CHAPTER

9 COORDINATION COMPOUNDS

Syllabus

- *Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).*

Trend Analysis

List of concept names	2018	2019		2020	
	D/OD	D	OD	D	OD
Structural formula, IUPAC name	–	1Q (2 marks)	–	–	–
Isomerism	1Q (3 marks)	–			1Q (1 mark)
Coordination Number and Oxidation state	1Q (1 mark)	–		1Q (1 mark)	1Q (1 mark)
Hybridization, Magnetic Character, Spin, Number of Unpaired Electrons and Isomers of Complex	1Q (3 marks)	1Q (2 marks)	1Q (2 marks)	1Q (2 marks)	1Q (2 marks)
Write the formula for IUPAC name	1Q (3 marks)		1Q (2 marks)	–	–
Properties	–	–		1Q (1 mark)	

TOPIC-1
Coordination Compounds : Properties and IUPAC Name

TOPIC - 1
Coordination Compounds : Properties and IUPAC Name .... **P. 247**

TOPIC - 2
Werner's Theory, Bonding, VBT, CFT .... **P. 259**

Revision Notes

- **Coordination Compound :** A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. There is a coordinate bond between metal atom and these ions or molecules, *e.g.*, $[Cu(NH_3)_4]^{2+}$.
- **Double Salt :** When two or more salts are added to form a stable solid together and break into constituent ions when dissolved in water or any solvent, *e.g.*, $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt).
- **Properties of double salts :**
  (i) They give simple ions in aqueous solution because they are ionic compounds.

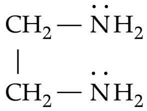
(ii) They do not contain coordinate bonds.
(iii) They exist only in solid state as double salt.
(iv) They are soluble in water.

- **Coordinate bonds :** A type of covalent bond in which one of the atoms supplies both the electrons. It can be considered as a combination of transfer and sharing of electrons. Coordinate bonds are also called semipolar bonds.
- **Central metal atom or ion :** The metal atom or ion surrounded by fixed number of ions or molecules is called central metal atom or ion, *e.g.,* in $K_4[Fe\ (CN)_6]$, Fe^{2+} is central metal ion.
- **Ligand :** The neutral molecules or ions (usually anions) which are attached with the central metal atom or ion in complex compound. *e.g.,* Cl^-, OH^-, CN^-, CO, NH_3, H_2O, etc. A ligand may be neutral or charged species. It is always act as a Lewis base.
  - **Types of ligands :**

(a) On the basis of number of donor sites :

(i) Unidentate ligands : Contain one donor atom. *e.g.,* $\ddot{N}H_3, H_2\ddot{O}:$

(ii) Bidentate ligands : Contain two donor atoms. *e.g.,* $(COO^-)_2$,



$$\begin{array}{l} CH_2-\ddot{N}H_2 \\ | \\ CH_2-\ddot{N}H_2 \end{array}$$

(iii) Polydentate ligands : Contain several donor atoms. *e.g.,* EDTA.

(b) On the basis of charge :

(i) Cationic ligands : Carry positive charge. *e.g.,* NO_2^+, $N_2H_5^+$.

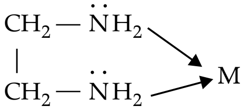
(ii) Anionic ligands : Carry negative charge. *e.g.,* X^-(halo), CN^-(cyano).

(iii) Neutral ligands : Do not carry any charge. *e.g.,* $\ddot{N}H_3$ (ammine), $H_2\ddot{O}:$ (aqua).

(c) On the basis of nature of ligand:

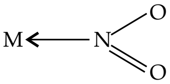
(i) Chelate ligands : A bidentate or polydentate uses its two or more donor atoms to bind a single metal ion, then a ring like structure is obtained. It is called chelate and the ligand is known as chelate ligand.

e.g.,



(ii) Ambidentate ligand : A ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal/ion is called ambidentate ligand.

e.g.,



Nitrito— N
(N donor atom)

$M \leftarrow SCN$

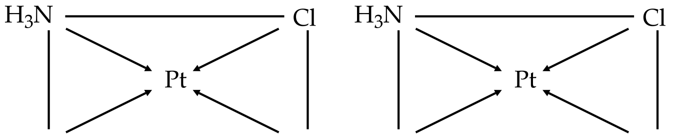
Thiocyanato
(S donor atom)

$M \leftarrow NCS$

Isothiocynate
(N donor atom)

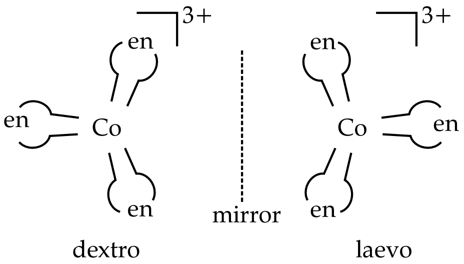
- **Coordination number :** Number of monodentate ligands attached to central metal ion in a complex is called coordination number. It may also be defined as total number of chemical bonds formed between central metal ion and donor atom of ligand *e.g.,* in $[Ni(NH_3)_6]^{2+}$, the coordination number of Ni is 6.
- **Coordination polyhedron :** The spatial arrangement of the ligand atoms which are directly attached to the central atoms or ions define a coordination polyhedron about the central atom *e.g.,* $[Pt\ Cl_4]^{2-}$ is square planar.
- **Charge on the complex ion :** The charge on the complex ion is equal to the algebric sum of the charges on all the ligands coordinated to the central metal ion.
- **Donor atom :** An atom in the Lewis base that forms the bond with the central atom/ion is called donor atom because it donates the pair of electrons.
- **Denticity :** The number of ligating groups or coordinating atoms in a ligand is called denticity *e.g.,* unidentate, bidentate, etc.
- **Applications of chelates :**
  (i) In the softening of hard water.
  (ii) In the separation of lanthanoids and actinoids.
  (iii) In the detection as well as estimation of some metal ions such as nickel (II) ion.
- **Coordination sphere :** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as coordination sphere *e.g.,* in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$.
- **Flexidentate character of ligands :** Certain polydentate ligands have flexible character and are called flexidentates. *e.g.,* EDTA is hexadentate in nature but in some cases, it may act as pentadentate or tetradentate ligand.
- **Oxidation number of central atom :** It is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. It is represented by Roman numerical.

- **Homoleptic and Heteroleptic complexes :** Complexes in which the metal atom or ion is linked to only one type of ligands are called homoleptic complexes, *e.g.*, $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes. *e.g.*, $[Co(NH_3)_4Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$.
- **Homonuclear and Polynuclear complexes :** Complexes in which only one metal atom is present are known as homonuclear complexes. *e.g.*, $[Co(NH_3)_6]Cl_3$ and $[Cu(NH_3)_4]SO_4$. Complexes in which more than one metal atom is present are known as polynuclear complexes.
- **Counter ions :** The ions which are not included in the primary coordination sphere are known as counter ions. *e.g.*, in $K_4[Fe(CN)_6]$, K^+ ions are counter ions.
- **Coordination ions :** The coordination entity with charge is called as coordination ion.
- **Nomenclature of Coordination compounds :**
  - **(i)** The cation whether simple or complex is named first followed by anion.
  - **(ii)** Ligands are named in alphabetical order.
  - **(iii)** For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used (di, tri, tetra, etc.). For ligands containing any of these prefixes in their names, their numbers are indicated by prefixes bis, tris, tetrakis, etc. Anionic ligands end in –o. Neutral retain their names while cationic end in -ium.
  - **(iv)** The coordination sphere is written in square bracket.
  - **(v)** In naming, ligands are named first in alphabetical order followed by metal atom and then the oxidation state of metal by a Roman numeral in parenthesis.
  - **(vi)** Name of coordination compounds starts with a small letter and the complex part is written as one word.
  - **(vii)** Oxidation number of central atom is indicated in Roman numerals. No space is left between the number and the rest of the name.
- **Isomers:** Two or more coordination compounds which have the same molecular formula but differ in the arrangement of ligands around the central metal atom or ion are called isomers. This phenomenon is called isomerism.
- **Types of isomerism:** Two types of isomerism are observed in coordination compounds.
  - **Structural Isomerism is of the following types:**
    - **(i) Ionization isomerism:** In this type of isomerism, isomers have same molecular formula but gives different ions in solution. e.g., $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$.
    - **(ii) Coordination isomerism:** This type of isomerism is shown by those complexes in which both the cation and the anion are complex ions and they differ in the coordination of ligands. e.g., $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$.
    - **(iii) Solvate isomerism:** Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. e.g.,$[Cr(H_2O)_5Cl]Cl_2.H_2O$,$[Cr(H_2O)_6]Cl_3$.
    - **(iv) Linkage isomerism:** Isomers having the same molecular formula but different linking atom, this is due to the presences of ambident ligands. e.g.,$[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$.
  - **Stereo isomerism is of following types:**
    - **(i) Geometrical isomerism or cis-trans isomerism:** In tetra coordinated square planar complexes, the cis-isomer has the same groups on the side whereas trans-isomer has same groups on opposite sides. e.g.



cis-diamminedichloro-platinum (II) *trans*-diamminedichloro-platinum (II)

    - **(ii) Optical isomerism:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) or laevo (l) depending upon the direction in which they rotate the plane of polarized light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involoving bidentate ligands



Optical isomers (*d* and *l*) of $[Co(en)_3]^{3+}$

Mnemonics

Spectrochemical Series

- **Concept:** Ligands causing Crystal Field Splitting are arranged in order of increasing field strength-Spectrochemical Series
- **Mnemonic: I Br**ought **SC**a**N**ned **Cl**assnotes to **S**tudy **F**undamentals **of Ch**emistry.
- **He N**urtured **E**xcellence in **NH**ew (New) **C**oordinatio**N CO**mpounds chapter.
- Interpretation: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_2 < CN^- < CO$

I^- = I

Br^- = Brought

SCN- = SCaNned

Cl^- = Classnotes

S^- = Study

F^- = Fundamentals

OH^- = Of

$C_2O_4^{2-}$ = Chemistry (Chromate ion)

H_2O = He

NCS^- = Nurtured

$EDTA^{4-}$ =Excellence

NH_3 = NHew

CN^- = CoordinatioN

CO = Compounds (Carbonyl group)

Know the Terms

- **Coordination chemistry :** The study of the coordination compounds is known as coordination chemistry.
- **Labile complex :** A complex in which ligand substitution is fast.
- **Inert complex :** A complex in which ligand substitution is slow.
- **Synergic bonding :** A ligand donates a pair of electrons to the metal atom or ion and then accepts a pair of electrons back in its vacant orbital also from *d*-orbitals of the metal or ion. This is called synergic bonding and the ligands involved are known as π-donor ligands.
- **Effective Atomic Number (EAN) :** It can be calculated for the metal atom or ion in the coordination complex by using following relation :

  EAN = Atomic no. (Z) of metal atom – Oxidation number + 2 C.N. where, C.N. is coordination number.
- **Facial or fac isomer :** When three ligands with donor atoms are on the same triangular face of the octahedron, the geometrical isomer is known as **facial or fac isomer.**
- **Meridional or mer isomer :** When three ligands with donor atoms are on the same equatorial plane of the octahedron or around the meridian of the octahedron, the isomer is called meridional or mer isomer.
- **Perfect or penetrating complexes :** These are the complexes in which complex ion is fairly stable and either completely or feebly dissociates in solution.
- **Imperfect or abnormal complexes :** These are the complexes in which the complex ion is less stable and is dissociated reversibly to give enough simple ions.

How is it done on the GREENBOARD?

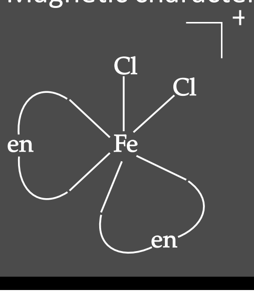
Q. For the complex ion $[Fe(en)_2Cl_2]^+$ write the hybridization type and magnetic behaviour. Draw one of the geometrical isomer of the complex ion which is optically active. [Atomic No.: Fe = 26]

Solutions:

STEP-1: Hybridisation: d^2sp^3

STEP-2: Magnetic character: Paramagnetic

STEP-3:



Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. The oxidation of Ni in $[Ni(CO_4)]$ is

(a) 0 (b) 2 (c) 3 (d) 4

$\boxed{\text{A\&E}}$ **[CBSE Delhi Set-1 2020]**

Ans: Correct option: (a)

Explanation : CO is a neutral ligand and its oxidation state is zero. Since the overall charge on the complex is zero too, hence oxidation state of Ni is 0.

Q. 2. Which of the following will give a white precipitate upon reacting with $AgNO_3$?

(a) $K_2\,[Pt(en)_2Cl_2]$ (b) $[Co[NH_3)_3Cl_3]$

(c) $[Cr(H_2O)_6]Cl_3$ (d) $[Fe(H_2O)_3Cl_3]$

$\boxed{\text{R}}$ **[CBSE Delhi Set-2 2020]**

Ans: Correct option: (c)

Explanation : $AgNO_3 + [Cr(H_2O)_6]Cl_3 \rightarrow$ AgCl ppt $+ NO_3^-$

Since Cl is outside the coordination sphere, it can react with $AgNO_3$ forming the white AgCl precipitate.

Q. 3. The formula of the complex triamminetri(nitrito-O) Cobalt (III) is

(a) $[Co(ONO)_3(NH_3)_3]$

(b) $[Co(NO_2)_3(NH_3)_3]$

(c) $[Co(ONO_2)_3(NH_3)_3]$

(d) $[Co(NO_2)(NH_3)_3]$

$\boxed{\text{U}}$ **[CBSE Delhi Set-3 2020]**

Ans: Correct option: (a)

Explanation : **$[Co(ONO)_3\,(NH_3)_3]$**

Q. 4. How many ions are produced from the complex $[Co(NH_3)_5Cl]Cl_2$ in solution?

(a) 4 (b) 2 (c) 3 (d) 5

$\boxed{\text{A}}$ **[CBSE OD Set-1 2020]**

Ans: Correct option: (c)

Explanation :

$[Co(NH_3)_5Cl]Cl_2 \rightarrow [CO(NH_3)_5Cl](aq) + 2Cl^-(aq)$

Q. 5. The pair $[Co(NH_3)_4Cl_2]Br_2$ and $[Co(NH_3)_4Br_2]Cl_2$ will show

(a) Linkage isomerism

(b) Hydrate isomerism

(c) Ionization isomerism

(d) Coordinate isomerism

$\boxed{\text{U}}$ **[CBSE OD Set-1 2020]**

Ans: Correct option: (c)

Explanation : Ionization isomers have identical central ion and the other ligands except for a ligand that has exchanged places with an anion or neutral molecule that was originally outside the coordination complex.

$[Co(NH_3)_4Cl_2]Br_2 \rightarrow [Co(NH_3)_4Cl_2]^+ + 2Br^-$

$[Co(NH_3)_4Br_2]Cl_2 \rightarrow [Co(NH_3)_4Cl_2]^+ + 2Cl^-$

Q. 6. The coordination number of 'Co' in the complex $[Co(en)_3]^{3+}$ is

(a) 3 (b) 6 (c) 4 (d) 5

$\boxed{\text{A\&E}}$ **[CBSE OD Set-2 2020]**

Ans: Correct option: (b)

Explanation : Coordination number is the number of ligands joined to the central metal ion or atom. Since ethylenediamine is a bidentate ligand, Co has coordination number of 6.

Q. 7. Which of the following is the most stable complex?

(a) $[Fe(CO)_5]$ (b) $[Fe(H_2O)_6]^{3+}$

(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[Fe(CN)_6]^{3-}$

$\boxed{\text{A\&E}}$ **[CBSE OD Set-3 2020]**

Ans: Correct option: (c)

Explanation : $[Fe(C_2O_4)_3]^{3-}$ acts as the chelating ligands. because $C_2O_4^{2-}$ is a bidentate ligand.

Q. 8. What type of isomerism is shown by the pair $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]\ Cl_2 . H_2O$?

(a) Ionisation isomerism
(b) Coordination isomerism
(c) Solvate isomerism
(d) Linkage isomerism

A&E **[CBSE OD Set-3 2020]**

Ans: Correct option: (c)

Explanation : Solvate / Hydrate isomerism

Solvate or hydrate isomers have the same composition but differ with respect to the number of solvent ligand molecules as well as the counter ion in the crystal lattice.

Q. 9. Ambidentate ligands like NO_2^- and SCN^- are :

(a) unidentate
(b) didentate
(c) polydentate
(d) has variable denticity

OR

The formula of the coordination compound Tetraamminеaquachloridocobalt(III) chloride is

(a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(b) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
(c) $[Co(NH_3)_2(H_2O)Cl]Cl_2$
(d) $[Co(NH_3)_4(H_2O)Cl]Cl$ R **[CBSE SQP 2021]**

Ans: Correct option : (a)

Explanation : Tetraammineaquachloridocobalt (III) chloride is $[CO(NH_3)_4(H_2O)Cl]Cl_2$.

Central atom – Cobalt(III)

Coordination sphere ligands-

Tetraammine - 4 NH_3 groups neutral ligand

Aqua – 1 H_2O groups neutral ligand

Chlorido -1 Cl group, negatively charged ligand, one negative charge

Counter ion- Chloride ions, 2

Since Cobalt is 3+, one valency is satisfied with Cl in coordination sphere and 2 by chlorine counter ions.

Hence the formula of the coordination compound is $[CO(NH_3)_4(H_2O)Cl]Cl_2$.

[B] ASSERTIONS AND REASONS:

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is correct statement but reason is correct statement.

Q. 1. Assertion (A) : Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason (R) : Actinoids can utilize their 5d orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.

Ans. Correct option: (d)

Explanation : Actinoids are more reactive and form relatively more stable complexes in comparison to lanthanoids as Actinoids can utilize their 5d orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbitals for bonding.

Q. 2. Assertion (A) : Toxic metal ions are removed by the chelating ligands.

Reason (R) : Chelate complexes tend to be more stable.

Ans. Correct option: (a)

Explanation : When a solution of chelating ligand is added to solution containing toxic metal ligands chelates the metal ions by formation of stable complex.

Q. 3. Assertion (A) : Linkage isomerism arises in coordination compounds containing ambidentate ligand.

Reason (R) : Ambidentate ligand has two different donor atoms.

Ans. Correct option: (a)

Explanation : Linkage isomerism arises due to two different donor atoms in ambidentate ligand.

[C] VERY SHORT ANSWER TYPE QUESTIONS:

Q. 1. What is the IUPAC name of the complex $[Ni(NH_3)_6]Cl_2$? A **[CBSE Comptt. Delhi 2015]**

Ans. Hexaamminenickel (II) Chloride. **[1]**
[CBSE Marking Scheme, 2015]

Q. 2. What is meant by chelate effect?

R **[CBSE Comptt. OD Delhi 2015]**

Ans. Formation of stable complex with a polydentate ligand due to stronger bonding is known as chelate effect. **[1]**
[CBSE Marking Scheme, 2015]

OR

Formation of stable complex with a polydentate ligand due to stronger bonding than the non chelate complexes is known as chelate effect.

Q. 3. Which of the following is more stable complex and why?

$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$.

U **[CBSE Comptt. OD Delhi 2015]**

Ans. $[Co(en)_3]^{3+}$: Because (en) is a chelating ligand/ bidentate ligand. [½ + ½]
[CBSE Marking Scheme, 2015]

Q. 4. How many ions are produce from the complex, $[Co(NH_3)_6]Cl_2$ in solution? A **[CBSE SQP 2016]**

Ans. Three ions $[CO(NH_3)_6]^{2+}$, $2Cl^-$ **[1]**
[CBSE Marking Scheme, 2015]

Q. 5. Write the IUPAC name of the following coordination compound $[NiCl_4]^{2-}$.

A **[CBSE Comptt. Delhi 2016]**

Ans. Tetrachloridonickelate (II) ion. **[1]**
[CBSE Marking Scheme, 2016]

Q. 6. Write IUPAC name of the complex: $[CoCl_2(en)_2]^{2+}$.
A [CBSE Comptt. OD Set-1, 3 2017]

Ans. Dichloridobis (ethane-1, 2-diamine) cobalt (III) ion. **[1]**
[CBSE Marking Scheme, 2017]

Commonly Made Error

- There is confusion in oxidation state of central metal ion.

Answering Tip

- Practice and understand writing nomenclature and oxidation state of ligands.

Q. 7. Write IUPAC name of the complex: $[Co(NH_3)_4Cl(NO_2)]^+$.
A [CBSE Comptt. OD Set-2 2017]

Ans. Tetraamminechloridonitrocobalt (III) ion. **[1]**
[CBSE Marking Scheme, 2017]

Q. 8. Write the coordination isomer of $[Cu(NH_3)_4]$ $[PtCl_4]$.
A [CBSE Comptt. Delhi/OD 2018]

Ans. $[Pt(NH_3)_4][CuCl_4]$ **[1]**
[CBSE Marking Scheme, 2018]

Q. 9. Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2Cl_2]$.
A [CBSE Comptt. Delhi/OD 2018]

Ans. Coordination Number = 6,
Oxidation State = +2 [½ + ½]
[CBSE Marking Scheme, 2018]

Q. 10. Out of Cis-$[Pt(en)_2Cl_2]^{2+}$ and Trans-$[Pt(en)_2Cl_2]^{2+}$, which one is optically active?

Ans. cis $[Pt(en)_2Cl_2]^{2+}$. [½ + ½]

Short Answer Type Questions-I (2 marks each)

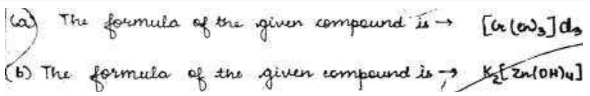
Q. 1. Using IUPAC norms write the formulae for the following:
(i) Sodium dicyanidoaurate (I)
(ii) Tetraamminechloridonitrito-N-platinum (IV) sulphate
A [CBSE OD Set-1 2017]

Ans. (i) $Na[Au(CN)_2]$ 1
(ii) $[Pt(NH_3)_4Cl(NO_2)]SO_4$ 1
[CBSE Marking Scheme 2017]

Q. 2. Using IUPAC norms write the formulae for the following:
(i) Tris(ethane-1,2-diamine)chromium(III) chloride
(ii) Potassium tetrahydroxozincate(II)
A [CBSE OD Set-2 2017]

Ans. (i) $[Cr(en)_3]Cl_3$ 1
(ii) $K_2[Zn(OH)_4]$ 1
[CBSE Marking Scheme 2017]

OR


(a) The formula of the given compound is → $[Cr(en)_3]Cl_3$
(b) The formula of the given compound is → $K_2[Zn(OH)_4]$

[Topper's Answer 2017] 2

AI Q. 3. Using IUPAC norms write the formulae for the following:
(i) Potassium trioxalatoaluminate (III)
(ii) Dichloridobis(ethane-1,2-diamine)cobalt(III)
A [CBSE OD Set-3 2017]

Ans. (i) $K_3[Al(C_2O_4)_3]$ 1
(ii) $[CoCl_2(en)_2]^+$ 1
[CBSE Marking Scheme 2017]

AI Q. 4. (i) Write the IUPAC name of the isomer of the following complex:
$[Pt(NH_3)_2Cl_2]$
(ii) Write the formula for the following:
Tetraammineaquachloridocobalt (III) nitrate
A [CBSE Foreign Set-1 2017]

Ans. (i) cis/trans-diamminedichloridoplatinum (II) 1
(ii) $[Co(NH_3)_4(H_2O)Cl]$ $(NO_3)_2$ 1
[CBSE Marking Scheme 2017]

Q. 5. (i) Write the IUPAC name of the isomer of the following complex:
$[Co(NH_3)_5Cl]SO_4$
(ii) Write the formula for the following:
Diamminechloridonitrito-N-platinum(II)
A [CBSE Foreign Set-2 2017]

Ans. (i) Pentaamminechlorocobalt (III) sulphate 1
(ii) $[Pt(NH_3)_2Cl(NO_2)]$ 1
[CBSE Marking Scheme 2017]

AI Q. 6. (i) Write the IUPAC name of the following complex:
$[Co(NH_3)_4Cl(NO_2)]Cl$
(ii) Write the formula for the following:
Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
A [CBSE Foreign Set-3 2017]

Ans. **(i)** Tetraamminechloridonitrito-N-cobalt (III) chloride. 1
(ii) $[CoCl_2(en)_2]Cl$ **1**
[CBSE Marking Scheme 2017]

Q. 7. (i) Write down the IUPAC name of the following complex :
$[Cr(NH_3)_2Cl_2(en)_2]Cl$ (en = ethylenediamine)

(ii) Write the formula for the following complex : Pentaamminenitrito-O-Cobalt (III).

A [CBSE Delhi 2015]

Ans. (i) Diamminedichloridobisethylenediaminechromium (III) chloride

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

[CBSE Marking Scheme 2015] 1+1

Q. 8. (i) Write down the IUPAC name of the following complex : $[Co(NH_3)_5Cl]^{2+}$

(ii) Write the formula for the following complex : Potassium tetrachloridonickelate (II)

A [CBSE Delhi 2015]

Ans. (i) Pentaamminechloridocobalt (III) ion 1

(ii) $K_2[NiCl_4]$ 1

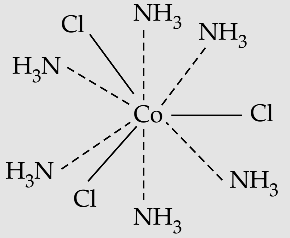
Q. 9. When a coordination compound $CoCl_3.6NH_3$ is mixed with $AgNO_3$, 3 moles of AgCl are precipitated per mole of the compound. Write

(i) Structural formula of the complex,

(ii) IUPAC name of the complex.

A [CBSE OD 2016]

Ans. (i) $[Co(NH_3)_6]Cl_3$



1

(ii) IUPAC name : Hexamminecobalt (III) chloride. 1

[CBSE Marking Scheme 2016]

Commonly Made Error

- Students often make errors in naming the central atom and ligand in the coordinate compounds.

Answering Tip

- Understand and practice the naming of coordinate compounds.

Q. 10. When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write

(i) Structural formula of the complex.

(ii) IUPAC name of the complex. A [CBSE Delhi 2016]

Ans. **(i)** $[Cr(H_2O)_5Cl]Cl_2.H_2O$ 1

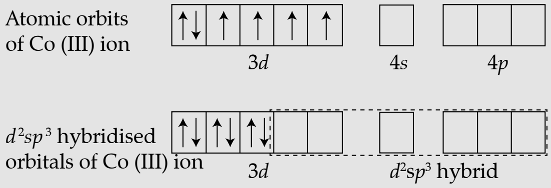
(ii) Pentaaquachloridochromium (III) chloride monohydrate. 1

[CBSE Marking Scheme 2016]

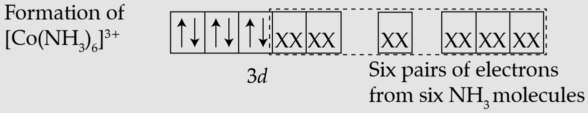
Q. 11. Discuss the bonding in the coordination entity $[Co(NH_3)_6]^{3+}$ on the basis of valence bond theory. Also, comment on the geometry and spin of the given entity. (Atomic no. of Co = 27)

Ans. Bonding in $[Co(NH_3)_6]^{3+}$

d^2sp^3 hybridisation ½



½



½

Geometry : Octahedral ½

Diamagnetic ½

[CBSE SQP Marking Scheme 2020]

Q. 12. Using IUPAC norms write the formulae for the following :

(i) Hexaamminecobalt(III) sulphate

(ii) Potassium trioxalatochromate(III)

A [CBSE Delhi Set-1 2019]

Ans.

(i) $[Co(NH_3)_6]_2(SO_4)_3$ 1

(ii) $K_3[Cr(C_2O_4)_3]$ **[CBSE Marking Scheme, 2019] 1**

Q. 13. Define the following terms with a suitable example of each :

(a) Polydentate ligand

(b) Homoleptic complex

Ans. (i) A ligand having several donor atoms. Example-EDTA 1

(ii) A complex in which a metal is bound to only one kind of donor groups / ligands. Example-$[Co(NH_3)_6]^{3+}$ 1

(or any other correct example)

[CBSE Marking Scheme, 2019]

Detailed Answer :

(a) A ligand which contains several donor atoms in a single ligand is known as polydentate ligand. Example, $N(CH_2\ CH_2\ NH_2)_3$.

(b) Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic complexes. Example, $[Co(NH_3)_6]^{3+}$.

Q. 14. Using IUPAC norms, write the formulae for the following complexes:

(a) Potassium tri(oxalate)chromate(III)

(b) Hexaaquamanganese(II) sulphate

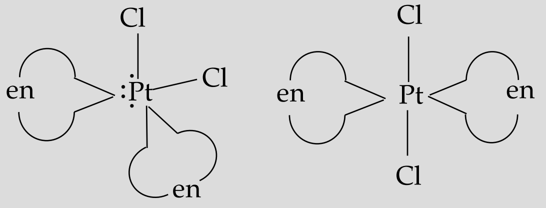
A [CBSE Delhi Set-3 2019]

(i) $K_3[Cr(C_2O_4)_3]$ 1

(ii) $[Mn(H_2O)_6]SO_4$ **[CBSE Marking Scheme, 2019] 1**

Q. 15. Write IUPAC name of the complex $[Pt(en)_2Cl_2]$. Draw structures of geometrical isomers for this complex. [2]

Ans. Bis(ethan-1,2-diamine)dichloridoplatinum (II) **1**



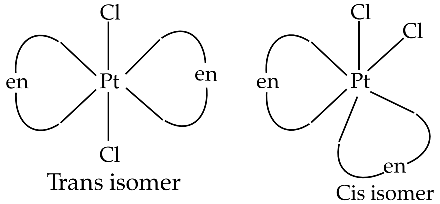
Cis-isomer   Trans-isomer

½ + ½

[CBSE Marking Scheme, 2019]

Detailed Answer:

IUPAC names of the complex $[Pt(en)_2Cl_2]$ is Dichlorobis(ethylenediamine) platinum (II). The geometrical isomers of $[Pt(en)_2Cl_2]$ is



Trans isomer   Cis isomer

Q. 16. Using IUPAC norms write the formulae for the following :

(i) Hexaamminecobalt(III) sulphate

(ii) Potassium trioxalatochromate(III)

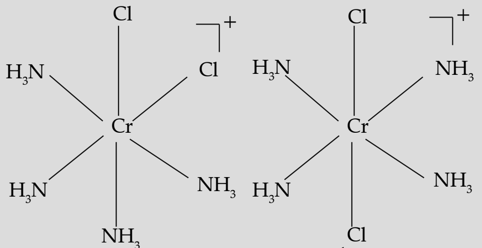
Ans.

(i) $[Co(NH_3)_6]_2(SO_4)_3$ **1**

(ii) $K_3[Cr(C_2O_4)_3]$ **[CBSE Marking Scheme, 2019] 1**

Q. 17. Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex.

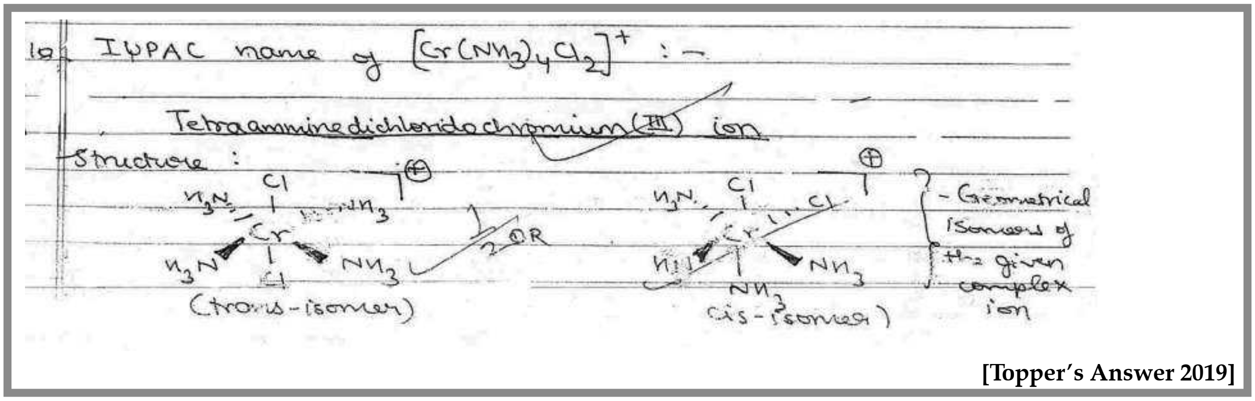
Ans. Tetraamminedichloridochromium(III) ion **1**



cis   trans

½ + ½

[CBSE Marking Scheme, 2019]



10. IUPAC name of $[Cr(NH_3)_4Cl_2]^+$:-

Tetraamminedichloridochromium(III) ion

Structure :

(trans-isomer) OR (cis-isomer)

} - Geometrical isomers of the given complex ion

[Topper's Answer 2019]

Q. 18. Using IUPAC norms write the formulae for the following :

(i) Pentaammine nitrito-o-cobalt (III) Chloride

(ii) Potassium tetracyanonickelate (II) **[2]**

Ans.

(i) $[Co(NH_3)_5ONO]Cl_2$ **1**

(ii) $K_2[Ni(CN_4)]$ **[CBSE Marking Scheme, 2019] 1**

Q. 19. Write IUPAC name of the complex $[Co(en)_2(NO_2)Cl]^+$. What type of structural isomerism is shown by this complex?

Ans. Chloridobis(ethane-1,2-diamine)nitrito-N-cobalt(III) ion

Linkage isomerism **1 + 1**

Q. 20. Using IUPAC norms, write the formulae for the following complexes :

(a) Hexaaquachromium(III) chloride

(b) Sodium trioxalatoferrate(III)

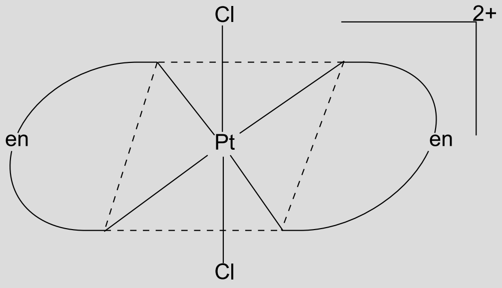
Ans. (a) $Cr(H_2O)_6]Cl_3$

(b) $Na_3[Fe(ox)_3]$ **1 + 1**

[CBSE Marking Scheme, 2019]

Q. 21. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl]^{2+}$ which is optically inactive. Also write the name of this entity according to the IUPAC nomenclature.

Ans.



trans-$[Pt(en)_2Cl_2]^{2+}$ **1**

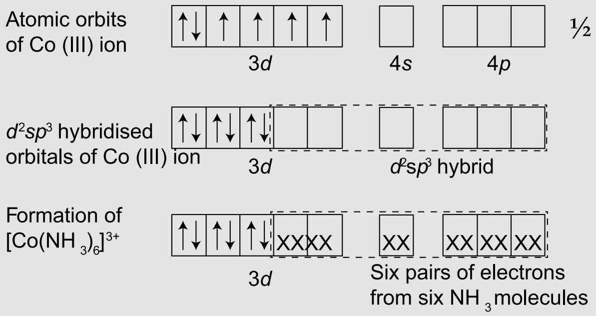
IUPAC Name of the entity :

Dichloridobis (ethane-1,2-diamine) platinum (IV) ion 1

Q. 22. Discuss the bonding in the coordination entity $[Co(NH_3)_6]^{3+}$ on the basis of valence bond theory. Also, comment on the geometry and spin of the given entity. (Atomic no. of Co = 27)

Ans. Bonding in $[Co(NH_3)_6]^{3+}$

d^2sp^3 hybridisation



Geometry : Octahedral ½

Diamagnetic ½

[CBSE SQP Marking Scheme 2020]

Q. 23. (a) Write the IUPAC name and hybridisation of the complex $[Fe(CN)_6]^{3-}$.

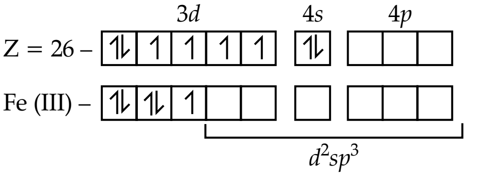
(Given : Atomic number of Fe = 26)

(b) What is the difference between an ambidentate ligand and a chelating ligand?

A [CBSE Delhi Set-1 2020]

Ans. (a) $[Fe(CN)_6]^3$ – hexacyanoferrate (III) ion

hybridization – d^2sp^3



six pairs of e^- from CN^- ions

(b) Ambidentate ligand can bond through different atoms to form different coordination compounds. e.g. NO_2^- can bind to the central atom or ion at either the nitrogen atom or one of the oxygen atom.

Chelating ligand : If the ligands with two or more electron donor groups positioned in such a way that they form five or six membered ring with central metal ion are called chelating ligands. e.g. ethane - 1, 2-diamine (en)

1+1 = 2

Q. 24. Write the IUPAC name and hybridization of the following complexes :

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

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

(Given : Atomic number of Ni = 28, Fe = 26)

A [CBSE OD Set-1 2020]

Ans. (i) $[Ni(CN)_4]^{2-}$ – tetracyanonickelate (II)

hybridization – dsp^2

(ii) $[Fe(H_2O)_6]^{2+}$ – hexaquairon (II)

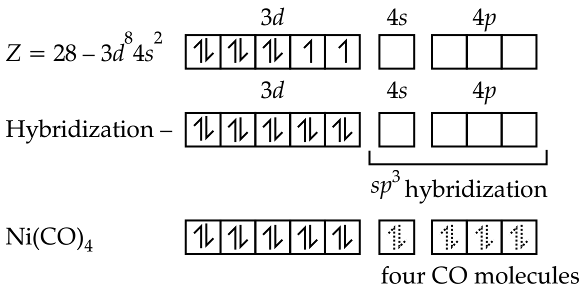
hybridization – sp^3d^2 **1 + 1 = 2**

Q. 25. Write IUPAC name and hybridization of the following complexes :

(i) $[Ni(CO)_4]$, (ii) $[CoF_6]^{3-}$ (Atomic number Ni = 28, Co = 27) A [CBSE OD Set-2 2020]

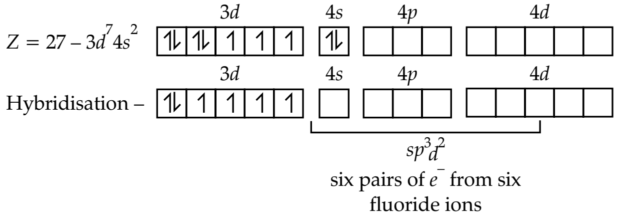
Ans. (i) $[Ni(CO)_4]$ – Tetracarbonylnickel

Hybridization - sp^3



(ii) $[CoF_6]^{3-}$ – Hexafluorocobaltate (III)

Hybridization - sp^3d^2



1 + 1 = 2

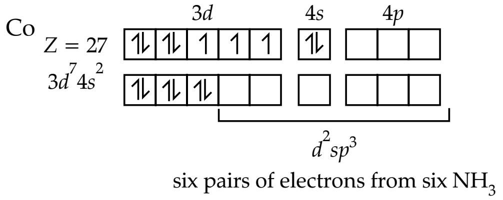
Q. 26. Write IUPAC name and hybridization of the following complexes :

(i) $[Co(NH_3)_6]^{3+}$ **(ii)** $[NiCl_4]^{2-}$

(Atomic number Ni = 28, Co = 27)

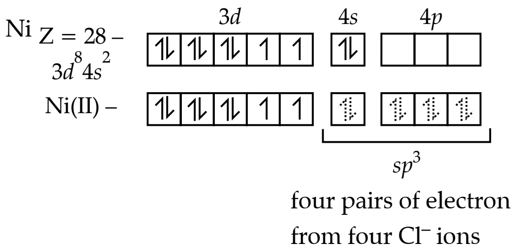
Ans. (i) $[Co(NH_3)_6]^{3+}$: Hexaamminecobalt (III)

Hybridization - d^2sp^3



(ii) $[NiCl_4]^{2-}$: Tetrachloronickelate (II)

Hybridization - sp^3



1 + 1 = 2

Short Answer Type Questions-II (3 marks each)

Q. 1. Write the IUPAC name of the following :

(i) $[Co(NH_3)_6]Cl_3$

(ii) $[NiCl_4]^{2-}$

(iii) $K_3[Fe(CN)_6]$ $\boxed{A}$ **[CBSE Comptt. OD 2015]**

Ans. (i) Hexaamminecobalt (III) chloride. 1

(ii) Tetrachloridonickelate (II) ion. 1

(iii) Potassiumhexacyanoferrate (III) 1

[CBSE Marking Scheme 2015]

Q. 2. 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 = ethylenediamine)

(iii) $[Pt(NH_3)_2Cl_2]$ $\boxed{A}$ **[CBSE Comptt. Delhi 2015]**

Ans. (i) Linkage isomerism. 1

(ii) Optical isomerism. 1

(iii) Cis - trans / Geometrical isomerism 1

[CBSE Marking Scheme 2015]

Commonly Made Error

- Some students write 'ligand isomerism' instead of 'linkage isomerism'.

Answering Tip

- Learn and understand different types of isomerism with examples.

Q. 3. (i) For the complex $[Fe\ (CN)_6]^{3-}$, write the hybridization, magnetic character and spin nature of the complex. (At. number : Fe = 26).

(ii) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically active.

$\boxed{A}$ **[CBSE Delhi 2016]**

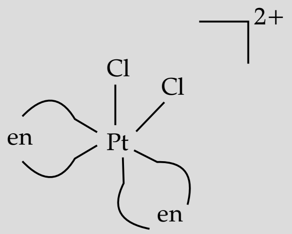
Ans. (i) Hybridization : d^2sp^3

Magnetic character : Paramagnetic

Spin nature of the complex : Low spin.

1 + ½ + ½

(ii)



cis-isomer **1**

[CBSE Marking Scheme, 2016]

Q. 4. (a) For the complex $[Fe(CN)_6]^{4-}$, write the hybridization, magnetic character and spin type of the complex. (At. number : Fe = 26).

(b) Draw one of the geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ which is optically active. $\boxed{A}$ **[CBSE OD Set-2 2016]**

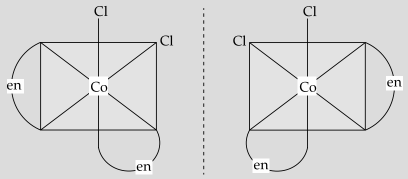
Ans.

(a) Hybridization : d^2sp^3

Magnetic character : Diamagnetic

Spin type : Low spin complex.

(b) Cis-$[Co(en)_2Cl_2]^+$ is optically active.



[CBSE Marking Scheme. 2016]

Q. 5. Write the hybridization, shape and magnetic character of $[Fe(CN)_6]^{4-}$.

$\boxed{A}$ **[CBSE Comptt. Delhi 2016]**

Ans. Hybridization : d^2sp^3 isomerism.

Shape : Octahedral

Magnetic character : Diamagnetic **1 + 1+ 1**

[CBSE Marking Scheme, 2016]

Q. 6. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6]\ [Cr(CN)_6]$?

(ii) 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). **[KVS]**

(iii) Write the IUPAC name of the following complex : $[Co(NH_3)_5(CO_3)]$ Cl.

$\boxed{A}$ **[CBSE Delhi Set-1, 2 2017]**

Ans. (i) Co-ordination isomerism. 1

(ii) Unpaired electrons in $[Ni(H_2O)_6]^{2+}$/*d-d* transition. 1

(iii) Pentaamminecarbonatocobalt (III) chloride. 1

[CBSE Marking Scheme, 2017]

Detailed Answer:

(ii) $[Ni(CN)_4]^{2-}$ has no unpaired electron in its d-subshell therefore d-d transition is not possible whereas $[Ni(H_2O)_6]^{2+}$ has unpaired electron in its d-subshell resulting in d-d transition imparting colour.

Q. 7. (i) What type of isomerism is shown by the complex $[Co(en)_3]\ Cl_3$?

(ii) Write the hybridisation and magnetic character of $[Co(C_2O_4)_3]^{3-}$. (At. no. of Co = 27)

(iii) Write IUPAC name of the following Complex $[Cr(NH_3)_3Cl_3]$.

Ans. **(i)** Optical isomerism **1**

(ii) d^2sp^3, diamagnetic **½ + ½**

(iii) Triamminetrichloridochromiun (III) **1**

[CBSE Marking Scheme, 2017]

Q. 8. (a) What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$?

(b) Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic ? (Atomic number of Ni = 28)

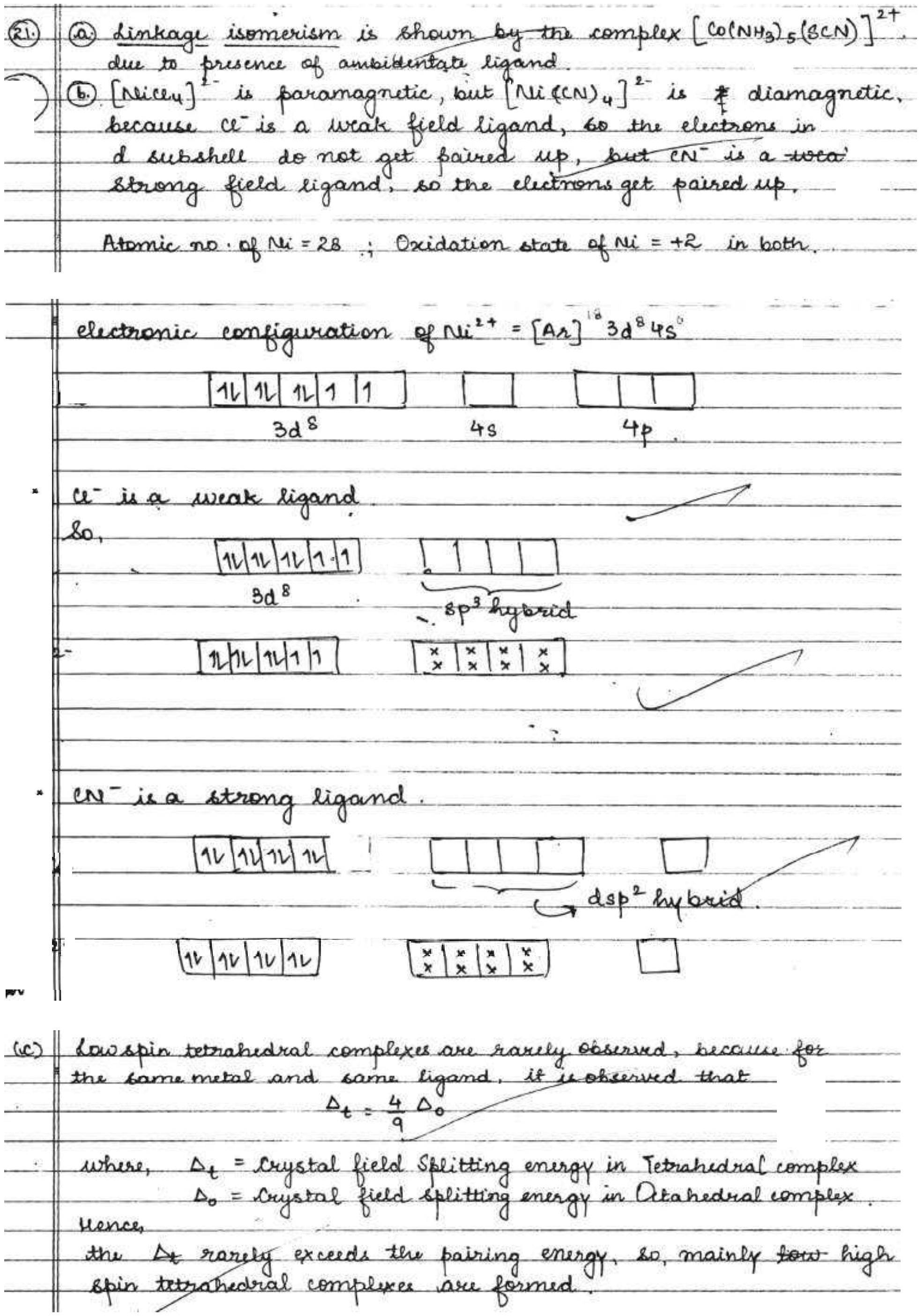
(c) Why are low spin tetrahedral complexes rarely observed ? A **[CBSE OD Set-1, 2, 3 2017]**

Ans. (a) Linkage isomerism. **1**

(b) In $[NiCl_4]^{2-}$, due to the presence of Cl^-, a weak field ligand no pairing occurs whereas in $[Ni(CN)_4]^{2-}$, CN^- is a strong field ligand and pairing takes place / diagrammatic representation. **1**

(c) Because of very low CFSE which is not able to pair up the electrons. **1**

[CBSE Marking Scheme, 2017]



(21.) (a) Linkage isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$. due to presence of ambidentate ligand.

(b.) $[NiCl_4]^{2-}$ is paramagnetic, but $[Ni(CN)_4]^{2-}$ is diamagnetic, because Cl^- is a weak field ligand, so the electrons in d subshell do not get paired up, but CN^- is a ~~wea~~ strong field ligand, so the electrons get paired up.

Atomic no. of Ni = 28 ; Oxidation state of Ni = +2 in both.

electronic configuration of $Ni^{2+} = [Ar]^{18} 3d^8 4s^0$

Cl^- is a weak ligand.

So,

CN^- is a strong ligand.

(c) Low spin tetrahedral complexes are rarely observed, because for the same metal and same ligand, it is observed that

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

where, Δ_t = Crystal field Splitting energy in Tetrahedral complex

Δ_o = Crystal field splitting energy in Octahedral complex.

Hence,

the Δ_t rarely exceeds the pairing energy, so, mainly ~~low~~ high spin tetrahedral complexes are formed.

[Topper's Answer, 2017]

Q. 9. For the complex ion $[CoF_6]^{3-}$ write the hybridization type, magnetic character and spin nature. [Atomic number: Co = 27]

A [CBSE Comptt. Delhi Set-1, 2 2017]

Ans. Hybridisation : sp^3d^2 1

Magnetic character : Paramagnetic 1

Spin nature : High spin 1

[CBSE Marking Scheme 2017]

Q. 10. For the complex ion $[Ni(CN)_4]^{2-}$ write the hybridization type, magnetic character and spin nature. [Atomic number: Ni = 28]

A [CBSE Comptt. Delhi Set-3 2017]

Ans. Hybridisation : dsp^2 1

Magnetic character : Diamagnetic 1

Spin nature : Low spin 1

[CBSE Marking Scheme 2017]

AI Q. 11. When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$ solution, 3 moles of AgCl are precipitated per mole of the compound. Write:

(i) Structural formula of the complex

(ii) IUPAC name of the complex

(iii) Magnetic and spin behaviour of the complex

A [CBSE Comptt. OD Set-3 2017]

Ans. (i) $[Cr(H_2O)_6]Cl_3$ 1

(ii) Hexaaquachromium(III) chloride 1

(iii) Paramagnetic and high spin ½+½

[CBSE Marking Scheme 2017]

Q. 12. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia whereas B gives a pale yellow precipitate soluble in concentrated ammonia.

Ans. (i) Isomer A: $[Cr(NH_3)_4BrCl]Cl$ ½

Isomer B: $[Cr(NH_3)_4Cl_2]Br$ ½

(ii) Hybridisation of Cr in isomer A and B is d^2sp^3. 1

(iii) Number of unpaired electrons in $Cr^{3+}(3d^3)$ is 3

Magnetic moment = $\sqrt{n(n+2)}$

= $\sqrt{3(3+2)}$

= 3.87 BM 1

(deduct half mark for wrong unit/unit not written)

[CBSE Marking Scheme 2018]

Q. 13. Write IUPAC name for each of the following complexes:

(i) $[Ni(NH_3)_6]Cl_2$

(ii) $K_3[Fe(CN)_6]$

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

A [CBSE Comptt. Delhi/OD 2018]

Ans. (i) Hexaamminenickel (II) chloride 1

(ii) Potassium hexacyanidoferrate (III) 1

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

[CBSE Marking Scheme 2018]

Q. 14. (a) Write the formula of the following co-ordination compound :

Iron(III) hexacyanoferrate(II)

(b) What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$?

(c) Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic No. of Co = 27)

Ans. (a) $Fe_4[Fe (CN)_6]_3$ 1

(b) Ionisation isomerism 1

(c) sp^3d^2, octahedral complex with 4 unpaired electrons 1

[CBSE Marking Scheme, 2018]

Q. 15. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia whereas B gives a pale yellow precipitate soluble in concentrated ammonia.

(i) State the hybridisation of chromium in each of them.

(ii) Calculate the magnetic moment (spin only value) of the isomer A.

A [CBSE SQP 2018-2019]

Ans. (i) Hybridisation of Cr in isomer A and B is d^2sp^3. 1½

(ii) Number of unpaired electrons in $Cr^{3+}(3d^3)$ is 3

Magnetic moment = $\sqrt{n(n+2)}$

= $\sqrt{3(3+2)}$

= 3.87 BM 1½

(deduct half mark for wrong unit/unit not written)

[CBSE Marking Scheme 2018]

TOPIC-2

Werner's Theory, Bonding, VBT, CFT

Revision Notes

➢ **Werner's Theory of Coordination compounds :**

Different postulates of Werner's coordinatron theory are given below:

(i) Metal ions possess two types of valency (a) primary or ionisable valency and (b) Secondary or non ionisable valency.

(ii) Every metal ion has a fixed number of secondary valency and this is known as coordination number.

(iii) **Primary valencies** are satisfied by anions while secondary valancies are satisfied by negative group or neutral molecules with lone pair of electrons.

(ii) **Secondary valencies** are directed in space towards internal positions.

- **Limitations of Werner's theory :** This theory does not explain the following queries—

(i) Why is the complex forming tendency limited to a few elements only ?

(ii) Why bonds in the coordination complexes are of directional nature ?

(iii) Why are certain complexes of magnetic nature and show geometrical and optical isomerism ?

- **Valence Bond theory :** It was developed by Pauling. The brief points are :

(i) A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bond with the ligands.

(ii) Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon total number of ligands.

(iii) The hybridised orbitals are allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.

(iv) The outer orbitals (high spin) or inner orbitals (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

- **Limitation of Valence bond theory :**

(i) It cannot explain the detailed magnetic properties of complex compounds.

(ii) It cannot explain the optical absorption spectra of coordination compounds.

(iii) It cannot predict property whether a particular 4 coordinate complex is square planar or tetrahedral in nature.

(iv) It fails to make distinction between strong and weak ligands.

(v) It does not explain thermodynamic or kinetic stabilities of coordination compounds.

- **Crystal field theory (CFT) :**

(i) The ligand is considered as point charge or point dipole.

(ii) Interaction between metal ion and ligand is considered as electrostatic in nature.

(iii) Metal ion is supposed to be present at the origin of the axis. Ligands approach to metal ion along the axis of octahedral complex between the axis of tetrahedral complex and in the case of square planar complex four ligand approach to metal ion along *x*, *y* plane.

(iv) Due to the approach of the ligand *hence* due to the electrostatic interaction between ligands electrons and metal *d*-orbital electron, degeneracy of *d*-orbital is lost and spliting of *d*-orbitals occurs.

(v) Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d*-orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below and called as spectrochemical series :

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

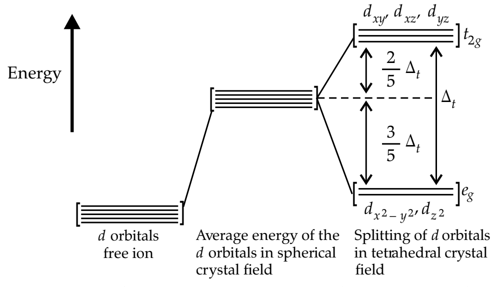


Fig. 2 : ***d*** orbital splitting in a tetrahedral crystal field

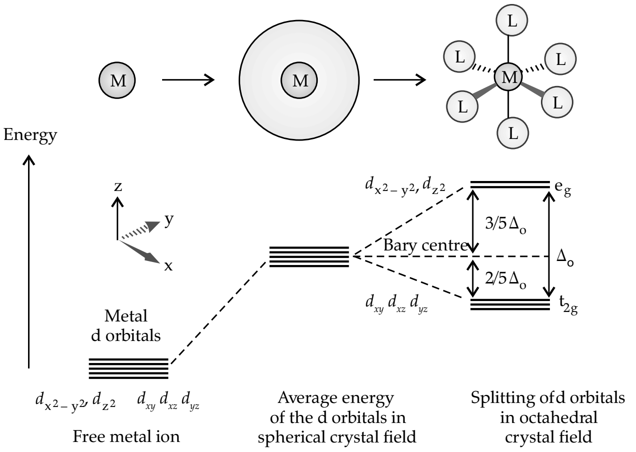


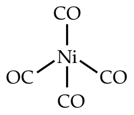
Fig. 1: *d* orbital splitting in an octahedral crystal field

***d*-orbital splitting in a tetrahedral crystal field** ***d*-orbital splitting in an octahedral crystal field**

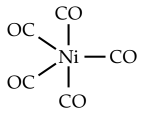
(vi) Explanation of colour and magnetic behaviour in complexes is possible by crystal field theory.

- **Metal carbonyls :** Homoleptic carbonyls are formed by *d*-block elements and contain carbonyl ligands only. *e.g.*, $V(CO)_6$, $Cr(CO)_6$, $[Mo(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO_8)]$, $[Co_4(CO)_{12}]$, $[Ni(CO)_4]$, etc. Metal carbonyls of outside the central part of *d*-block are unstable.

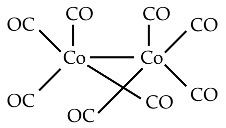
  Properties of metal carbonyls :
  - **(i)** Metal carbonyls are mostly solids at room temperature and pressure. Exceptions being iron and nickel carbonyls which are liquids.
  - **(ii)** The mononuclear carbonyls are volatile and toxic.
  - **(iii)** Most of metal carbonyls are soluble in hydrocarbon solvents except $[Fe_2(CO)_9]$.
  - **(iv)** Mononuclear carbonyls are either colourless or light coloured.
  - **(v)** They are highly reactive due to metal centre and the CO ligands.
  - **(vi)** Metal carbonyls are used as industrial catalyst and as precursor in organic synthesis.



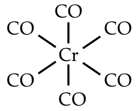
$Ni(CO)_4$
Tetrahedral



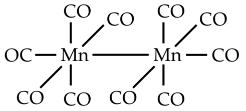
$Fe(CO)_5$
Trigonal bipyramidal



$[Co_2(CO)_8]$



$Cr(CO)_6$
Octahedral



$[Mn_2(CO)_{10}]$

- **Bonding in metal carbonyls :** It also involves both σ- and π-bond. σ-bond is formed by overlapping of lone pair on CO to the vacant *d*-orbitals of metal whereas π-bond is formed by back donation of pair of *d*-electrons to vacant anitbonding orbital of carbonyl.
- **Factors affecting the stability of 'coordination' complexes :**
  - **(i)** **Nature of the central ion :** Greater the charge density on the central metal ion, greater is the stability of the complex.
  - **(ii)** **Nature of the ligand :** More basic ligands have a tendency to donate the electron pairs to central metal ion more easily resulting in a stable complex.
  - **(iii)** **Chelate effect :** Entropy increases when chelation occurs and so the formation of the complex becomes more favourable.
- **Applications of Complex compounds :**
  - **(i)** They are used in photography, *i.e.*, AgBr forms soluble complex with sodium thiosulphate in photography.
  - **(ii)** $K[Ag(CN)_2]$ is used for electroplating of silver, $K[Au(CN)_2]$ is used for gold plating.
  - **(iii)** Some of ligands oxidise Co^{2+} to Co^{3+} ion.
  - **(iv)** EDTA is used for estimation of Ca^{2+} and Mg^{2+} in hard water.
  - **(v)** Silver and gold are extracted by treating Zn with their cyanide complexes.
  - **(vi)** Ni^{2+} is tested and estimated by DMG (dimethyl glyoxime).
  - **(vii)** *cis*-platin $[Pt(NH_3)_2Cl_2]$ is used as antitumor agent in the treatment of cancer.
  - **(viii)** EDTA is used to remove Pb by forming Pb-EDTA complex which is eliminated in urine.
  - **(ix)** Haemoglobin contains Fe, chlorophyll contains (Mg) and vitamin B_{12} contain Co^{2+} 'which are all coordination compounds'.
  - **(x)** Bauxite is purified by forming complex with NaOH.
  - **(xi)** Coordination compounds are used as catalysts for many industrial processes.

Know the Terms

- **Homogeneous Catalysis :** Organometallic compounds or intermediates derived from soluble transition metal complexes catalyse a variety of reaction in solutions. This is known as **homogeneous catalysis.**
- **Macrocyclic effect :** Multidentate ligands happen to be cyclic in nature without causing any steric hindrance, the stability of the complexes is further increased. This is known as **macrocyclic effect.**
- **Stability constants (K) :** The relative stabilities of coordination complexes can be compared in terms of stability constant (K) also denoted by β (Beta).
- **Metal carbonyl :** Organometallic compounds in which carbon monoxide acts as the ligand.

How is it done on the GREENBOARD?

Q. (i) Describe the type of hybridisation for the complex ion [Fe(H2O)6]2+.

(ii) Write the IUPAC name of the ionisation isomer of the coordination compound [Co(NH3)5Br]SO4. Give one chemical test to distinguish between the two compounds.

Solutions:

STEP-1: (i) Fe exists as Fe^{2+}. Fe (II) in $[Fe(H_2O)_6]^{2+}$ = $3d^6\ 4s^0\ 4p^0\ 4d^0$

STEP-2: As water is a weak ligand, pairing does not occur and the 6 lone pairs available from each water molecule moves to one 4s, three 4p and two 4d orbitals. Thus, the hybridisation involved is sp^3d^2.

(marks to be granted if hybridisation is depicted diagrammatically)

STEP-3: (ii) The ionisation isomer is $[Co(NH_3)_5SO_4]Br$. The IUPAC name is Pentaamminesulphatocobalt (III) bromide.

STEP-4: The isomer $[Co(NH_3)_5Br]SO_4$ gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution whereas the isomer $[Co(NH_3)_5SO_4]$ Br does not form this precipitate. (or any other relevant test)

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. The crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complexes is related as

(a) $\Delta_t = \frac{2}{9}\Delta_o$

(b) $\Delta_t = \frac{5}{9}\Delta_o$

(c) $\Delta t = \frac{4}{9}\Delta_o$

(d) $\Delta_t = 2\Delta_o$

R **[CBSE OD Set-2 2020]**

Ans. Correct option : (c)

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

Q. 2. Which set of ions exhibit specific colours?(Atomic number of Sc=21, Ti=22, V=23, Mn=25, Fe=26, Ni=28, Cu=29 and Zn=30)

(a) Sc^{3+}, Ti^{4+}, Mn^{3+}

(b) Sc^{3+}, Zn^{2+}, Ni^{2+}

(c) V^{3+}, V^{2+}, Fe^{3+}

(d) Ti^{3+}, Ti^{4+}, Ni^{2+} A&E **[CBSE SQP 2021]**

Ans. Correct option : (c)

Explanation : V^{3+}, V^{2+}, Fe^{3+} ions exhibit specific colours.

Atomic number of V = 23,
Electronic configuration of V – $[Ar]3d^34s^2$
Electronic configuration of V^{2+} – $[Ar]3d^3$
Electronic configuration of V^{3+} – $[Ar]3d^2$

Atomic number of Fe = 26
Electronic configuration of Fe – $[Ar]3d^64s^2$
Electronic configuration of Fe^{3+} – $[Ar]3d^5$

Since these ions have partially filled d-subshells , they exhibit colour. Most transtition metal ions have a partially filled d subshell.
As for other ions,
Atomic number of Sc = 21
Electronic configuration of Sc – $[Ar]3d^14s^2$
Electronic configuration of Sc^{3+} – $[Ar]3d^0$

Q. 3. Atomic number of Mn, Fe and Co are 25, 26, 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?

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

(b) $[Mn(CN)_6]^{3-}$

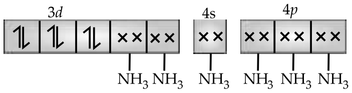
(c) $[Fe(CN)_6]^{3-}$

(d) None of the above

Ans. Correct option : (a)

Explanation :

Molecular orbital electronic configuration of Co^{3+} in $[Co(NH_3)_6]^{3+}$ is



Number of unpaired electron = 0
Magnetic property = Diamagnetic

[B] ASSERTIONS AND REASONS :

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices

- **(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.**
- **(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.**
- **(c) Assertion is correct statements but reason is wrong statement.**
- **(d) Assertion is wrong statements but reason is correct statement.**

Q. 1. Assertion : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Reason : Because it has d^2sp^3 type hybridisation.

R **[NCERT Exemplar]**

Ans. Correct option : (d) **1**

Explanation : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

Q. 2. Assertion : $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.
Reason : Unpaired electrons are present in their d-orbitals.

R **[NCERT Exemplar]**

Ans. Correct option : (b) **1**

Explanation : In the complexes, Co exists as Co^{2+} and Fe as Fe^{2+}. Both of the complexes become satble by oxidation of metal ion to Co^{3+} and Fe^{3+}.

Q. 3. Assertion : Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
Reason : Geometrical isomerism is not shown by complexes of coordination number 6.

U **[NCERT Exemplar]**

Ans. Correct option : (b) **1**

Explanation : For complexes of MX_6 and MX_5L type, different geometric arrangements of the ligands are not possible due to presence of plane of symmetry.

Q. 4. Assertion : Low spin tetrahedral complexes are rarely observed.
Reason : Crystal field splitting is less than pairing energy for tetrahedral complexes.

R **[CBSE Delhi Set-1 2020]**

Ans. Correct option : (a) **1**

Explanation : In tetrahedral complexes, the splitting of the d-orbitals is inverted and is smaller in comparison to octahedral complexes.The Crystal field splitting energy is not large enough to force pairing and hence, low spin complexes are rarely observed.

[C] VERY SHORT ANSWER TYPE QUESTIONS :

AI **Q. 1. Why are low spin tetrahedral complexes not formed?**

A&E **[CBSE Comptt. Delhi Set-1, 2, 3 2017]**

Ans. Orbital splitting energies are not sufficiently large for forcing pairing. **1**

[CBSE Marking Scheme 2017]

Q. 2. Low spin configuration are rarely observed in tetrahedral coordination entity formation. Explain.

A&E **[CBSE SQP 2018-2019]**

Ans. The Orbital splitting energies, Δ_t, are not sufficiently large for forcing pairing of electrons in the tetrahedral coordination entity formation. **1**

[CBSE Marking Scheme 2018]

Q. 3. A coordination compound with molecular formula $CrCl_3.4H_2O$ precipitates one mole of AgCl with $AgNO_3$ solution. Its molar conductivity is found to be equivalent to two ions. What is the structura; formula and name of the compound? [A][CBSE SQP 2017]

Ans. $[Cr(H_2O)_4Cl_2]Cl$
Tetraaquadichloridochromium (III) chloride. **1**

[CBSE Marking Scheme 2017]

Q. 4. On the basis of crystal field theort, write the electronic configuration of d^6 in terms of t_{2g} and eg in an octahedral field when $\Delta_0 < P$.

A **[CBSE SQP 2018-2019]**

Ans. $t^3_{2g}e^3_g$ **1**

Short Answer Type Questions-I

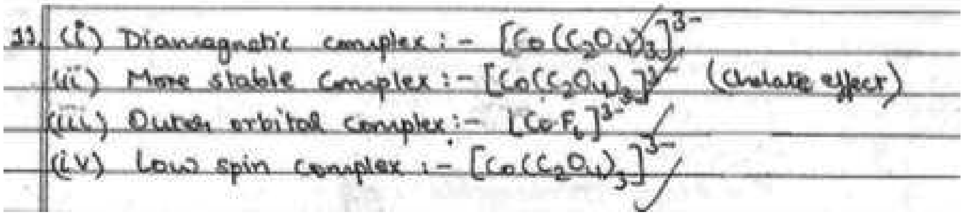
(2 marks each)

Q. 1. Out of $\left[CoF_6\right]^{3-}$ and $\left[Co(en)_3\right]^{3+}$, which one complex is,
- **(i) Paramagnetic,**
- **(ii) More stable,**
- **(iii) Inner orbital complex and**
- **(iv) High spin complex**

(Atomic number of Co = 27)

A&E **[CBSE Delhi Set 1 2019]**

Ans. (i) $[CoF_6]^{3-}$
(ii) $[Co(en)_3]^{3+}$
(iii) $[Co(en)_3]^{3+}$
(iv) $[CoF_6]^{3-}$ **[CBSE Marking Scheme, 2019]** ½ × 4



11. (i) Diamagnetic complex :- $[Co(C_2O_4)_3]^{3-}$
(ii) More stable Complex :- $[Co(C_2O_4)_3]^{3-}$ (Chelate effect)
(iii) Outer orbital complex :- $[CoF_6]^{3-}$
(iv) Low spin complex :- $[Co(C_2O_4)_3]^{3-}$

[Topper's Answer 2019]

Q. 2. 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 number of Co = 27)

A&E [CBSE Delhi Set 2 2019]

Ans. (i) $[Co(C_2O_4)_3]^{3-}$
(ii) $[Co(C_2O_4)_3]^{3-}$
(iii) $[CoF_6]^{3-}$
(iv) $[Co(C_2O_4)_3]^{3-}$

[CBSE Marking Scheme, 2019] ½ × 4

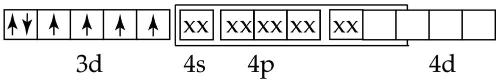
Q. 3. Write the hybridization and magnetic character of the following complexes:
- **(i) $[Fe(H_2O)_6]^{2+}$**
- **(ii) $[Fe(CO)_5]$** **U [CBSE Delhi Set 2 2019]**

Ans. (i) sp^3d^2, Paramagnetic ½ + ½
(ii) sp^3d^2, Paramagnetic

[CBSE Marking Scheme, 2019] ½ +½

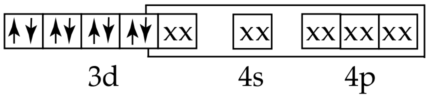
Detailed Answer :

(i) In $[Fe(H_2O)_6]^{2+}$ the oxidation state of Fe is +2. The outermost electronic configuration of Fe is $3d^64s^24p^0$. H_2O is weak field ligand and do not cause pairing up of electrons.



In this complex, there are 4 unpaired electrons. Therefore, it involves sp^3d^2 hybridisation and is paramagnetic.

(ii) In $[Fe(CO)_5]$ the oxidation state of Fe is zero. The outermost electronic configuration of Fe is $3d^64s^24p^0$. CO is strong field ligand, causes pairing up of 4s electrons into the 3d orbitals.



In this complex, there is no unpaired electron. Therefore, it involves dsp^3 hybridisation and is diamagnetic. **2**

Q. 4. Define the following terms with a suitable example of each :
- **(a) Chelate complex**
- **(b) Ambidentate ligand**

Ans. (a) A complex formed by bi or polydentate ligands with metal. Example- $[Co(en)_3]^{3+}$. ½ + ½
(b) A ligand which can ligate through two different donor atoms. Example-SCN^-. ½ + ½

[CBSE Marking Scheme, 2019] ½ +½

Detailed Answer :

(a) Chelate complex is the complex formed when a di – or polydentate ligand uses its two or more donor atoms to bind a single metal atom.

(b) Ligand which can ligate through two different atoms is called ambidentate ligand.

Q. 5. Using IUPAC norms, write the formula for the following complexes :
- **(a) Tetraamminediaquacobalt(III) chloride**
- **(b) Dibromidobis(ethane-1,2-diamine)platinum(IV) nitrate** **A [CBSE OD Set-2 2019]**

(i) $[Co(NH_3)_4(H_2O)_2]Cl_3$ **1**
(ii) $[Pt\,Br_2(en)_2](NO_3)_2$

[CBSE Marking Scheme, 2019] 1

Q. 6. (a) Using valence bond theory, write the hybridization and magnetic character of the complex $[Fe(CN)_6]^{4-}$. (Atomic no. of Fe=26)

(b) Write the electronic configuration of d^6 on the basis of crystal field theory when :
- (i) $\Delta_0 < P$ and
- (ii) $\Delta_0 > P$ **A [CBSE OD Set-2 2019]**

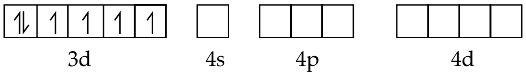
Ans. (a) d^2sp^3, diamagnetic ½ + ½
(b) (i) $t_{2g}{}^4e_g{}^2$ **(ii)** $t_{2g}{}^6e_g{}^0$ ½ + ½

[CBSE Marking Scheme, 2019]

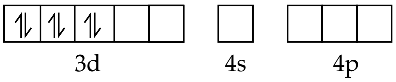
Detailed Answer :

(a) Oxidation number of Fe is + 2 in $[Fe(CN)_6]^{4-}$

$Fe^{2+} - 3d^6$



CN^- being strong ligand pairs with 3*d* orbital of Fe^{2+}



Six CN^- ions give their six pairs of electron to the empty orbitals. The orbitals utilized for hybridization is d^2sp^3.

Magnetic character – Diamagnetic

Q. 7. (a) Although both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ have sp^3 hybridisation yet $[NiCl_4]^{2-}$ is paramagnetic and $[Ni(CO)_4]$ is diamagnetic. Give reason. (Atomic no. of Ni = 28)

(b) Write the electronic configuration of d^5 on the basis of crystal field theory when.

(i) $\Delta_o < P$ and **(ii)** $\Delta_o > P$

U **[CBSE OD Set-3 2019]**

Ans. (a) In $[NiCl_4]^{2-}$, Cl^- is a weak field ligand due to which there are two unpaired electrons in 3*d* orbital whereas in $[Ni(CN)_4]^{2-}$, CN- is a strong field ligand due to which pairing leads to no unpaired electron in 3*d*- orbital/ or structural representation. ½ + ½

(b) (i) $t_{2g}^3 e_g^2$ (ii) $t_{2g}^5 e_g^0$ ½ + ½

[CBSE Marking Scheme, 2019]

Detailed Answer :

(a) In $[NiCl_4]^{2-}$ Ni is in +2 oxidation state and each Cl^- donates a pair of electron. So, Cl^- acts as a weak ligand and does not cause any forced pairing. Thus, electrons remains unpaired making it paramagnetic.

In $[Ni(CO)_4]$, Ni is in zero oxidation state and CO acts as a strong ligand causing forced pairing. Thus, no electron remains unpaired making it diamagnetic.

Q. 8. (i) Using crystal field theory, write the electronic configuration of iron ion in the following complex ion. Also predict its magnetic behaviour:
$[Fe(H_2O)_6]^{2+}$

(ii) Write the IUPAC name of the coordination complex: $[CoCl_2(en)_2]NO_3$

Ans. (i) $t_{2g}^4 e_g^2$ Paramagnetic [½ + ½]

(ii) Dichloridobis (ethane-1,2-diamine)cobalt (III) nitrate **[1]**

Q. 9. (i) Predict the geometry of $[Ni(CN)_4]^{2-}$

(ii) Calculate the spin only magnetic moment of $[Cu(NH_3)_4]^{2+}$ ion. [A&E][CBSE SQP 2021]

Ans. (i) Square planar [1]

(ii) $Cu^{2+} = 3d^9$ unpaired electron so

$\sqrt{(3)} = 1.73\,\text{BM}$ **[1]**

Short Answer Type Questions-II

(3 marks each)

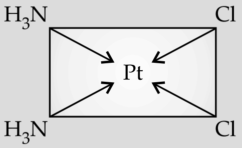
Q. 1. (i) Draw the geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$.

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

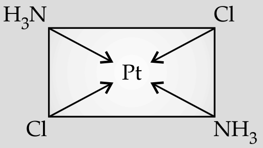
(iii) Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$. (At. no. of Ni = 28)

A **[CBSE Delhi 2015]**

Ans. (i)

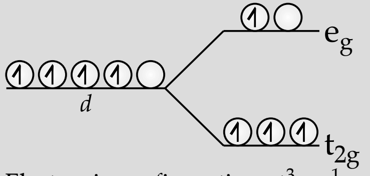


Cis-diamminedichloro platinum (II)



Trans-diamminedichloro platinum (II)

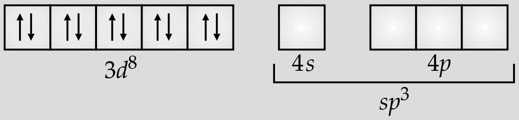
(ii) When $\Delta_o < P$, it is weak field and high spin situation. As a result, one electron entered in e_g orbital and 3 electrons in t_{2g}. 1



Electronic configuration : $t^3_{2g}\, e^1_g$ 1

(iii) $Ni(CO)_4$: The outermost electronic configuration will be $3d^8\, 4s^2\, 4p^o$.

CO is the strong ligand, causes pairing up of the 4s electrons into the 3d electrons



Thus, the hybridization will be sp^3 (tetrahedral) $Ni(CO)_4$ will be diamagnetic in nature.

Q. 2. (i) What type of isomerism is shown by the complex $[Cr(H_2O)_6]Cl_3$?

(ii) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o > P$.

(iii) Write the hybridization and shape of $[CoF_6]^{3-}$. (Atomic number of Co = 27)

A **[CBSE OD 2015]**

Ans. (i) Hydration isomerism 1

(ii) Electronic configuration is t^4_{2g} or by diagram. 1

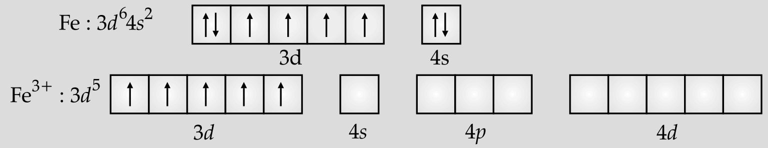
(iii) Hybridization is sp^3d^2 and shape is octahedral. ½ + ½

Q. 3. (i) For the complex $[Fe(CN)_6]^{3-}$, write the hybridization, magnetic character and spin nature of the complex. (At. number : Fe = 26).

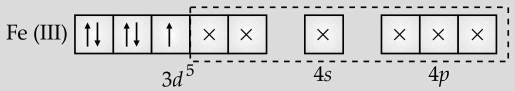
(ii) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically active.

A **[CBSE Delhi 2016]**

Ans. (i) $[Fe(CN)_6]^{3-}$

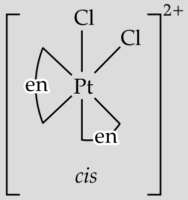


Since CN⁻ is strong field ligand, pairing takes place.



Hybridization – d^2sp^3(octahedral), Magnetic character – Paramagnetic, Spin nature – Low spin complex

(ii)



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Commonly Made Error

- Some students write incorrect electronic configuration of ions.

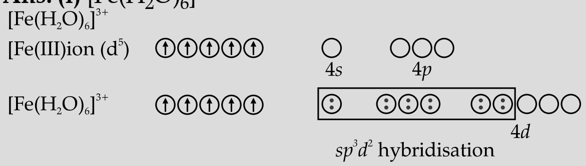
Answering Tip

- Do practice for writing the electronic configuration of metal atom in coordination compounds.

Q. 4. (i) For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number : Fe = 26).

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

Ans. (i) $[Fe(H_2O)_6]^{3+}$



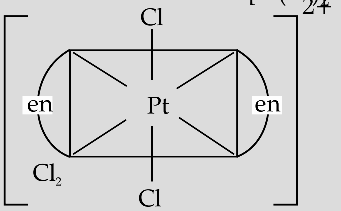
Since H_2O is a weak field ligand, it cannot cause pairing of electrons. Therefore, the number of unpaired electrons is 5.

$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.92\,\text{BM}$$

Thus, it is strongly paramagnetic (due to presence of unpaired electrons).

In $[Fe(H_2O)_6]^{3+}$ outer d-orbitals are used in hybridization to form high spin complex.

(ii) Geometrical isomers of $[Pt(en)_2Cl_2]^{2+}$



trans-$[PtCl_2(en)_2]^{2+}$ is optically inactive

Q. 5. (i) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.

(ii) $[Ni(CN)_4]^{2-}$ is colourless whereas $[Ni(H_2O)_6]^{2+}$ is green. Why? (At. no. of Ni = 28)

A&E **[CBSE Foreign Set-1 2017]**

Ans. (i) It is the magnitude of difference in energy between the two sets of *d* orbital i.e. t_2g and e_g **1**

$t^3_{2g}e^1_g$ **1**

(ii) In $[Ni(H_2O)_6]^{2+}$, $Ni^{+2}(3d^8)$ has two unpaired electrons which do not pair up in the presence of weak field ligand H_2O. **1**

[CBSE Marking Scheme 2017]

Detailed Answer:

(i) The difference in energy between the two sets of *d*-orbital (t_{2g} and e_g) caused by splitting of the degenerate levels due to the presence of ligands in a definite geometry.

Electronic configuration: $t^3_{2g}e^1_g$

(ii) In $[Ni(H_2O)_6]^{2+}$, Ni is present in +2 state with the configuration $3d^8$. It has two unpaired electrons which do not pair up in the presence of the weak H_2O ligand. Therefore, it is green in colour. While undergoing d–d transition, red light is absorbed and complementary light emitted is green.

In case of $[Ni(CN)_4]^{2-}$, Ni is in +2 state with the configuration $3d^8$ but in presence of the strong CN^- ligand, the two unpaired electrons in the 3d orbitals undergoes pairing. As there is no unpaired electron present, it is colourless.

Q. 6. (i) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o > P$.

(ii) $[Ni(CN)_4]^{2-}$ is diamagnetic whereas $[NiCl_4]^{2-}$ is paramagnetic. Give reason. (At. no. of Ni = 28)

R + A + A&E **[CBSE Foreign Set-2 2017]**

Ans. (i) It is the magnitude of difference in energy between the two sets of *d* orbital i.e. t_2g and e_g **1**

$t^4_{2g}e_g^0$ **1**

(ii) In $[Ni(CN)_4]^{2-}$, CN^- is a strong field ligand and pairing takes place whereas in $[NiCl_4]^{2-}$, due to the presence of Cl^-, a weak field ligand no pairing occurs/diagrammatic representation. **1**

[CBSE Marking Scheme 2017]

AI Q. 7. A metal ion M^{n+} having d^4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_o > P$.

(i) Write the electronic configuration of d^4 ion..

(ii) What type of hybridisation will M^{n+} ion has?

(iii) Name the type of isomerism exhibited by this complex. **A [CBSE SQP 2017]**

Ans. (i) $t_{2g}^4 e_g^0$ **1**

(ii) sp^3d^2 **1**

(iii) optical isomerism **1**

[CBSE Marking Scheme 2017]

Q. 8. (a) Write the formula of the following coordination compound : Iron(III) hexacyanoferrate(II)

(b) What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$?

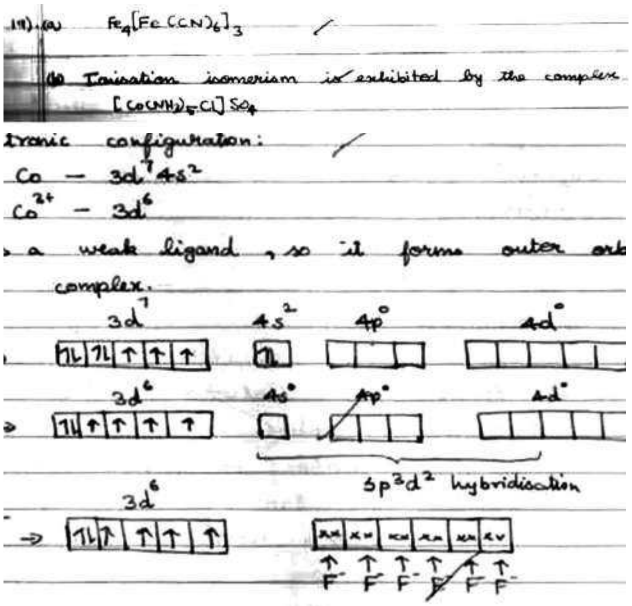
(c) Write the hybridization and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic No. of Co = 27) **A [CBSE 2018] 3**

Ans. (a) $Fe_4[Fe(CN)_6]_3$ **1**

(b) ionisation isomerism **1**

(c) sp^3d^2, 4

[CBSE Marking Scheme 2018] ½, ½



19). (a) $Fe_4[Fe(CN)_6]_3$ ✓

(b) Ionisation isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$

tronic configuration: ✓

$Co - 3d^7 4s^2$

$Co^{3+} - 3d^6$

a weak ligand, so it forms outer orb

complex.

[Topper's Answer 2018]

Visual Case based Questions

(4 marks each)

Q. 1. Read the passage given below and answer the following questions: **(1×4=4)**

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

Ans: Correct option: (c)

Explanation : $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$ **[1]**

(ii) The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be

(a) 18,000 cm^{-1} **(b)** 16,000 cm^{-1}

(c) 8,000 cm^{-1} **(d)** 20,000 cm^{-1}

Ans: Correct option: (c)

Explanation : 8,000 cm^{-1} **[1]**

(iii) An aqueous pink solution of cobalt(II) chloride changes to deep blue on addition of excess of HCl. This is because _____________.

(a) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_6]^{4-}$

(b) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$

(c) tetrahedral complexes have larger crystal field splitting than octahedral complex.

(d) None of the above

Ans: Correct option: (b)

Explanation : $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$. **[1]**

(iv) A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?.

(a) thiosulphato **(b)** oxalato

(c) glycinato **(d)** ethane-1,2-diamine **[1]**

Ans: Correct option: (a)

Explanation : Thiosulphato is a monodentate ligand whereas Oxalato, glycinato and ethylene diamine are bidentate ligands and can form rings with the central metal ion. So, they all are also chelating ligands. Thiosulphato is a monodentate ligand and hence, cannot form chelate rings. Hence, it is not a chelating ligand

Q. 2. According to Valence Bond Theory, the metal atom or ion under the influence of ligands can use its (n−1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

In these questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement

(d) Assertion is wrong statement but reason is correct statement.

(i) Assertion : In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state.

Reason : Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals.

Ans : Correct option: (b)

Explanation : In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$.

(ii) Assertion : $[NiCl_4]^{2-}$ is an inner orbital complex.

Reason : An inner orbital or low spin or spin paired complex uses inner d orbitals of the metal ion for hybridisation.

Ans : Correct option: (d)

Explanation : $[NiCl_4]^{2-}$ is high spin complex.

(iii) Assertion : In the square planar complexes, the hybridisation involved is dsp2.

Reason : In $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$.

Ans : Correct option: (b)

(iv) Assertion : The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4d) in hybridisation (sp^3d^2).

Reason : It is a high spin complex.

Ans : Correct option: (c)

Explanation : The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4d) in hybridisation (sp^3d^2). It is a low spin complex.

Q. 3. Read the passage given below and answer the following questions: (1×4=4)

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called isomers. Isomers are compounds with the same molecular formula but different structural formulas and do not necessarily share similar properties. There are many different classes of isomers, like stereoisomers, enantiomers, and geometrical isomers. There are two main forms of isomerism: structural isomerism and stereoisomerism. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Indicate the complex ion which shows geometrical isomerism.

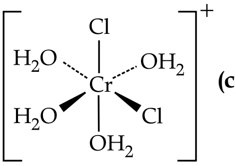
(a) $[Cr(H_2O)_4Cl_2]^+$ **(b)** $[Pt(NH_3)_3Cl]$

(c) $[Co(NH_3)_6]^{3+}$ **(d)** $[Co(CN)_5(NC)]^{3-}$

Ans: Correct option: (a)

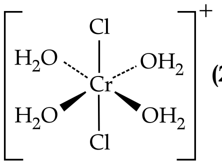
Explanation :

(1)



and

(c) doc b



(2)

[1]

(ii) What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (greyish-green)?

(a) linkage isomerism **(b)** solvate isomerism

(c) ionisation isomerism **(d)** coordination isomerism

Ans: Correct option: (b)

Explanation : solvate isomerism **[1]**

(iii) Which of the following complexes show linkage isomerism?

(a) $[Co(H_2O)_5CO]^{3+}$ **(b)** $[Cr(NH_3)_5SCN]^{2+}$

(c) $[Fe(en)_2Cl_2]^+$ **(d)** All of the above

Ans: Correct option: (b)

Explanation : Linkage isomerism is the existence of coordination compounds that have the same composition differing with the connectivity of the metal to a ligand. Typical ligands that give rise to linkage isomers are: thiocyanate, SCN −, isothiocyanate, NCS − **[1]**

(iv) Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are

(a) linkage isomers **(b)** coordination isomers

(c) ionisation isomers **(d)** geometrical isomers

Ans: Correct option: (a)

Explanation : Same as above **[1]**

Self Assessment Test-9

Time : 1 Hour **Max. Marks : 25**

AI **1. Read the passage given below and answer the following questions : (1 × 4 = 4)**

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand. Thus, the dx^2y^2 and dz^2 orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the *dxy, dyz* and *dxz* orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.

Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement

(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion:** The degeneracy of the d orbitals is removed in the octahedral complexes.

Reason: The degeneracy is removed due to ligand electron-metal electron repulsions.

(ii) **Assertion:** The crystal field splitting, Δo , depends upon the field produced by the ligand and charge on the metal ion.

Reason: The energy of the two e_g orbitals will increase by (3/5) Δ_o and that of the three t_{2g} will decrease by $(2/5)\Delta_o$.

(iii) **Assertion:** Spectrochemical series is theoretically determined series based on the absorption of light by complexes with different ligands.

Reason: Ligands can be arranged in a series in the order of increasing field strength called the spectrochemical series.

(iv) **Assertion:** In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Reason: The orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed in tetrahedral complexes.

OR

AI **Assertion:** $[Fe(CN)_6]^{3-}$ complex is paramagnetic.

Reason: Cyanide ion is strong field ligand hence favouring Spin pairing.

Following questions (No. 2 to 5) are Multiple Choice Questions Carrying 1 mark each.

Q. 2 The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is

(a) Diamminedichloridoplatinum (II)

(b) Diamminedichloridoplatinum (IV)

(c) Diamminedichloridoplatinum (I)

(d) Diamminedichloridoplatinum (IV) A

Q 3. Which of the following complexes are homoleptic?

(a) $[Co(NH_3)_4Cl_2]^+$

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

(c) $[NI(NH_3)_4Cl_2]$

(d) All of the above U

Q 4. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?

(a) $[Fe(CO)_5]$

(b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(C_2O_4)_3]^{3-}$

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

Q 5. Which of the following species is not expected to be a ligand?

(a) NO

(b) NH_4^+

(c) $NH_2CH_2CH_2NH_2$

(d) CO U

The following questions (Q. no. 6 & 7), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement

(d) Assertion is wrong statement but reason is correct statement.

AI **Q 6. Assertion:** $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons.

Reason: This difference is due to the presence of strong ligand CN^- and weak ligand H_2O in these complexes. U

Q 7. Assertion: $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic and the latter is diamagnetic.

Reason: The reason is presence of neutral ligands. R

Q. No. 8 & 9 are Short Answer Type-I Carrying 2 marks each.

Q 8. Write the IUPAC name of the complex $[Cr(NH_3)4Cl_2]+$. What type of isomerism does it exhibit? A **[2]**

Q 9. Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

Q. No. 10 & 11 are Short Answer Type-II Carrying 3 marks each.

Q. 10. (i) On the basis of crystal field theory, write the electronic configuration for 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) A **[3]**

Q. 11. (i) Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$.

(ii) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. nos. : Cr = 24, Co = 27, Ni = 28)

Q.No 12 is Long Answer Type Carrying 5 marks each.

Q 12. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex :

(a) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$

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

(c) $[CrCl_3(py)_3]$

(d) $Cs[FeCl_4]$

(e) $K_4[Mn(CN)_6]$ A **[NCERT]**

OR

Specify the oxidation numbers of the metals in the following coordination entities :

(a) $[Co(H_2O)(CN)(en)_2]^{2+}$

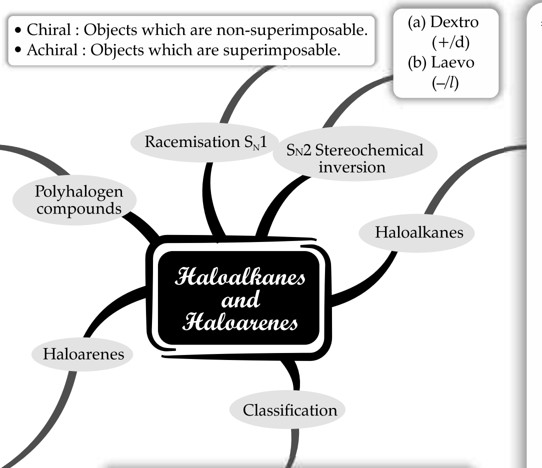
(b) $[CoBr_2(en)_2]^{+}$

(c) $[PtCl_4]^{2-}$

(d) $K_3[Fe(CN)_6]$

(e) $[Cr(NH_3)_3Cl_3]$ A

●●



- Chiral : Objects which are non-superimposable.
- Achiral : Objects which are superimposable.

(a) Dextro (+/d)
(b) Laevo (–/l)

Polyhalogen compounds

Chloroform
- Solvent for fats, alkaloids, I etc.
- Production of freon.

Iodoform
Antiseptic

Carbon tetrachloride
- Manufacture of refrigerants and propellants.
- Cleaning fluid.

Freons
For aerosol propellants, refrigeration and air conditioning purposes.

DDT
As insecticide

Dichloromethane
- Paint remover.
- Propellant in aerosols.
- Metal cleaning and finishing solvent.

Haloalkanes

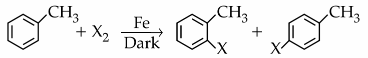
=>Preparation
- From alcohol :

$$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$$
$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3$$
$$ROH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

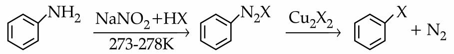
- From hydrocarbons :
  (a) By free radical halogenation

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

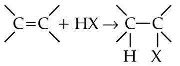
  (b) By electrophilic substitution



  (c) Sandmeyer's reaction



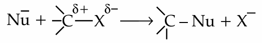
  (d) From alkenes



$$H_2C{=}CH_2{+}Br_2 \xrightarrow{CCl_4} BrCH_2\text{–}CH_2Br$$

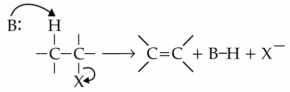
- Halogen exchange :
  R–X + NaI → R – I + NaX

=>Properties
- Physical : Colourless, volatile, sweet smell.
  Lower members are gases at room temperature while higher are solids.
  B.P : RI > RBr > RCl > RF.
  M.P : Para isomers have high m.p. than ortho and meta – isomers.
  Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.
  Solubility : Very slightly soluble in water.
- Chemical :
  (a) Nucleophilic substitution



For S_N2 reaction
Tertiary, Secondary, Primary
For S_N1 reaction

  (b) Elimination reaction



B = Base; X = Leaving group

  (c) Reaction with metals

$$CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$$

Wurtz reaction :

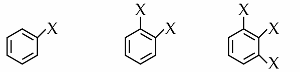
$$2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$$

Classification

- No. of halogen atoms

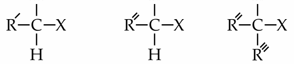
C_2H_5X Monohaloalkane

CH_2X–CH_2X Dihaloalkane

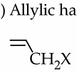


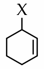
Monohaloarene Dihaloarene Trihaloarene

- Compounds containing sp^3 C–X bond
  (a) Alkyl halides

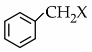


  (b) Allylic halides



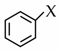


  (c) Benzylic halides

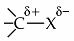


- Compounds containing sp^2 C–X bond
  (a) Vinylic halides

  (b) Aryl halides

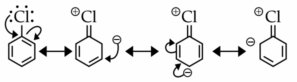


- Nomenclature
  Common name : Alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.
  IUPAC name : Numerals are used.
- Nature of C –X bond
  : Carbon –halogen bond is polarized.

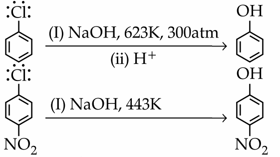


Haloarenes

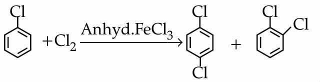
- Reactions :
  (a) Nucleophilic substitution
    (i) Resonance effect

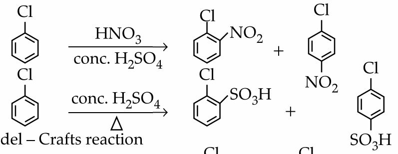


    (ii) Hybridisation of C in C-X bond :
      Haloalkane –sp^3; Haloarence –sp^2
    (iii) Phenyl cation unstabilised by resonance

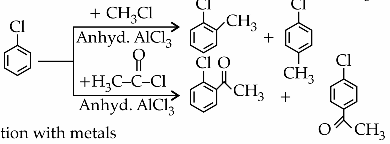


  (b) Electrophilic substitution

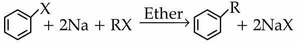




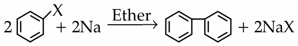
Friedel – Crafts reaction



  (c) Reaction with metals
    Wurtz – Fitting reaction



    Fittig reaction



Trace the Mind Map
- First Level
- Second Level
- Third Level