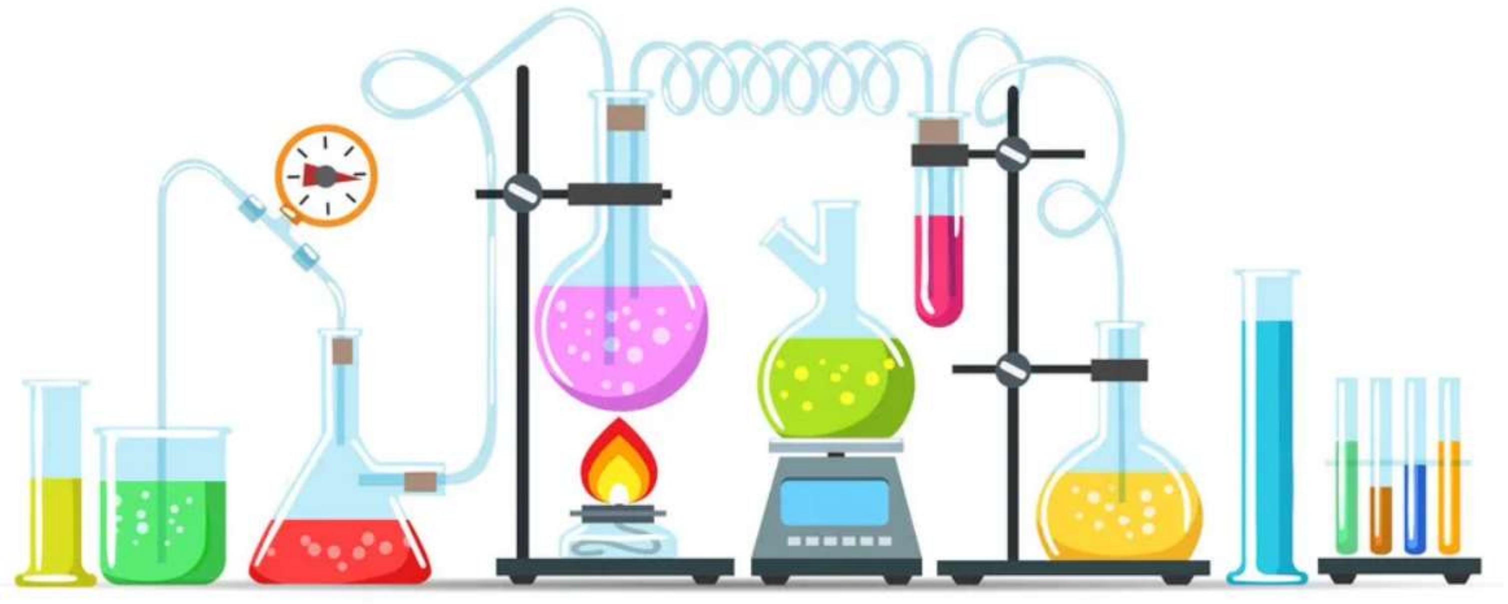
CHEMISTRY



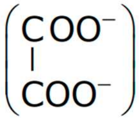
COORDINATION COMPOUNDS

COORDINATION COMPOUNDS

- **Differences between coordination compound and double bond**

Coordination compound	Double salt
A coordination compound contains a central metal atom or ion surrounded by several oppositely charged ions or neutral molecules. These ions or molecules re-bonded to the metal atom or ion by a coordinate bond.	When two salts in stoichiometric ratio are crystallised together from their saturated solution, they are called double salts.
Example: $K_4[Fe(CN)_6]$	**Example:** $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt)
They do not dissociate into simpleions when dissolved in water.	They dissociate into simple ions when dissolved in water.

- **Coordination entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: In $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ represents a coordination entity.
- **Central atom or ion:** In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement is called the central atom or ion. Example: In $K_4[Fe(CN)_6]$,Fe^{2+} is the central metal ion.
- **Ligands:** A molecule, ion or group which is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called a ligand. It may be neutral, positively ornegatively charged. Examples: H_2O, CN^-, NO^+ etc.
- **Donor atom:** An atom of the ligand attached directly to the metal is called the donor atom. Example:In the complex $K_4[Fe(CN)_6]$, carbon is a donor atom.
- **Coordination number:** The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. Example: In the complex $K_4[Fe(CN)_6]$, the coordination number of Fe is 6.
- **Coordination sphere**: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed the coordination sphere. Example: In the complex $K_4[Fe(CN)_6]$,$[Fe(CN)_6]^{4-}$ is the coordination sphere.
- **Counter ions:** The ions present outside the coordination sphere are called counter ions. Example: Inthe complex $K_4[Fe(CN)_6]$, K^+ is the counter ion.

- **Coordination polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. Examples: $[PtCl_4]^{2-}$ is square planar, $Ni(CO)_4$ is tetrahedral and $[Cu(NH_3)_6]^{3+}$ is octahedral.
- **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of thecharges on all the ligands coordinated to the central metal ion.
- **Denticity:** The number of ligating (linking) atoms present in a ligand is called denticity.
- **Unidentate ligands:** The ligands whose only donor atom is bonded to a metal atom are calledunidentate ligands. Examples: H_2O, NH_3, CO, CN^-
- **Didentate ligands:** The ligands which contain two donor atoms or ions through which they are bonded to the metal ion. Example: Ethylene diamine ($H_2NCH_2CH_2NH_2$) has two nitrogen atoms, and oxalate ion  $\left(\begin{array}{c} COO^- \\ | \\ COO^- \end{array}\right)$ has two oxygen atoms which can bind with the metal atom.
- **Polydentate ligand:** When several donor atoms are present in a single ligand, the ligand is called a polydentate ligand. Example: 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 twonitrogen and four oxygen atoms to a central metal ion.
- **Chelate:** An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points. An example is the complex ion formed between ethylene diamine and cupric ion $[Cu(NH_2CH_2NH_2)_2]^{2+}$.
- **Ambidentate ligands:** Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligands. Examples: NO^- and SCN^-. NO^- can link through N as well as O, while SCN^- can link through S as well as N.
- **Werner's coordination theory:** Werner was able to explain the nature of bonding in complexes. The postulates of Werner's theory are
  - Metal shows two kinds of valencies—primary valence and secondary valence.

Primary valence	Secondary valence
This valence is normally ionisable.	This valence is non-ionisable.
It is equal to the positive chargeon the central metal atom.	The secondary valency equals to the number of ligand atoms coordinated to the metal. It is also called the coordination number of the metal.
These valencies are satisfied by negatively charged ions.	It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.

Example: In $CrCl_3$, the primary valency is three. It is equal to the oxidation state of the centralmetal ion.	

- The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
- The most common geometrical shapes in coordination compounds are octahedral, square planarand tetrahedral.

- **Oxidation number of the central atom:** The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs whichare shared with the central atom.
- **Homoleptic complexes:** Those complexes in which metal or ion is coordinately bonded to only onekind of donor atom. Example: $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complexes:** Those complexes in which metal or ion is coordinately bonded to more thanone kind of donor atom. Example: $[CoCl_2(NH_3)_4]^+$, $[Co(NH_3)_5Br]^{2+}$
- **Isomers:** Two or more compounds which have the same chemical formula but different arrangementof atoms are called isomers.
- **Types of isomerism**
  - Structural isomerism
    - Linkage isomerism
    - Solvate isomerism or hydrate isomerism
    - Ionisation isomerism
    - Coordination isomerism
  - Stereoisomerism
    - Geometrical isomerism
    - Optical isomerism
- **Structural isomerism:** This type of isomerism arises due to the difference in structures of coordination compounds. Structural isomerism, or constitutional isomerism, is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.
  - **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

    Examples: $[Co(NH_3)_5Br]\ SO_4$ and $[Co(NH_3)_5\ SO_4]\ Br$
  - **Solvate isomerism:** It is isomerism in which the solvent is involved as the ligand. If the solvent is water, then it is called hydrate isomerism. Example: $[Cr(H_2O)_6]Cl_3$ and $[Crcl_2(H_2O)_4]\ Cl_2.2H_2O$
  - **Linkage isomerism:** Linkage isomerism arises in a coordination compound containing an ambidentate ligand. In the isomerism, a ligand can form linkage with metal through

different atoms.

Examples: $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$

- **Coordination isomerism:** This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. Examples: $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$

- **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.
  - **Geometrical isomerism:** It arises in heteroleptic complexes due to different possible geometricalarrangements of ligands.
  - **Optical isomerism:** Optical isomers are those isomers which are non-superimposable mirrorimages.

- **Valence bond theory:**

  According to this theory, the metal atom or ion under the influence of ligands can use its (n − 1)d, ns, np or ns, np or nd orbitals for hybridization to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral and square planar. These hybridised orbitals are allowed to overlap with ligand orbitals which can donate electron pairs for bonding.

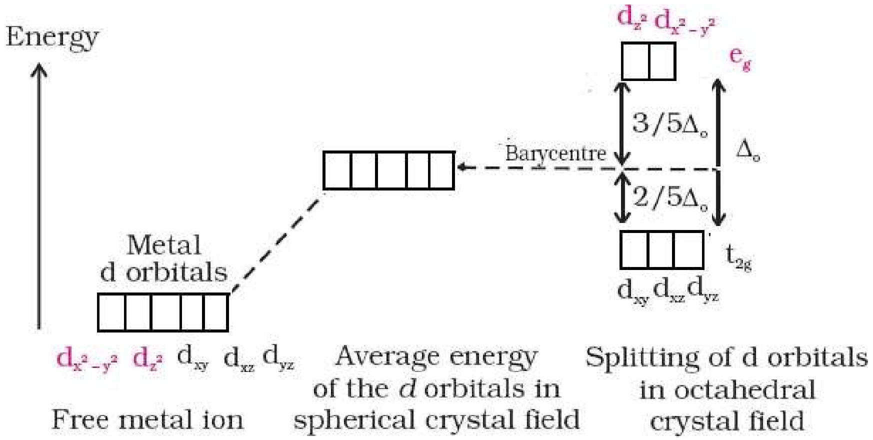
Coordinationnumber	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2 (nd orbitals are involved; outer orbital complex or high-spin or spin-free complex)	Octahedral
6	d^2sp^3 [(n − 1)d orbitals are involved; inner orbital complex or low-spin or spin-paired complex]	Octahedral

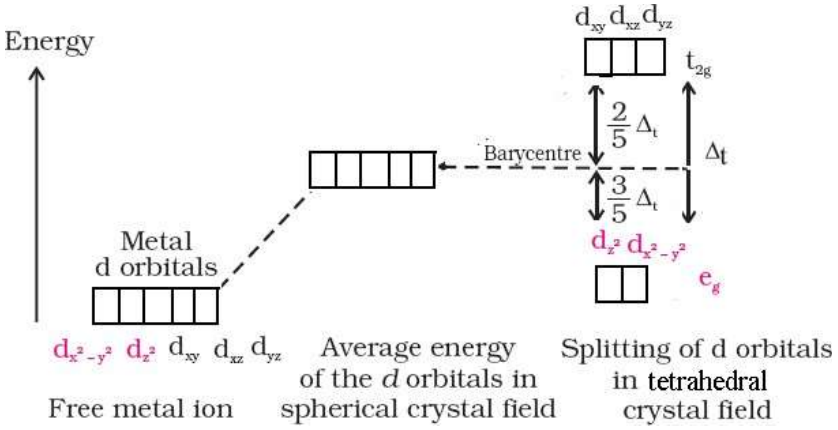
- **Magnetic properties of coordination compounds:** A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compoundare paired.

  Magnetic moment $\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons.

- **Crystal Field Theory:** It assumes the ligands to be point charges and there is an electrostatic force of attraction between ligands and the metal atom or ion. It is a theoretical assumption.

- **Crystal field splitting in octahedral coordination complexes**





- **Crystal field splitting in tetrahedral coordination complexes**
- For the same metal, the same ligands and metal–ligand distances, the difference in energy between $e_g$and t_{2g} level is

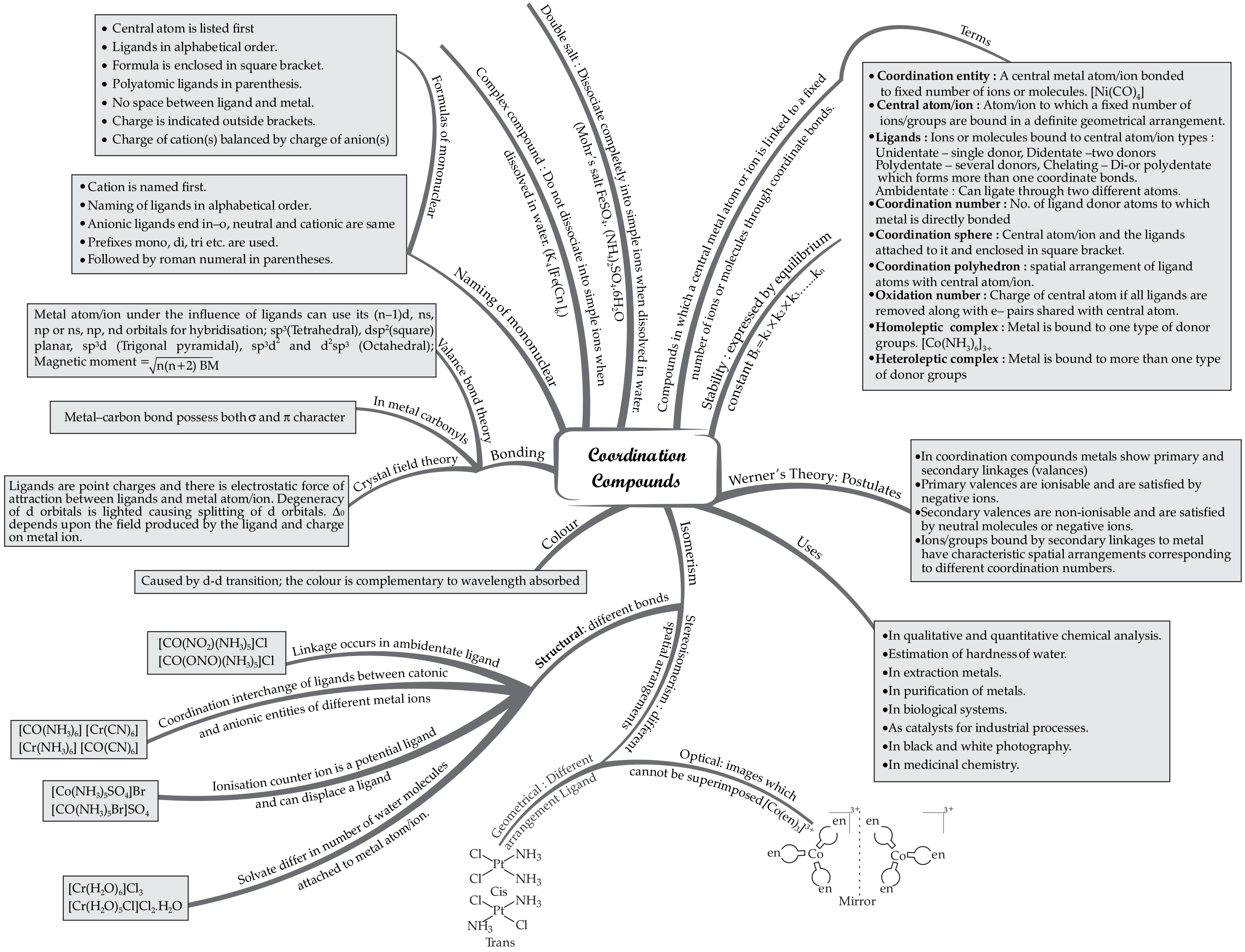
$$\Delta_t = \frac{4}{9}\Delta_0$$

- **Metal carbonyls:** Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts asthe ligand. Example: $Ni(CO)_4$

  The metal–carbon bond in metal carbonyls possesses both σ and π characters. The metal–carbon bond in metal carbonyls possess both *s* and *p* characters. The M–C σ bond is formed by the donation of a lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant anti-bonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 9



Coordination Compounds

Terms

- **Coordination entity :** A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- **Central atom/ion :** Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- **Ligands :** Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate –two donors Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
- **Coordination number :** No. of ligand donor atoms to which metal is directly bonded
- **Coordination sphere :** Central atom/ion and the ligands attached to it and enclosed in square bracket.
- **Coordination polyhedron :** spatial arrangement of ligand atoms with central atom/ion.
- **Oxidation number :** Charge of central atom if all ligands are removed along with e– pairs shared with central atom.
- **Homoleptic complex :** Metal is bound to one type of donor groups. $[Co(NH_3)_6]_{3+}$
- **Heteroleptic complex :** Metal is bound to more than one type of donor groups

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Stability : expressed by equilibrium constant $B_r = k_1 \times k_2 \times k_3 \ldots\ldots k_n$

Double salt : Dissociate completely into simple ions when dissolved in water. (Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$

Complex compound : Do not dissociate into simple ions when dissolved in water. $(K_4[Fe(Cn]_6)$

Naming of mononuclear

- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in–o, neutral and cationic are same
- Prefixes mono, di, tri etc. are used.
- Followed by roman numeral in parentheses.

Formulas of mononuclear

- Central atom is listed first
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s)

Bonding

Valance bond theory

Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(square) planar, sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment $=\sqrt{n(n+2)}$ BM

In metal carbonyls

Metal–carbon bond possess both σ and π character

Crystal field theory

Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lighted causing splitting of d orbitals. Δ_0 depends upon the field produced by the ligand and charge on metal ion.

Colour

Caused by d-d transition; the colour is complementary to wavelength absorbed

Werner's Theory: Postulates

- In coordination compounds metals show primary and secondary linkages (valances)
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Uses

- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Isomerism

Structural: different bonds

Linkage occurs in ambidentate ligand

$[CO(NO_2)(NH_3)_5]Cl$
$[CO(ONO)(NH_3)_5]Cl$

Coordination interchange of ligands between catonic and anionic entities of different metal ions

$[CO(NH_3)_6]$ $[Cr(CN)_6]$
$[Cr(NH_3)_6]$ $[CO(CN)_6]$

Ionisation counter ion is a potential ligand and can displace a ligand

$[Co(NH_3)_5SO_4]Br$
$[CO(NH_3)_5Br]SO_4$

Solvate differ in number of water molecules attached to metal atom/ion.

$[Cr(H_2O)_6]Cl_3$
$[Cr(H_2O)_5Cl]Cl_2.H_2O$

Stereoisomerism : different spatial arrangements

Geometrical : Different arrangement Ligand

Optical: images which cannot be superimposed $[Co(en)_3]^{3+}$

Important Questions

Multiple Choice questions-

1. IUPAC name of $[Pt(NH_3)_3 Br (NO_2) Cl] Cl$ isw
(a) triamminechlorodibromidoplatinum (IV) chloride
(b) triamminechloridobromidonitrochloride- platinum (IV) chloride
(c) triamminebromidochloridonitroplatinum (IV) chloride
(d) triamminenitrochlorobromoplatinum (IV) chloride

2. Trunbull's blue is
(a) Ferricyanide
(b) Ferrous ferricyanide
(c) Ferrous cyanide
(d) $Fe_3[Fe(CN)_6]_4$

3. Primary and secondary valency of Pt in $[Pt(en)_2Cl_2]$ are
(a) 4, 4
(b) 4, 6
(c) 6, 4
(d) 2, 6

4. The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5 (ONO)]^{2+}$ are called
(a) Ionization isomers
(b) Linkage isomers
(c) Co-ordination isomers
(d) Geometrical isomers

5. Which of the following has square planar structure?
(a) $[NiCl_4]^{2-}$
(b) $[Ni(CO)_4]$
(c) $[Ni(CN)_4]^{2-}$
(d) None of these

6. Which of the following has magnesium?
(a) Chlorophll
(b) Haemocyanin
(c) Carbonic anhydrate
(d) Vitamin B_{12}

7. Mohr's salt is
(a) $Fe_2(SO_4) 3 . (NH_4)_2SO_4 . 6H_2O$
(b) $FeSO_4 . (NH_4)_2 . SO_4 . 6H_2O$

(c) $MgSO_4 . 7H_2O$
(d) $FeSO_4 . 7H_2O$

8. Which of the following shall form an octahedral complex?
(a) d^4 (low spin)
(b) d^8 (high spin)
(c) d^6 (low spin)
(d) All of these

9. EDTA is used for the estimation of
(a) Na^+ and K^+ ions
(b) Cl^- and Br^- ions
(c) Cu^{2+} and Cs^+ ions
(d) Ca^{2+} and Mg^{2+} ions

10. The solution of the complex $[Cu(NH_3)_4] SO_4$ in water will
(a) give the tests of Cu^{2+} ion
(b) give the tests of NH_3
(c) give the tests of SO_4^{2-} ions
(d) not give the tests of any of the above

Very Short Questions-

1. What is the shape of $[Fe(CO)_5]$?
2. What do you understand by stability of a complex and instability constant of coordination compounds?
3. How is EDTA used in estimation of hardness of water?
4. Explain the role of complexes in metallurgy with an example.
5. How is excess of copper and iron removed from body?
6. Define – isomerism.

7. Indicate the types of isomerisms shown by the complex $-K[Fe(H_2O)_2(en)_2Cl_2]$?
8. Give an example of coordination isomerism?
9. What are complex compounds?
10. Give some examples of coordination compounds.

Short Questions-

1.Explain the synergic bonding in metal carbonyls.
2. Give some examples showing importance of complexes in biological system?
3.Give examples of complexes in
a) Chemical analysis

b) Industries
4.Distinguish between homoleptic and heteroleptic ligands.
5.What are the different shapes or coordination polyhedral in the complexes?
6.What is the difference between a double salt and a complex? Explain with an example.
7. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.
8. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

9. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

10.A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Long Questions-

1. What are ligands? Explain different types of ligands.
2. Write the formulas for the following coordination compounds:
(i) Tetraamminediaquacobalt (III) chloride

(ii) Potassium tetracyanonickelate (II)

(iii) Tris(ethane-1,2-diamine) chromium (III) chloride

(iv) Amminebromidochloridonitrito-N-platinate (II)

(v) Dichloridobis (ethane-1,2-diamine)platinum(IV) nitrate

(vi) Iron (III) hexacyanoferrate (II)

3. Write the IUPAC names of the following coordination compounds:
(i) $[Co(NH_3)6]Cl_3$ (ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $K_3[Fe(CN)_6]$ (iv) $K_3[Fe(C_2O_4)_3]$
(v) $K_2[PdCl_4]$ (vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

4. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:
(i) $K[Cr(H_2O)_2(C_2O_4)_2]$

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

(iii) $[Co(NH_3)_5(NO_2)(NO_3)_2]$

(iv) $[Pt(NH_3)(H_2O)Cl_2]$

5. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

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

7. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3}$ is weakly paramagnetic. Explain.

8. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Assertion and Reason Questions-

1. 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.

Assertion: Zeise's salt is a ππ-bonded organometallic compound.

Reason: The oxidation number of platinum in Zeise's salt is +2.

2. 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.

Assertion: The second and third transition series elements have lesser tendency to fonn low spin complex as compared to the first transition series.

Reason: The CFSE (Δ_0) is more for 5d and 4d.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both **σ** and **π** character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty **π** or **π**–orbital. These types of ligands are called **π**–accepter or **π**–acid ligands. These interactions increases the Δ_0 value.

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

(i) What is the oxidation state of metal in $[Mn_2(CO)_{10}]$?

a) +1
b) -1
c) +2
d) 0

(ii) Among the following metal carbonyls, the C-O bond order is lowest in:

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

(iii) Which of the following can be reduced easily?

a. $V(CO)_6$
b. $Mo(CO)_6$
c. $[Co(CO)_4]^-$
d. $Fe(CO)_5$

(iv)The oxidation state of cobalt in $K[Co(CO)_4]$ is:

a. +1
b. +3
c. -1
d. 0

(v) Structure of decacarbonyl manganese is:

a. Trigonal bipyramidial
b. Octahedral
c. Tetrahedral
d. Square pyramidal

2. Read the passage given below and answer the following questions:

Coordination compounds are formulated and named according to the IUPAC system.

Few rules for naming coordination compounds are:

I. In ionic complex, the cation is named first and then the anion.
II. In the coordination entity, the ligands are named first and then the central metal ion.
III. When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.

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

(i) The IUPAC name of the complex $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ is:

a) Triamminechlorobromonitroplatinum (IV) chloride.
b) Triamminebromonitrochloroplatinum (IV) chloride.
c) Triamminebromidochloridonitroplatinum (IV) chloride.
d) Triamminenitrochlorobromoplatinum (IV) chloride.

(ii) The IUPAC name of $[Ni(CO)_4]$ is:

a) Tetracarbonylnickel (II).
b) Tetracarbonylnickel (0).
c) Tetracarbonylnickelate (II).
d) Tetracarbonylnickelate (0).

(iii) As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is:

a) Tetraaquadiamminecobalt (II) chloride.

b) Tetraaquadiamminecobalt (III) chloride.
c) Diamminetetraaquacobalt (II) chloride.
d) Diamminetetraaquacobalt (III) chloride.

(iv) Which of the following represents correct formula of dichloridobis(ethane -1, 2-diamine)cobalt (III) ion?

a) $[CoCl_2(en)]^{2+}$
b) $[CoCl_2(en)_2]^{2+}$
c) $[CoCl_2(en)]^{+}$
d) $[CoCl_2(en)_2]^{+}$

(v) Correct formula of pentaamminenitro-O-cobalt (III) sulphate is:

a) $[Co(NO_2)(NH_3)_5]SO_4$
b) $[Co(ONO)(NH_3)_5]SO_4$
c) $[Co(NO_2)(NH_3)_4](SO_4)_2$
d) $[Co(ONO)(NH_3)_4](SO_4)_2$

MCQ Answers-

1. Answer: c

2. Answer: b

3. Answer: d

4. Answer: b

5. Answer: c

6. Answer: a

7. Answer: b

8. Answer: b

9. Answer: d

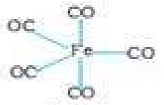
10. Answer: c

Very Short Answers-

Ans 1.

$[Fe\ (CO)_5]$

Geometry = Trigonal bipyramidal/span>



$Fe(CO)_5$
Trigonal bipyramidal

Ans 2. The stability of a complex in solution is the degree of association between the two species involved in the state of equilibrium. The instability constant is reciprocal of the formation constant. It is also called dissociation constant.

Ans 3. Hard water is titrated with $Na_2 - EDTA$ complex for estimation of its hardness. During the process, the $Ca^{2+} and\ Mg^{2+}$ ions form complex with EDTA replacing Na^+. The method is based on the difference in the stability constant of calcium and magnesium complexes.

Ans 4. Some extraction processes make use of complex formation e.g. during metallurgy of Gold, it combines with cyanide in the presence of oxygen and water to form the complex $[Au\ (CN)_2]-$ in aqueous solution by addition of zinc.

Ans 5. Excess of copper and iron are removed by chelating Ligands D – penicillamine and deferoxamine B through the formation of coordination compounds.

Ans 6. Isomerism is the phenomenon of existence of two or more compounds with same chemical formula but a different arrangement of atoms.

Ans 7. Both geometrical and optical isomerisms will be present.

Ans 8. Example of coordination isomerism is

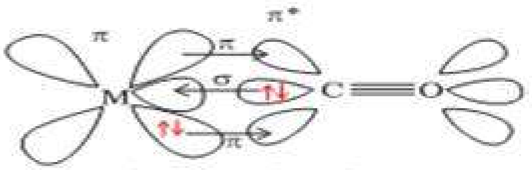
$[Cr\ (NH_3)_6]\ [Co\ (CN)_6]$ and $[Co\ (NH_3)_6]\ [Cr\ (CN)_6]$

Ans 9. Complex compounds or coordination compounds are those compounds in which the metal atoms are bound to a number of anions or neutral molecules.

Ans 10. Examples of coordination compounds are chlorophyll, haemoglobin, and vitamin B_{12}

Short Answers-

Ans 1. The metal – carbon bond in metal carbonyls has both s & P- character. The M – C σ bond is formed by donation of lone pair of electrons of carbonyl carbon into a vacant orbital of metal. The M – C π bond is formed by the donation of a pair of electrons from a filled d- orbital of metal to the vacant π orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect that strengthens the bond.



Synergic bonding

Ans 2. Examples of complexes in biological system-

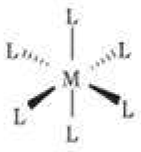
1. Chlorophyll is a complex of Mg.
2. Haemoglobin is a complex of iron.
3. Cyanocobalamin, Vit B_{12}, is a complex of cobalt.

Ans 3. (a) Chemical analysis – Qualitative and Quantitative analysis methods involve use of Ligands like EDTA, DMG etc.

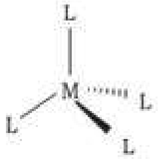
(b) Industries - Hydrogenation of alkenes is done by using a sodium complex called Wilkinson catalyst. In black and white photography, silver complexes are used.

Ans 4. Homoleptic complexes are those in which only one type of ligand or donor group is present e.g. $\left[Pt(NH_3)_6\right]^{3+}$ has only NH_3 as ligand. Whereas heteroleptic complexes are those in which different types of ligands are present eg. $\left[Pt(NH_3)_4 Cl_2\right]^{+}$ has two type of ligands- NH_3 and Cl^-.

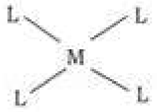
Ans 5. The various coordination polyhedra are –



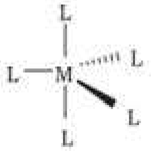
Octahedral



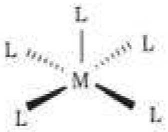
Tetrahedral



Square planar



Trigonal bipyramidal

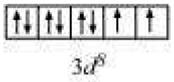


Square pyramidal

Ans 6. Double salts dissociate completely into simple ions when dissolved in water e.g., Mohr salt, $FeSO_4(NH_4)_2SO_4, 6H_2O$ will dissolve in water and give ferrous, ammonium and sulphate ions. On the other hand, the complex ions do not completely dissociate into all constituent ions e.g. $K_4[Fe(CN)_6]$ will dissociate to give potassium ions and $[Fe(CN)_6]^{4-}$ ions only.

Ans 7. $[Pt(CN)_4]^{2-}$

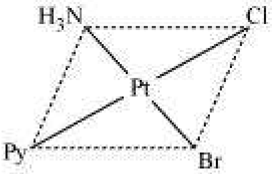
In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes dsp^2 hybridization. Now, the electronic configuration of Pd(+2) is $5d^8$.

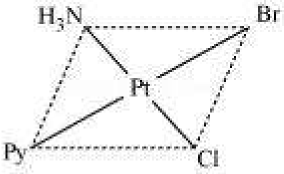


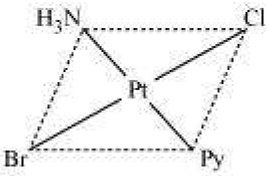
CN^- being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in $[Pt(CN)_4]^{2-}$.

Ans 8.

$[Pt(NH_3)(Br)(Cl)(py)]$







From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Ans 9. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values. The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands. Also, strong field ligands cause higher splitting in the *d* orbitals than weak field ligands.

$$\mathrm{I-} < \mathrm{Br}^- < \mathrm{S}^{2-} < \mathrm{SCN}^- < \mathrm{Cl}^- < \mathrm{N}_3 < \mathrm{F}^- < \mathrm{OH}^- < \mathrm{C_2O_4^{2-}}$$

$$\sim \mathrm{H_2O} < \mathrm{NCS}^- \sim \mathrm{H}^- < \mathrm{CN}^- < \mathrm{NH_3} < \mathrm{en} \sim \mathrm{SO_3^{2-}} < \mathrm{NO_2^-} < \mathrm{phen} < \mathrm{CO}$$

Ans 10. In $\left[\mathrm{Ni(H_2O)_6}\right]^{2+}$, $\mathrm{H_2\ddot{O}}$ is a weak field ligand. Therefore, there are unpaired electrons in $\mathrm{Ni^{2+}}$. In this complex, the *d* electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of *d* – *d* transition is present. Hence, $\left[\mathrm{Ni(H_2O)_6}\right]^{2+}$ is coloured.

In $\left[\mathrm{Ni(CN)_4}\right]^{2-}$, the electrons are all paired as $\mathrm{CN^-}$ is a strong field ligand. Therefore, *d*-*d* transition is not possible in $\left[\mathrm{Ni(CN)_4}\right]^{2-}$. Hence, it is colourless.

Long Answers-

Ans 1. The ions or molecules bound to central atom or ion in the coordination entity are ligands e.g $\left[Fe(CN)_6\right]^{4-}$ has six CN^- ligands.

Types: -

(1) On the basis of charges on them ligands can be negative, positive (e.g. H_3O^+, NH_4^+ etc.) or neutral (e.g. CO, NH_3, H_2O).

(2) On the basis of their donor atoms ligands can be monodentate or unidentate (one donor atom) e.g-H_2O, NH_3, Cl^- etc, or didentate ligands (two donor atoms) $H_2NCH_2CH_2NH_2$ or $C_2O_4^{2-}$ etc. or polydentate (several donor atoms) e.g $[EDTA]^{4-}$ is a hexadentate ligand.

(3) Ligands which can ligate through two different atoms are called ambidentate ligands eg. NO_2^- and SCN^- ions. Whereas when a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is called chelate ligand.

Ans 2.

(i) $[CO(H_2O)_2(NH_3)_4]Cl_3$

(ii) $K_2[Ni(CN)_4]$

(iii) $[Cr(en)_3]Cl_3$

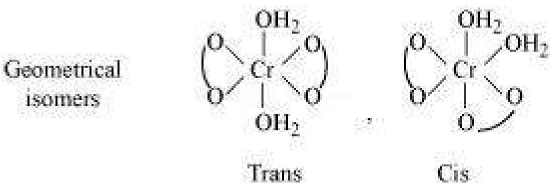
(vi) $[Pt(NH)_3BrCl(NO_2)]^-$

(v) $[PtCl_2(en)_2](NO_3)_2$

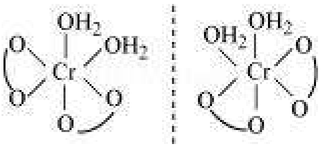
(vi) $Fe_4[Fe(CN)_6]_3$

Ans 3. (i) Hexaamminecobalt(III) chloride
(ii) Pentaamminechloridocobalt(III) chloride
(iii) Potassium hexacyanoferrate(III)
(iv) Potassium trioxalatoferrate(III)
(v) Potassium tetrachloridopalladate(II)
(vi) Diamminechlorido(methylamine)platinum(II) chloride

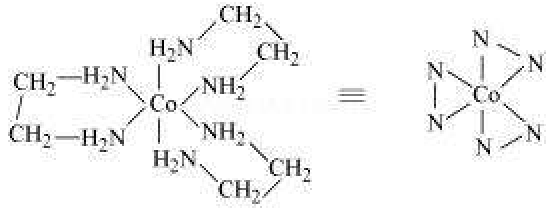
Ans 4. Both geometrical (*cis*-, *trans*-) isomers for $K[Cr(H_2O)_2(C_2O_4)_2]$ can exist. Also, optical isomers for cis isomer exist.



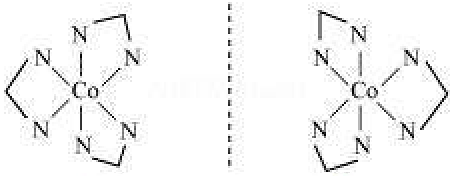
Trans-isomer is optically inactive. On the other hand, cis isomer is optically active.



(ii) Two optical isomers for $[CO(en)_3]Cl_3$ exist.

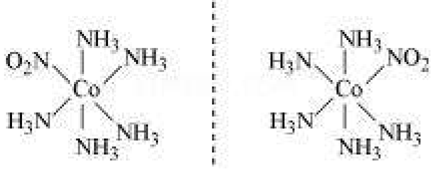


Two optical isomers are possible for this structure.



(iii) $[CO(NH_3)_5(NO_2)](NO_3)_2$

A pair of optical isomers:



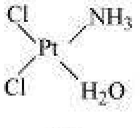
It can also show linkage isomerism.

$[CO(NH_3)_5(NO_2)](NO_3)_2$ and $[CO(NH_3)_5(ONO)](NO_3)_2$

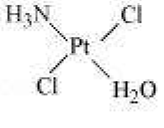
It can also show ionization isomerism.

$[Co(NH_3)_5(NO_2)](NO_3)_2$ $[CO(NH_3)_5(NO_3)](NO_3)(NO_2)$

(iv) Geometrical (*cis*-, *trans*-) isomers of $[Pt(NH_3)(H_2O)Cl_2]$ can exist.

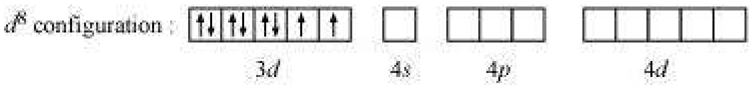


Cis

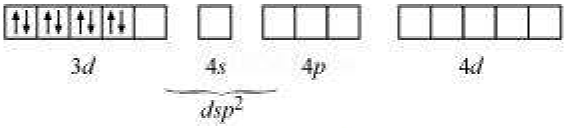


Trans

Ans 5. Ni is in the +2-oxidation state i.e., in d^8 configuration.

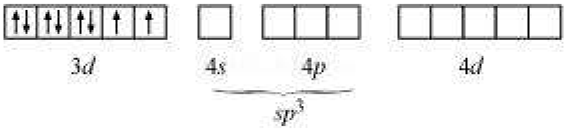


There are 4 CN^- ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since CN^- ion is a strong field ligand, it causes the pairing of unpaired 3*d* electrons.



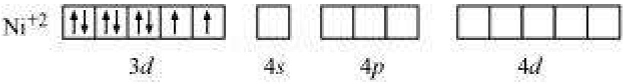
It now undergoes dsp^2 hybridization. Since all electrons are paired, it is diamagnetic.

In case of $[NiCl_4]^{2-}$, CN^- ion is a weak field ligand. Therefore, it does not lead to the pairing of unpaired 3*d* electrons. Therefore, it undergoes sp^3 hybridization.

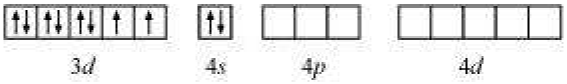


Since there are 2 unpaired electrons in this case, it is paramagnetic in nature.

Ans 6. Though both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral, their magnetic characters are different. This is due to a difference in the nature of ligands. CN^- is a weak field ligand and it does not cause the pairing of unpaired 3*d* electrons. Hence, $[NiCl_4]^{2-}$ is paramagnetic.

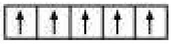


In $Ni(CO)_4$, Ni is in the zero-oxidation state i.e., it has a configuration of $3d^8 4s^2$.

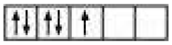


But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3*d* electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

Ans 7. In both $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, Fe exists in the +3-oxidation state i.e., in d^5 configuration.

d^5 

Since CN^- is a strong field ligand, it causes the pairing of unpaired electrons. Therefore, there is only one unpaired electron left in the *d*-orbital.



Therefore,

$\mu = \sqrt{n(n+2)}$

$= \sqrt{1(1+2)}$

$= \sqrt{3}$

=1.732 BM

On the other hand, H_2O is a weak field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

Therefore,

$\mu = \sqrt{n(n+2)}$

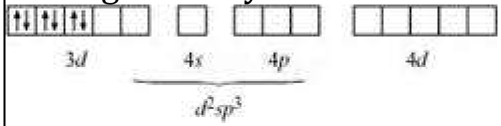
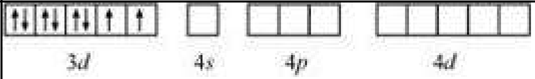
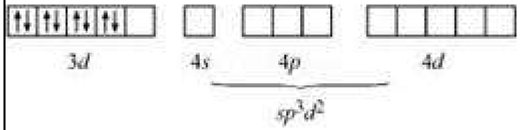
$= \sqrt{5(5+2)}$

$= \sqrt{35}$

= 6 BM

Thus, it is evident that $\left[Fe(H_2O)_6\right]^{3+}$ is strongly paramagnetic, while $\left[Fe(CN)_6\right]^{3}$ is weakly paramagnetic.

Ans 8.

$\left[Co(NH_3)_6\right]^{3+}$	$\left[Ni(NH_3)_6\right]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt = d^6	Electronic configuration of nickel = d^8
 NH_3 being a strong field ligand causes the pairing. Therefore, Cobalt can undergo d^2sp^3 hybridization.  Hence, it is an inner orbital complex.	 If NH_3 causes the pairing, then only one 3*d* orbital is empty. Thus, it cannot undergo d^2sp^3 hybridization. Therefore, it undergoes sp^3d^2 hybridization.  Hence, it forms an outer orbital complex.

Assertion and Reason Answers-

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

Explanation:

In these complexes, the metal and ligand fonn a bond that involves the ππ-electrons of the ligand and so it is a ππ-bonded organometallic compound.

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

Explanation:

4d and 5d elements have greater tendency to form low spin complex (allows better pairing of electrons) in comparison to 3d because the difference in energy of t_{2g} and e_g (CFSE, Δ_0) increases in 4d and 5d.

Case Study Answers-

1. Answer :

(i) (d) 0

Explanation:

Oxidation state of Mn in $[Mn_2(CO)_{10}]$ is zero.

(ii) (d) $[V(CO)_6]^-$

Explanation:

In $[V(CO)_6]^-$, the anionic carbonyl complex can delocalise more electron density to antibonding **π**–orbital (**dπ–pπ** back bonding) of CO and thus lowers the bond order.

(iii) (a) $V(CO)_6$

Explanation:

$V(CO)_6$ can be easily reduced to $[V(CO)_6]^-$. $V(CO)_6$ has a total of 17 bonding electrons, hence it is very reactive and unstable. $[V(CO)_6]^-$ on the other hand has complete set of 18 bonding electrons as an electron is added into the bonding orbital when $V(CO)_6$ gets reduced to $[V(CO)_6]^-$. All others have 18 bonding electrons.

(iv) (c) -1

Explanation:

$K[Co(CO)_4]$

$+1 + (x) + 4(0) = 0$ or $x = -1$

(v) (d) Square pyramidal.

Explanation:

$Mn_2(CO)_{10}$ is made up of two square pyramidal $Mn(CO)_5$ units joined by Mn-Mn bond.

2. Answer :

(i) (c) Triamminebromidochloridonitroplatinum (IV) chloride.

Explanation:

Ligands are named in alphabetical order irrespective of their charge.

(ii) (b) Tetracarbonylnickel (0).

(iii) (d) Diamminetetraaquacobalt (III) chloride.

(iv) (d) $[CoCl_2(en)_2]^+$

(v) (b) $[Co(ONO)(NH_3)_5]SO_4$

Explanation:

Ligand NO_2^- is ambidentate ligand as it can donate electrons through either nitrogen (NO_2) or oxygen (ONO).