UNIT 9

Coordination Compounds

Points to Remember

Introduction : Coordination compounds are those molecular compounds which retain their identify in solid as well as in solution

Example,

$K_4[Fe(CN)_6] + H_2O \rightarrow 4K^+ (aq) + [Fe(CN)_6]^{4-} (aq)$

Types of Complex

(I) Anionic complex

$K_3[Fe(C_2O_4)_3] \rightarrow 3K^+ + [Fe(C_2O_4)_3]^{3-}$

Anionic complex

(ii) Cationic complex

$[CoCl_2(en)_2] Cl \rightarrow [CoCl_2(en)_2]^+ + Cl^-$

Cationic complex

(iii) Neutral complex

$[Ni(CO)_4]$

Neutral complex

Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Types of Ligands

Unidentate :

A ligand which is bound to a metal ion through a single donor atom.

e.g., H_2O, NH_3, CO, Cl^-, NH_2^- etc

Bidentate :

A ligand which is bound to a metal ion through two donor atoms.

Example:

COO^- $\vert$ COO^-	$CH_2\text{-}NH_2$ $\vert$ $CH_2\text{-}NH_2$
Oxalate ion	Ethane-1,2-diamine

Polydentate :

A ligand which is bound to a metal ion through several donor atoms.

e.g., ethylenediamine tetraacetate ion $[EDTA]^{4-}$.

Ambidentate ligands, which can bind through two different donor sites but binds through one site only

e.g., - NO_2^- & -ONO^-

SCN^- & SNC^-

CN^- & NC^-

Chelate ligands: These may be a di- or polydentate ligand which form closed ring with central metal ion. Complex such formed are known as chelate complex. More the number of chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

Homoleptic Complexes	Heteroleptic Complexes
Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic.	Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic.
e.g., $[Co(NH_3)_6]^{3+}$	e.g., $[Co(NH_3)_4Cl_2]^{+}$

Nomenclature of Coordination Compounds

Neutral Complex
$[Pt(NH_3)_2Cl(NO_2)]$
Diamminechloridonitrito - N - platinum (II)
(I) Name of ligands in alphabetical order
(II) Central metal atom and oxidation state

Anionic Complex
$K_3[Fe(CN)_6]$
Postassium hexacyanatoferrate (III)
(I) Name of ionisable metal
(II)Name of ligand in alphabetical order
(III) Central metal atom + ate and oxidation state

Cationic Complex

$[Cr(NH_3)_3(H_2O)_3]Cl_2$
Triamminetriaquachromium(III) chloride
1. Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.
2. Central metal atom and oxidation state indicated by Roman numerals in parenthesis.
3.Name of ionisable anion.

Isomerism in Coordination Compounds

Note: Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types :

Geometrical Isomerism

Optical Isomerism.

Optical Isomerism

- It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called dextro (d) and laevo (l).
- Optical isomerism is common in octahedral complexes but at least one didentate ligand must be present.

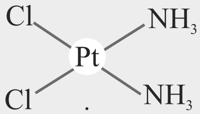
e.g., $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$etc.

Geometrical Isomerism

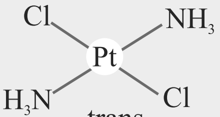
It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), The two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.

e.g., $[Pt(NH_3)_2Cl_2]$



cis



trans

Square planar complex of the type [MABXL](where A, B, X, L are unidentates) shows three isomers - two cis and one trans. **Such isomerism is not possible for terahedral complexes.**

e.g., $[Pt(NH_3)(Br)(Cl)(Py)]$

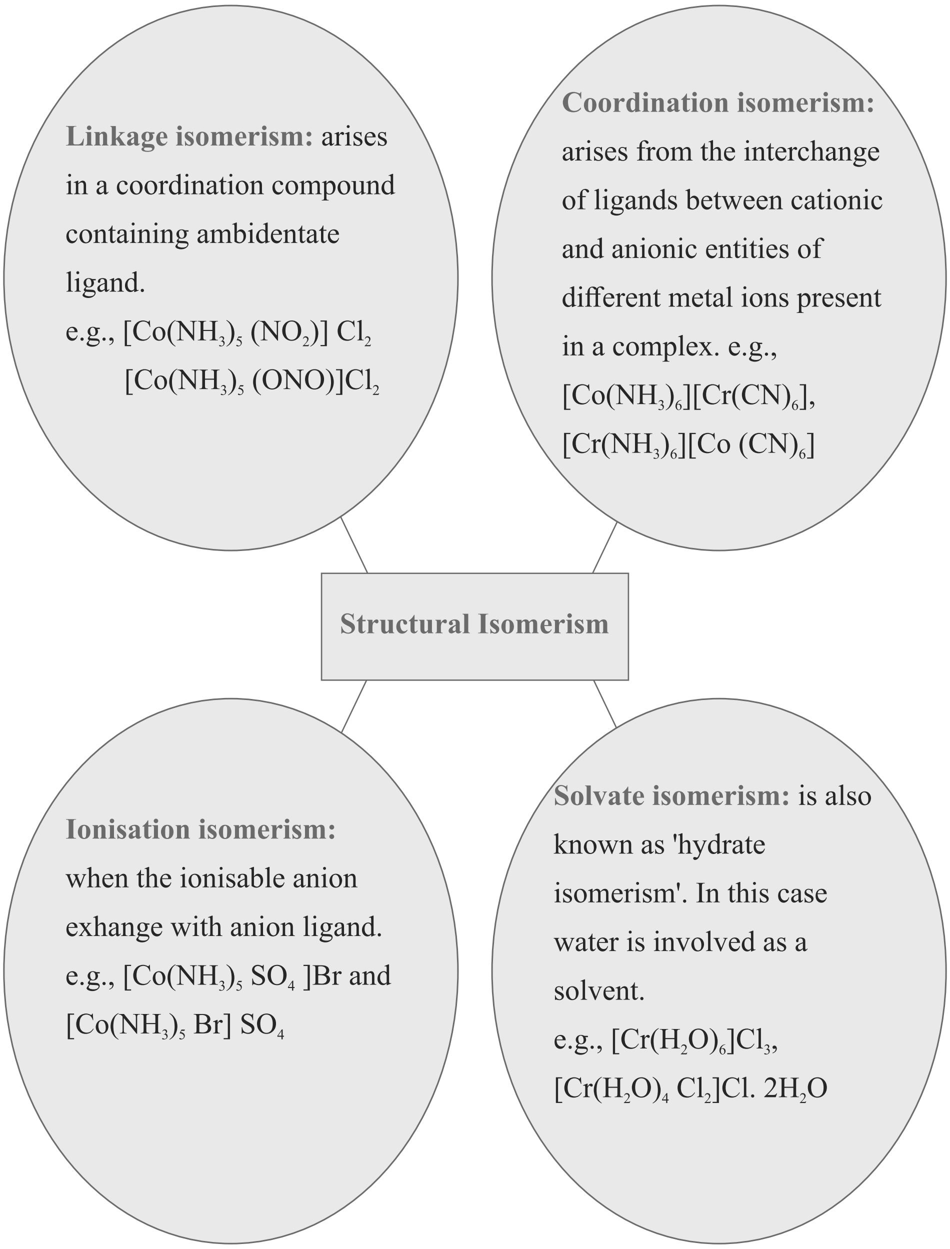
Octahedral complexes of formula $[MX_2A_2]$ where X are unidentates and A are didentate and form cis and trans isomers.

e.g., $[CoCl_2(en)_2]$

Octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented cis or trans to each other.

e.g., $[Co(NH_3)_4 Cl_2]^+$

Octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3 (NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



Structural Isomerism

Linkage isomerism: arises in a coordination compound containing ambidentate ligand.
e.g., $[Co(NH_3)_5 (NO_2)] Cl_2$
$[Co(NH_3)_5 (ONO)]Cl_2$

Coordination isomerism: arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. e.g., $[Co(NH_3)_6][Cr(CN)_6]$, $[Cr(NH_3)_6][Co (CN)_6]$

Ionisation isomerism: when the ionisable anion exhange with anion ligand. e.g., $[Co(NH_3)_5 SO_4]Br$ and $[Co(NH_3)_5 Br] SO_4$

Solvate isomerism: is also known as 'hydrate isomerism'. In this case water is involved as a solvent.
e.g., $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_4 Cl_2]Cl. 2H_2O$

Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies - primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non- ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

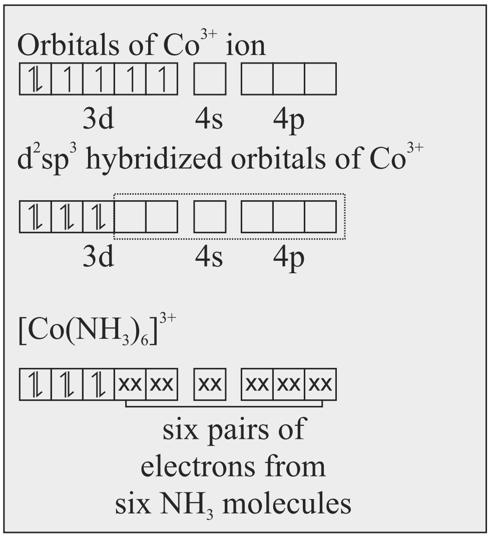
(i) **Six ligands (unidentate) (octahedral entity)** Generally central atom belongs 3d series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

Inner orbital complexes,
Which are formed due to participation of (n-1)d orbitals in hybridisation is (d^2sp^3) and shape of complex will be octahedral.

Outer orbital complexes,
Which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2).

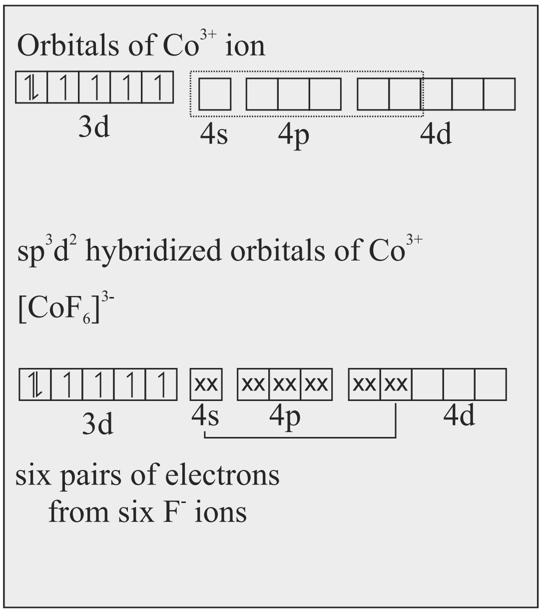
Generally halides (F^- Cl^- Br^- I^-), SCN^-,S^{2-} From outer orbital complexes and other ligands from inner orbital complexes.

e.g., Inner orbital complex, $[Co(NH_3)_6]^{3+}$



All electrons are paired therefore, complex will be diamagnetic in nature.

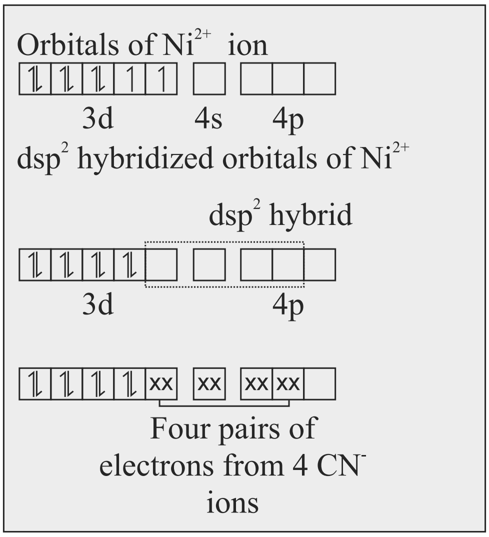
e.g., Outer orbital complex, $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

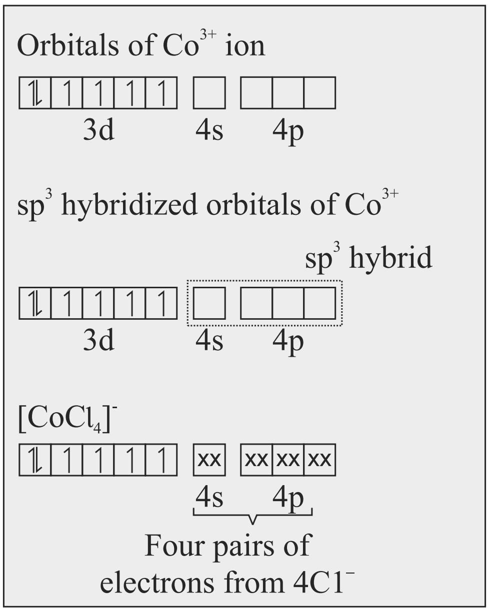
Complexes with coordination number: 4

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



All electrons are paired. Complex will be diamagnetic in nature.

2. **$[CoCl_4]^-$**

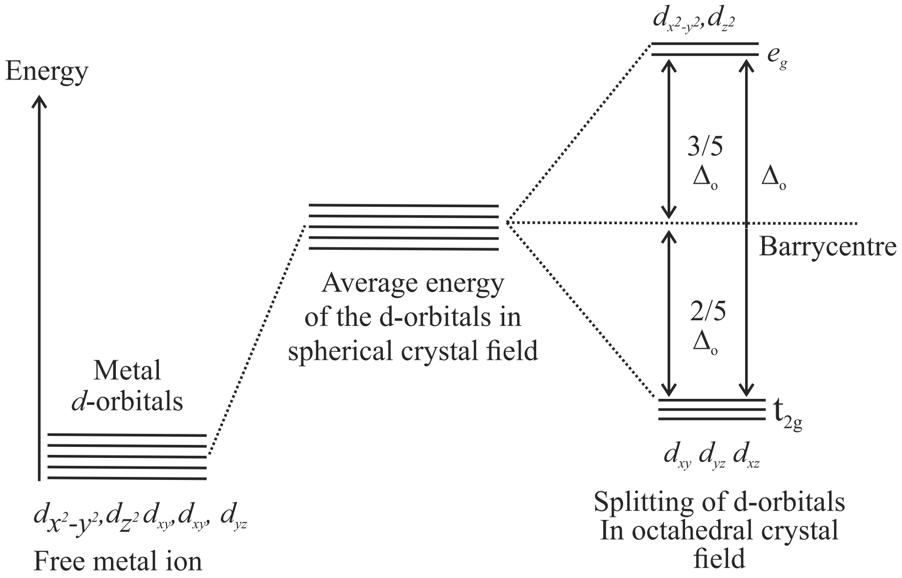


Complex has unpaired electrons. Complex will be paramagnetic in nature.

Crystal Field Theory

The five d-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field splitting. The five d-orbitals in a gaseous metal atom/ion have same energy.

(i) **Crystal field splitting in octahedral coordination entities**



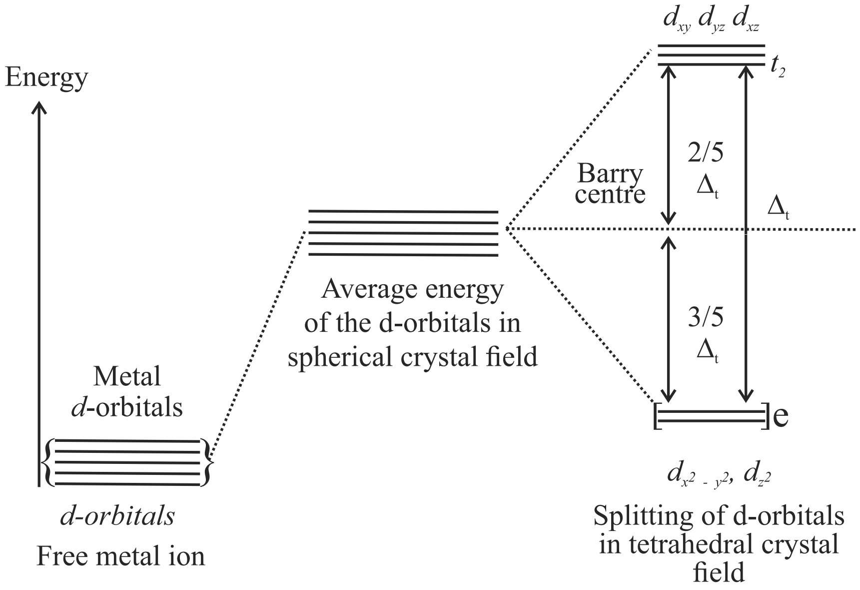
- Energy separation is denoted by Δ_o (the subscript o is for octahedral).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by $(3/5)\Delta_o$. and that of the three t_{2g} (lower energy orbitals) will decrease by $(2/5)\,\Delta_o$.
- If $\Delta_o < P$, the fourth electron enters one of the e_g, orbitals giving the configuration $t^3_{2g}\,e_g^1$.

  Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

- If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^o$.

Ligands which produce this effect are known as strong field ligands and form low spin complexes, where P represents the energy required for electron pairing in a single orbital.

(ii) **Crystal field splitting in tetrahedral coordination entities.**



- In tetrahedral coordination entities, $\Delta_t = (4/9)\Delta_o$.

Consequently the orbital splitting energies are not sufficiently large for forcing pairing, therefore, low spin configurations are rarely observed.

- Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

- In complex compounds d-orbitals split in two sets t_{2g} and e_g These have different energies. The electron jump from ground state t_{2g} level to higher state e_g level. This is known as d-d transition and it is responsible for colour of coordination compounds.
- d-d transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured. On the other hand, the ions d^0 and d^{10} configuration do not show d-d transition.

Importance and Applications of Coordination Compounds.

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with $EDTA^{2-}$.
- Some important extraction processes of metals, like those of silver and gold make use of complex formation.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium.

Supplementary List of Ligands

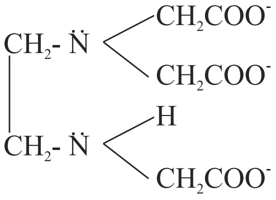
Ligand	F^-	$C1^-$	Br^-	I^-	OH^-	CN^-	O^{2-}	O_2^{2-}	O_2^-	CO_3^{2-}	PH_3
Name	fluoro	chloro	bromo	iodo	hy droxido	cyanido	Oxido	peroxido	super oxido	carbonato	phos phine
Ligand	SO_4^{2-}	NO_2^-	ONO	SCN^{-1}	NCS	CH_2COO^-	C_5H_5N	S^{2-}	$S_2O_3^{2-}$	NO_3	SO_3^{2-}
Name	suphato	nitro	aitrito	thiocyanato	isothiocyanato	acetato	pyridine (Py)	sulphido	thiosulphato	nitrato	sulphito
Ligand	NC^-	$(C_6H_5)_3P$	CS	NH_2^-	NH^{2-}	H_2NCSNH_2	$C_2O_4^{2-}$	H_2O	NH_3	CO	NO
Name	isocyano	triphenyl phosphine	thiocarbonyl	amido	imido	thiourea (tu)	oxalate (ox)	aqua	ammine	carbonyl	nitrosyl

$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$

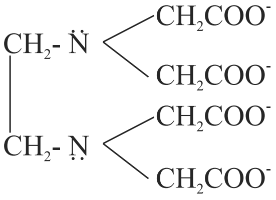
ethane-1, 2- diamine (en)

$H_2NCH_2CH_2NHCH_2CH_2NH_2$

Diethylenetriamine(diene)



Ethylenediaminetriacetate ion ($EDTA^{3-}$)



Ethylenediaminetetracetate ion ($EDTA^{4-}$)

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Which of the following compounds formed by Cu^{2+} ions is most stable?

(a) $Cu^{2+}+4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$;log K=11.6

(b) $Cu^{2+}+4CN^- \rightarrow [Cu(CN_4]^{2-}$;log K=27.3

(c) $Cu^{2+}+2en \rightarrow [Cu(en)_2]^{2+}$;log K=15.4

(d) $Cu^{2+}+4H_2O \rightarrow [Cu(H_2O)_4]^{2+}$;log K=8.9

2. The colour of the coordination compounds depends on the crystals 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) $[Co(CN)_6]^{3-}>[Co(NH_3)_6]^{3+}>[Co(H_2O)_6]^{3-}$

3. When 0.1 mol $CoCl_3 \cdot NH_3$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to-

(a) 1 : 3 electrolyte (b) 1 : 2 electrolyte

(c) 1 : 1 electrolyte (d) 3 : 1 electrolyte

4. The correct IUPAC name of $[Pt(NH_3)_2 Cl_2]$ is-

(a) Diamminedichloridoplatinum (II)

(b) Diamminedichloridoplatinum (IV)

(c) Diamminedichloridoplatinum (0)

(d) Diamminedichloridoplatinum (IV)

5. Out of the following the most stable complex species is

(a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(C_2O_4)_3]^{3+}$ (d) $[Fe(H_2O)_6]^{3+}$

6. 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}

7. Which of the following species is not likely to be a ligand?
   (a) NH_2^- (b) NH_4^+
   (c) $NH_2CH_2NH_2$ (d) CO

8. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is:
   (a) Platinum diaminechloritrite
   (b) Chloronitrito-N-ammine platinum(II)
   (c) Diamminechloridonitrito-N-platinum (II)
   (d) Diamminechlornitrite-N-platinate(II)

9. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex is diamagnetic?
   (a) $[Co(NH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{3-}$
   (c) $[Fe(CN)_6]^{4-}$ (d) $[Fe(CN)_6]^{3-}$

10. $[Fe(CN)_6]^{3-}$ complex is ....
   (a) sp^3 hybridised (b) sp^3d^2 hybridised
   (c) paramagnetic (d) diamagnetic

11. The denticity of 'PPh_3' and 'en' are respectively-
   (a) 1,1 (b) 2,1
   (c) 3,2 (d) 1,2

12. The type of isomerism exhibited by complex $[Co(NH_3)_4Br_2]Cl$?
   (a) Geometrical and Ionization (b) Geometrical and Optical
   (c) Optical and Ionization (d) Geometrial only

13. Complex which will be colourless is -
   (a) $[Ti(H_2O)_6]^{3+}$ (b) $[Ti(NO_3)_4]$
   (c) $[Cr(NH_3)_6]^+$ (d) $[Fe(CN)_6]^{4-}$

14. $K_3[CoF_6]$ is a high spin complex. The hybridisation of Co in complex will be-
   (a) sp^3d (b) sp^3d^2
   (c) d^2sp^3 (d) dsp^2

15. Complex which is paramagnetic as well as tetrahedral is-
   (a) $[Ni(CO)_4]$ (b) $[NiCl_4]^{2-}$
   (c) $[Ni(CN)_4]^{2-}$ (d) None of these

16. On dissolving $K_4[Fe(CN)_6]$ in water, presence of .... ions are detected.
   (a) K^+ only (b) Fe^{2+} only
   (c) CN^- only (d) Both K^+ and CN^-

17. The complex ion, which does not have any 'd' electron in central metal atom is-
    (a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$
    (c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

18. Two isomers of a complex are **A** and **B**. If **A** gives white precipitate on reacting with $BaCl_2$, while **B** gives precipitate of AgCl on reaction with $AgNO_3$. The complex **B** and type of isomerism exhibited by it are–
    (a) $[Co(NH_3)_5Cl]SO_4$, Ionization (b) $[Co(NH_3)_5 Cl]SO_4$, Coordination
    (c) $[Co(NH_3)_5SO_4]Cl$, Ionization (d) $[Co(NH_3)_5SO_4]Cl$, Coordination

19. The complex which shows optical isomerism is-
    (a) trans-$[Co(en)_2Cl_2]Cl$ (b) $[Co(NH_3)_4 Cl_2]Cl$
    (c) $[Co(NH_3)_3Cl_3]$ (d) cis-$[Co(en)_2Cl_2]Cl$

II FILL IN THE BLANKS

1. The IUPAC name of linkage isomer of $[Co(NH_3)_5NO_2]C1_2$ is...............................
2. The oxidation state of Ni in $K_2[Ni(CN)_4]$ is...........................
3. The metal present in vitamin B_{12} is....................
4. NO is named as.......................
5. Octahedral crystal field splitting of d-orbitals give the three d orbitals having lower energy are collectively called...................
6. The number of isomers of $[Pt(NH_3)_2Cl_2]$ are.........................
7. In complex $[Fe(H_2O)_6]^{3+}$ number of unpaired electrons are......................
8. Number of ions produced per mole of the complex $[Co(NH_3)_5Cl]Cl_2$ are ....
9. Out of *cis* and *trans* isomer of $[RhCl(en)_2]^+$, ...isomer shows optical activity.
10. Dentisity of $EDTA^{4-}$ ligand is ....

III ASSERTION REASON TYPE QUESTIONS

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

(a) Both assertion and reason are True, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are True, but reason is not the correct explanation of the assertion.

(c) Assertion is True, but reason is False.

(d) Both assertion and reason are False.

1. **ASSERTION:** Toxic metal ions are removed by the chelating ligands.
   REASON: Chelate complex tend to be more stable.
2. **ASSERTION:** $[(Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   REASON: Because it has d^2sp^3 type hybridisation.
3. **ASSERTION:** Carbon monoxide forms low spin complexes with metals.
   REASON: Carbon monoxide is neutral oxide.
4. **ASSERTION:** Carbon monoxide is a deadly poison.
   REASON: CO can form strong complexes with haemoglobin.
5. **ASSERTION :** Tetrahedral complexes cannot exhibit geometrical isomerism.
   REASON: Tetrahedral complexes are chiral in nature.
6. **ASSERTION:** An octahedral complex with two didentate ligands is always optically active.
   REASON: The cis - isomer of the octahedral complex is chiral.
7. **ASSERTION:** Ionisation isomerism is shown by complexes having ambidentate ligands.
   REASON: Ambidentate ligands have two possible ligating centres.
8. **ASSERTION:** $[Fe(CN)_6]^{3-}$ is more paramagnetic than$[FeF_6]^{3-}$.
   REASON: $[FeF_6]^{3-}$ has more number of unpaired electrons.
9. **ASSERTION:** $[Co(NH_3)_6]^{3+}$ is an inner orbital complex.
   REASON: $[Co(NH_3)_6]^{3+}$ forms an octahedral complex.
10. **ASSERTION:** $[Fe(ox)_3]^{3-}$ is more stable than $[Fe(H_2O)_6]^{3+}$
    REASON: $[Fe(ox)_3]^{3-}$ is a chelate complex.

IV ONE WORD TYPE QUESTIONS

1. What is the oxidation state of Ni in $[Ni(CO)_4]$?
2. Write IUPAC name of $[Ni(CN)_4]^{2-}$.
3. What is the hybridisation of Co in the complex $[CoF_6]^{3-}$?
4. Write the chemical formula of potassium trioxalatochromate(III).
5. Name the transition element present in haemoglobin.

6. What is denticityof triphenylphosphine?
7. Out of NH_3 and H_2O which is strong field ligand?
8. Write electronic configuration of Fe in complex $[Fe(CN)_6]^{4-}$.
9. What is the coordination number of Cr in $[Cr(en)_2Cl_2]Cl$?
10. How many geometrical isomers are possible for $[Cr(ox)_3]^{3-}$?
11. Give the linkage isomer of $[Pd(PPh_3)_2(NCS)_2]$?
12. How many unpaired electrons are present in $[Fe(NH_3)_6]Cl_3$?
13. Name the imperfect complex compound which ionizes completely in solutions.
14. Give an example of hexadentate ligand.
15. Write the coordination number of 'Fe' in $K[Fe(CN)_2(en)_2]$

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. What is ambidentate ligand ? Give one example.

Ans. Monodentate ligands contain more than one coordinating atoms. Example, CN^-.

Q.2 Write the IUPAC name of $[PtCl_2(en)_2(NO_3)_2]$.

Ans. Dichloridobis(ethane-1, 2-diamine)nitratoplatinum (IV)

Q.3. What is a chelate ligand ? Give one example.

Ans. The complex in which ligand binds through two or more donor sites simutaneously to form cyclic complexes. Example: ethane-1-2 diamine.

Q.4. How many geometrical isomers are possible for the $[Ni(NH_3)_4]^{2+}$?

Ans. Not possible, because all 4 ligands are same.

Q.5. Define coordination polyhedron.

Ans. The spatial arrangement of the ligand with the central metal ion.

Q.6. Give the chemical formula of potassium hexacyanidoferrate (II).

Ans. $K_4[Fe(CN)_6]$.

Q.7. Name the metal present in : (i) Chlorophyll (ii) cis platin

Ans. (i) Mg (ii) Pt

Q.8. Which of the two is more stable — $K_4[Fe(CN)_6]$ Or $K_3[Fe(CN)_6]$?

Ans. $K_4[Fe(CN)_6]$ because Fe has d^6 configuration in this case.

Q.9. Arrange the following complexes in order of increasing electrical conductivity : $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4]Cl_3$

Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_4]Cl_3$

More number of ions, more electrical conductivity

Q.10. Give an example of the role of coordination compounds in biological system.

Ans. Haemoglobin, the red pigment of blood acts as oxygen carrier. It is a coordination compound of iron.

Q.11. Why is CO a stronger ligand than Cl^-?

Ans. CO is a stronger ligand than Cl^- due to back bonding between its empty p-orbitals and filled d-orbitals of central metal ion which in turn increases Δ_o value.

Q.12. What do you understand by denticity of a ligand?

Ans. Denticity of a ligand is the number of coordinating or ligating groups sites present in a ligand.

Q.13. What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

Ans. Coordination number = Number of ligands x Denticity = 3 x 2 = 6

Q.14 Name two properties of the central metal atom/ion which enable it to form stable complex entities.

Ans. (a) Small size of metal ion

(b) High charge on the metal ion.

Q.15 Write the IUPAC name of the complex $[Cr(en)_3][Co(CN)_6]$.

Ans. Tris (ethane- 1, 2-diamine)chromium(III) hexacyanidocobaltate(III)

Q.16. A blue coloured solution of $[CoCl_4]^{2-}$ ion changes to pink on reaction with $HgCl_2$. Why ?

Ans. $CoCl_4^{2-} + HgCl_2 \longrightarrow Co[HgCl_4] + 2Cl^-$

[Blue] [Pink]

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q.1. Explain the following :

(i) NH_3 act as a ligand but NH_4^+ does not.

(ii) CN^- is a ambidentate ligand.

Ans. (i) NH_3 has one lone pair while NH_4^+ does not.

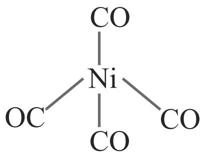
(ii) Because it has two donor atoms in a monodentate ligand, can bind through either C or N.

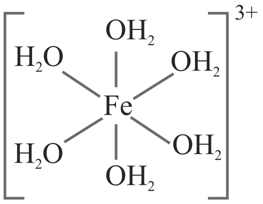
Q. 2. Mention the main postulates of Werner theory.

Ans. (i) Metal ion has two types of valency. (ii) Primary valency and secondary valency. (iii) Secondary valency is equal to coordination number.

Q. 3. Draw the structure of : (i) $[Ni(CO)_4]$ (ii) $[Fe(H_2O)_6]^{3+}$

Ans.





Q.4. How does EDTA help as a cure for lead poisoning ?

Ans. Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble complex Pb-EDTA is eliminated in urine.

Q.5. Define homoleptic and heteroleptic complexes.

Ans. Homoleptic : When metal atom/ion is linked with one type of ligands. Example, $[Ni(CO)_4]$.

Heteroleptic : When metal atom/ion is linked with the more than one kind of ligands. Example, $[Co(NH_3)_4Cl_2]^+$

Q.6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why ?

Ans. In $[NiCl_4]^{2-}$, Ni has $3d^8 4s^0$ configuration, Cl^- can not pair up while in $[Ni(CO)_4]$, Ni has $3d^8 4s^2$ configuration, CO pair up electrons

Q.7. The oxidation number of cobalt in the complex : (i) $K[Co(CO)_4]$ (ii) $[Co(C_2O_4)_3]^{3-}$

Ans. (i) - 1 (ii) + 3

Q.8. What are t_{2g} and e_g orbitals ?

Ans. In a free transition metal ion, the d-orbitals are degenerate. When it form complex, the degeneracy is split and d-orbitals split into t_{2g} and e_g orbitals.

Q.9. What is spectrochemical series ?

Ans. The arrangement of ligands in order of their increasing crystal field splitting field strength.

Q.10. What are the assumptions of Crystal Field theory.

Ans. (i) Ligand act as a point charge. (ii) Metal ion has electrostatic attraction force with the ligand. (Or any other)

Q.11. $CuSO_4$ is colourless while $CuSO_4 .5H_2O$ is coloured. Why ?

Ans. $CuSO_4$ does not has any ligand, so no splitting of d-orbital take place while $CuSO_4$ $5H_2O$ has water at ligand.

Q.12. Differentiate between inner and outer orbital complexes.

Ans. Inner sphere complex : When d-orbital of inner shell take part in hybridisation. Outer sphere complex : When d-orbital of outermost shell take part in hybridisation.

Q.13. How is stability of coordination compound determined in aqueous solution ?

Ans. By using stability constant. Higher the value of stability constant, more stability.

Q.14. In a complex ion $[Co(NH_3)_5NO_2]Cl_2$,

(i) Identify the ligand. (ii) Oxidation number of metal ion.

Ans. (i) NH_3 , NO_2^- . (ii) + 3

Q.15. Explain how the nature of ligand affects the stability of complex ion.

Ans. Strong ligand : More stability Weak ligand : Less stability

LONG ANSWER TYPE QUESTIONS (5 Marks)

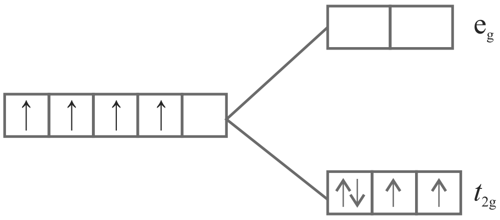
Q.1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_o > P$:

(i) Draw the diagram showing d-orbital splitting during this complex formation.

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

(iii) Name the type of isomerism exhibited by this complex.

Ans. (i) If $\Delta_o > P$ then



(ii) $d^2 sp^3$

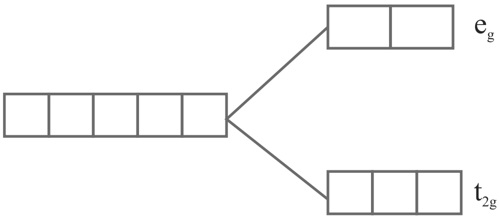
(iii) $[M(AA)_3]$ type complex show optical isomerism.

Q.2. (i) Discuss the nature of bonding in metal carbonyls.

(ii) Draw figure to show the splitting of d-orbitals in an octahedral crystal field and write electronic configuration of Mn^{2+} ion when : (a) $P > \Delta_o$ (b) $\Delta_o > P$

Ans. (i) The metal carbon bond in metal carbonyls possess both σ and π character. The M-C σ bond is formed by the M←C≡O while M-C π it bond is formed by the donation of a pair of electron from filled d-orbital of metal to antibonding π* orbital of CO.

(ii)



(a) $t_{2g}^{3} e_g^{2}$ (b) $t_{2g}^{5} e_g^{0}$

Q. 3. (i) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution. Why ?

(ii) A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio of 1 : 4. A 0.1m solution of this complex was found to be freeze at - 0.372 °C. What is the formula of the complex ? ($K_f = 1.86$ K kg mol^{-1})

Ans. (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN^- and H_2O has different crystal field splitting energy.

(ii) $\Delta T_f = i.K_f.$ m, $i = 2$ means complex dissociate into two ions. Hence the formula is $[Co(NH_3)_4 Cl_2]Cl$.

Q.4. $CoSO_4Cl.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$.

(i) Identify 'A' and 'B' and write their structural formulae. (ii) Name the type of isomerism involved. (iii) Give the IUPAC name of 'A' and 'B'.

Ans. (i) $A = [Co(NH_3)_5SO_4]Cl$, $B = [Co(NH_3)_5Cl]SO_4$

(ii) Ionisation iosmerism

(iii) (A) = Pentaamminesulphatocobalt(III) chloride

(B) = Pentaamminechloridocobalt(III) sulphate

Q.5. For the complexes $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ write -

(i) Oxidation state of Fe

(ii) IUPAC names

(iii) Magnetic behaviour

(iv) Spin type

(v) Which complex has higher λ_{max} of absorption?

Ans.

S.No.	$[Fe(CN)_6]^{4-}$	$[FeF_6]^{3-}$
(i)	+2	+3
(ii)	Hexacyanidoferrate (II)	Hexafluoridoferrate (III)
(iii)	Diamagnetic	Paramagnetic
(iv)	Low spin	High spin
(V)	lower λ_{max}	Higher λ_{max}

CASE STUDY BASED QUESTIONS

1. Read the passage and answer the following question.

According to the VBT , 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. The geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4d) in hybridisation (sp^3d^2). It is thus called outer orbital or high spin or spin free complex.

Source : NCERT

(A) Number of unpaired electrons present in $[CoF_6]^{3-}$ are :

(a) 4 (b) 3
(c) 2 (d) 1

(B) Out of following, paramagnetic complex is :

(a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(Cl)_4]^{2-}$
(c) $[Ni(CO)_4]$ (d) All of these

(C) Outer orbital complex is :

(a) $[CoF_6]^{3-}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Ni(CN)_4]^{2-}$ (d) None of these

(D) Inner orbital complex involves :

(a) nd orbitals (b) (n-1)d orbitals

(c) ns orbitals (d) None of these

2. Read the passage and answer the following question.

The degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o (the subscript o is for octahedral) . Thus, 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)Δ_o. The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. 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.

(A) The cause of removal of degeneracy of the d orbitals in coordination compunds is :

(a) higher nuclear charge

(b) ligand electron-metal electron repulsions

(c) Atomic size

(d) None of these

(B) The crystal field splitting is :

(a) The splitting of the degenerate levels due to the presence of ligands in a definite geometry.

(b) splitting of f- orbitals

(c) splitting of p- orbitals

(d) all of these

(C) Energy of two e_g orbitals in octahedral complexes increased by :

(a) $3/5\,\Delta_o$ (b) $2/5\,\Delta_o$

(c) $1/5\,\Delta_o$ (d) $5/3\,\Delta_o$

(D) The relationship between CFSE in tetrahedral field (Δ_t) and octahedral field (Δ_o) is

(a) $\Delta_t = 9/4\Delta_o$ (a) $\Delta_t = 4/9\Delta_o$

(c) $\Delta_t = 2\Delta_o$ (d) $\Delta_t = 5\Delta_o$

3. Read the passage and answer the following question.

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins. When a ligand is bound to a metal ion through a single donor atom, as with Cl^- H_2O or NH_3, the ligand is said to be unidentate. When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be didentate and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate.

Ethylenediaminetetraacetate ion $(EDTA)^{4-}$ is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Ligand which can ligate through two different atoms is called ambidentate ligand. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

(A) Ambidentate ligand is :

(a) CN^- (b) CO

(c) NH_3 (d) H_2O

(B) Total number of donor sites in ethane–1,2 –diamine is/are :

(a) 1 (b) 2
(c) 3 (d) 4

(C) Ligand with maximum denticity is-

(a) NC^- (b) $C_2O_4^{2-}$
(c) NH_3 (d) H_2O

(D) Chelating ligand is :

(a) $EDTA^{4-}$ (b) NH_3
(c) CN^- (d) H_2O

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (b) 2. (c) 3. (b) 4. (a) 5. (c) 6. (a) 7. (b) 8. (c) 9. (a) 10. (c)
11. (d) 12. (a) 13. (b) 14. (b) 15. (b) 16. (a) 17. (a) 18.(c) 19. (d)

II FILL IN THE BLANKS

1.pentaamminenitrito-O-cobalt(III) chloride 2. 2 3. Cobalt
4. Nitrosyl 5. t_{2g} 6. 4 7. 5 8. 3
9. cis 10. 6

III ASSERTION REASON TYPE QUESTIONS

1. (a) 2. (b) 3. (b) 4. (a) 5. (c) 6. (d) 7. (d) 8. (d) 9. (b) 10.(a)

IV ONE WORD QUESTION ANSWERS

1. 0 2. tetracynatonickelate(II) ion
3. $(CoF_6)^{3-}$, (sp^3d^2) 4. $(K_3[Cr(C_2O_4)_3])$
5. Iron 6. 1
7. NH_3 8. t_{2g}^{6}, e_g^{0}
9. 6 10. 0
11. $[Pd(PPh_3)_2(NCS)_2]$ 12. 1
13. Double salt 14. $[EDTA]^{4-}$
15. 6

CASE STUDY BASED QUESTIONS

1. (A) a (B) b
   (C) a (D) b
2. (A) b (B) a
   (C) a (D) b
3. (A) a (B) b
   (C) b (D) a

UNIT TEST-1

Coordination Compounds

Maximum Marks: 20 **Time Allowed : 1 hour**

1. Explain- $[Cr(en)_3]^{2+}$ is more stable than $[Cr(H_2O)_6]^{2+}$. 1
2. Give two examples of didentate ligands. 1
3. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_o > P$, write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.
4. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion. 1
5. For the complex $[CoBr_2(en)_2]^{2+}$, write coordination number and oxidation state of Co. 1
6. Name the isomerism exhibited by following coordination compounds: 2
   a) $[Co(NH_3)_5SO_4]Br$
   b) $[Fe(SCN)_6]^{3-}$
   c) $[Co(en)_3]^{2+}$
   d) $[Cr(en)_2(H_2O)_2]^{2+}$
7. Define following terms with suitable example. 2
   a) Spectrochemical Series
   b) Synergic Bonding
8. Write IUPAC names of following complexes: 2
   a) $[Fe(NH_3)_2(C_2O_4)_2]^{2-}$
   b) $[Cr(en)_2(H_2O)_2]^{2+}$
9. Explain hybridization, geometry, and magnetic behaviour of following complexes (Attempt any 2) 2
   a) $[Ni(CO)_4]$
   b) $[Mn(CN)_6]^{3-}$
   c) $[FeCl_6]^{3-}$
10. Arrange the following in increasing order of given properties: 3
    a) $[Co(NH_3)_3C1_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$ (Electrical Conductivity)
    b) $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$ (Wavelength of absorption)
    c) $[Co(NH_3)_6]^{3+}$, $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ (spin-only magnetic moment)
11. Explain following: 3
    a) $[Ni(H_2O)_6]^{2+}$ is green in colour while $[Ni(CN)_6]^{2-}$ is colourless.
    b) $[Fe(H_2O)_6]^{3+}$ is highly paramagnetic while $[Fe(CN)_6]^{3-}$ is weakly paramagnetic.
    c) $[NiCl_4]^{2-}$ is paramagnetic and $[Ni(CO)_4]$ is diamagnetic, even though both are tetrahedral

UNIT TEST-2

Coordination Compounds

Maximum Marks: 20 **Time Allowed : 1 hour**

1. Write coordination number and oxidation number of Cr in $[Cr(ox)_2Cl_2]^{3+}$. 1
2. Give two examples of ambidentate ligands. 1
3. Tetrahedral complexes does not exhibit geometrical isomerism. Explain.
4. Predict the hybridisation of $[FeCl_4]^-$ 1
5. Mention the denticity of $C_2O_4^{2-}$ & $EDTA^{4-}$ ligands. 1
6. Name the isomerism exhibited by following molecules: 2
   a) $[Fe(CN)_6]^{3-}$
   b) $[Co(NH_3)_5Cl]SO_4$
   c) $[Co(en)_3]^{3+}$
   d) $[Co(NH_3)_6][Cr(CN)_6]$
7. Define following terms giving examples: 2
   a) Ambidentate ligands
   b) Chelate effect
8. The molar conductivity of the complex $CrCl_3.4NH_3.\ 2H_2O$ is found to be same as that of 3:1 electrolyte. Write its structural formula, name and geometrical isomers of the complex. 2
9. Explain hybridization, geometry, and magnetic, behaviour of following Complexes (Attempt any 2) 3
   a) $[Ni(Cl)_4]^{2-}$
   b) $[Co(CN)_6]^{3-}$
   c) $[Cr(H_2O)_6]^{3+}$
10. a) Differentiate low spin and high spin complexes giving examples.
    b) How homoleptic complexes are different from heteroleptic complexes ?
    c) Write the chemical formula of potassium hexacyanatoferrate (II). 3
11. Explain following: 3
    a) CO is stronger ligand than NH_3 .
    b) Low spin octahedral complexes of nickel are not known.
    c) Aqueous solution of $[Ti(H_2O)_6]^{3+}$ is coloured.