Chapter–9

Coordination Compounds

basic concepts

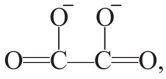
1. **Double Salts:** Double salts are the addition compounds which are stable in solid state but break up into constituent ions when dissolved in water or any other solvent. In these compounds the individual properties of constituent are not lost. Some common examples are:

Mohr's salt	$FeSO_4.(NH_4)_2SO_4.6H_2O$
Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Carnallite	$KCl.MgCl_2.6H_2O$

2. **Complex Ion:** An electrically charged species, carrying positive or negative charge, in which the central metal atom or ion is surrounded by fixed number of ions or molecules, *e.g.*, $[Co(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$, etc. The complex ion does not dissociate into simple ions in aqueous solutions.
3. **Coordination Compounds:** Coordination compounds are the compounds which contain complex ions, *e.g.*, $[Co(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$, etc. These compounds contain a central metal atom or cation which is attached with a fixed number of anions or molecules (called ligands) through coordinate bonds.
4. **Coordination Entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of molecules or ions (ligands), *e.g.*, $[Co(NH_3)_3Cl_3]$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, etc.
5. **Central Atom or Ion:** In a coordination entity, the atom or ion to which a fixed number of ions or molecules are bound in a definite geometrical arrangement. For example, in the complex ion $[CoCl(NH_3)_5]^{2+}$, the Co^{2+} ion is the central ion.
6. **Ligands:** Ligands are the atoms, molecules or ions which donate a pair of electrons to central metal atom or ion and form a coordinate bond with it. Depending upon the number of donor atoms available for coordination, the ligands may be classified as:

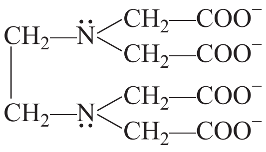
- **Unidentate ligands:** Contain one donor atom, *e.g.*, $\ddot{N}H_3$, $:\ddot{Cl}:^-$, etc.
- **Bidentate ligands:** Contain two donor atoms, *e.g.*,

$H_2\ddot{N}CH_2—CH_2\ddot{N}H_2$,



$$\overset{O^-}{\underset{|}{}}\; O{=}\overset{\overset{O^-}{|}}{C}—\overset{\overset{O^-}{|}}{C}{=}O$$, etc.

- **Polydentate ligands:** Contain several donor atoms, *e.g.*,



Ethylenediaminetetraacetate ion ($EDTA^{4-}$) (Hexadentate)

- **Ambidentate ligand:** A ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal atom/ion is called an ambidentate ligand. Some common examples are given below:

 **nitrito—N** **(N donor atom)**	M← O—N=O **nitrito—O** **(O donor atom)**
M ← SCN **thiocyanato** **(S donor atom)**	M ← NCS **isothiocyanato** **(N donor atom)**
M ← CN **cyano** **(C donor atom)**	M ← NC **isocyano** **(N donor atom)**

- **Chelating ligand:** When a bidentate or a polydentate ligand 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 chelating ligand. The chelating ligands form more stable complexes than the unidentate ligands. This is because when chelation occurs entropy increases and the process becomes more favourable.

7. **Coordination Number (CN):** The coordination number of a metal ion in a complex may be defined as the total number of ligand donor atoms to which the metal ion is directly bonded. For example, in the complex ions, $[Co(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$, the coordination numbers of both Co and Fe is 6.
8. **Coordination Sphere and Counter Ions:** The central metal atom or ion and the ligands directly attached to it are enclosed in a square bracket and is collectively termed as the coordination sphere. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $[Cr(NH_3)_3(H_2O)_3]Cl_3$, the coordination sphere is $[Cr(NH_3)_3(H_2O)_3]^{3+}$ and the counter ion is Cl^-.
9. **Coordination Polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion is known as the coordination polyhedron around the central atom/ion. Tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal are common shapes of coordination polyhedra.

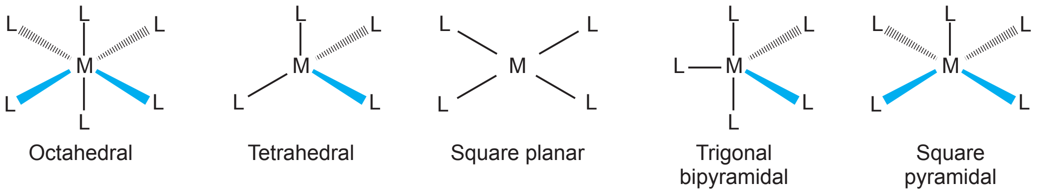


Fig. 9.1: Shapes of different coordination polyhedra.
M represents the central atom/ion and L, a unidentate ligand

10. **Oxidation Number of 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 that are shared with the central atom.
11. **Homoleptic Complex:** The complex in which metal atom is bound to only one kind of donor groups, *e.g.*, $[Cu(CN)_4]^{3-}$.
12. **Heteroleptic Complex:** The complex in which metal atom is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$.
13. **Table 9.1: Nomenclature of Some Coordination Compounds**

S. No.	Formula	Name
(*i*)	$[Pt(NH_3)_2ClNO_2]$	diamminechloridonitrito–N–platinum(II)
(*ii*)	$[CoCl_2(en)_2]Cl$	dichloridobis(ethane-1, 2–diamine) cobalt(III) chloride
(*iii*)	$K_3[Fe(C_2O_4)_3]$	potassium trioxalatoferrate(III)
(*iv*)	$[Ag(NH_3)_2]\ [Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I)

14. **Isomerism:** Two or more compounds having the same molecular formula but different arrangement of atoms and hence differ in one or more physical or chemical properties are called isomers and the phenomenon is called isomerism.

Isomerism in Coordination Compounds

Structural Isomerism

- Linkage isomerism
- Coordination isomerism
- Ionisation isomerism

Stereoisomerism

- Geometrical isomerism
- Optical isomerism

Structural isomers have different bonds. Stereoisomers have the same chemical formula and chemical bonds but differ in their spatial arrangements.

(*a*) Structural isomerism:

(*i*) Linkage isomerism: This type of isomerism arises due to the presence of an ambidentate ligand in a coordination compound. Some examples of linkage isomers are:

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

$[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$

(*ii*) Coordination isomerism: This type of isomerism arises due to interchange of ligands between the cationic and anionic entities of different metal ions present in a complex. Some examples are

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

$[Pt(NH_3)_4]\ [PtCl_4]$ and $[PtCl(NH_3)_3]\ [PtCl_3(NH_3)]$

(*iii*) Ionisation isomerism: Ionisation 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. Some examples are:

$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]\ SO_4$

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

$[Co(NH_3)_5NO_2]SO_4$ and $[Co(NH_3)_5SO_4]NO_2$

(*iv*) Solvate isomerism: Solvate isomers differ by whether or not a solvent molecule is directly bonded to metal ion or merely present as free solvent molecule in the crystal lattice. If water is the solvent then this form of isomerism is known as "hydrate isomerism".

Some examples in which hydrate isomerism is observed are:

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

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$

$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_2O$

(*b*) Stereoisomerism: Stereoisomerism is of two types:

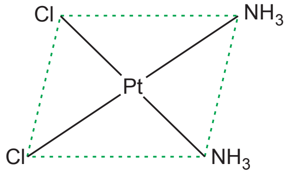
(*i*) Geometrical isomerism: This type of isomerism arises in heteroleptic complexes due to difference in geometrical arrangement of the ligand around the central metal ion. If the same kind of ligand occupy adjacent positions, the isomer is called *cis*, and if these are opposite to each other, the isomer is called *trans*.

This type of isomerism is very common in complexes with coordination number 4 and 6.

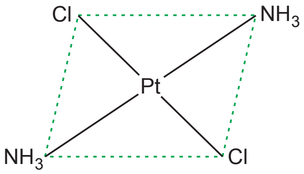
- **Isomerism in complexes with coordination number 4.**

  These complexes can either have a tetrahedral or square planar geometry. Tetrahedral complexes do not show geometrical isomerism as relative position of the ligands attached to central metal atom is same with respect to each other (adjacent). The square planar complexes on the other hand show this type of isomerism as given below:

- Tetra coordinated square planar complexes of the type $[MA_4]$, $[MA_3X]$, $[MAX_3]$ are incapable of showing geometrical isomerism because all possible arrangements of ligands in each of these complexes are exactly the same.
- **Type $[MA_2X_2]$:** $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2(NO_2)_2]$, $[Pt(Py)_2Cl_2]$

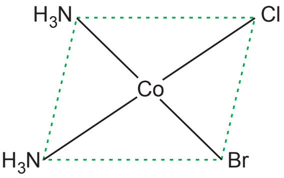


***cis*-isomer**
(similar groups on adjacent position)

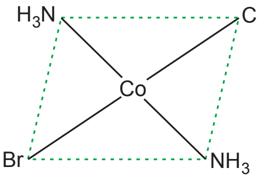


***trans*-isomer**
(similar groups on opposite position)

- **Type $[MA_2XY]$:** $[Co(NH_3)_2ClBr]$, $[Pt(Py)_2(NH_3)Cl]$

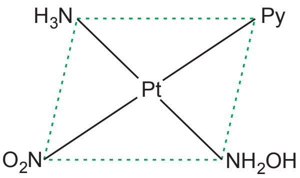


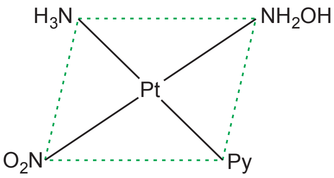
***cis*-isomer**

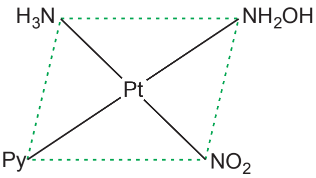


***trans*-isomer**

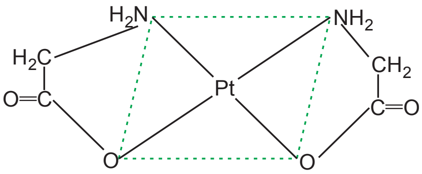
- **Type [MABXY]:** $[Pt(NH_3)Py(NH_2OH)(NO_2)]^+$



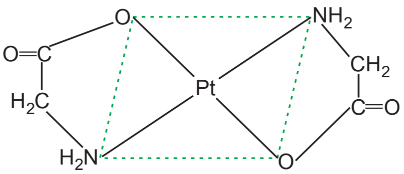




- **Type $[M(AB)_2]$:** $[Pt(gly)_2]$ where gly = $H_2NCH_2COO^-$

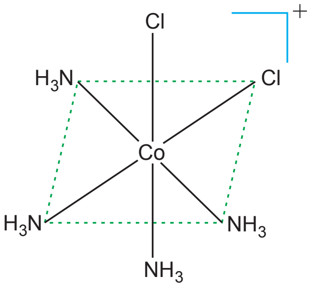


***cis*-isomer**

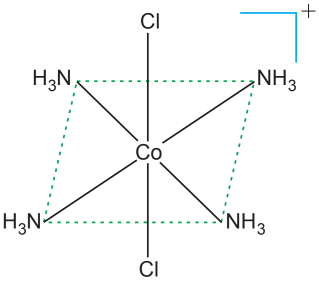


***trans*-isomer**

- **Isomerism in complexes with coordination number 6.**
  - Octahedral complexes of the type $[MA_6]$ and $[MA_5X]$ are incapable of showing geometrical isomerism.
  - **Type $[MA_4X_2]$ or $[MA_2X_4]$:** $[Co(NH_3)_4Cl_2]^+$, $[Cr(NH_3)_4Cl_2]^+$ ion

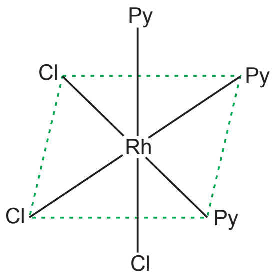


***cis*-isomer**

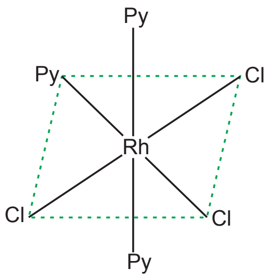


***trans*-isomer**

- **Type $[MA_3X_3]$:** $[Rh(Py)_3Cl_3]$, $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_3(NO_2)_3]$

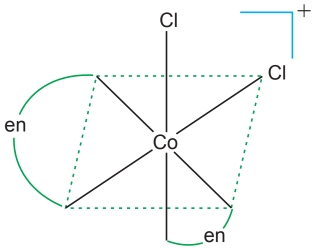


facial or fac-isomer

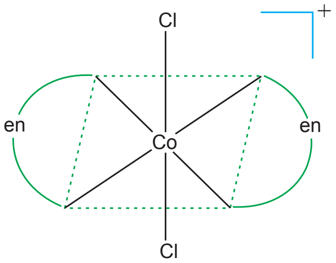


meridional or mer-isomer

- **Type $[M(AA)_2X_2]$ or $[M(AA)_2XY]$:** $[Co(en)_2Cl_2]^+$, $[Ni(ox)_2Cl_2]^+$



cis-isomer

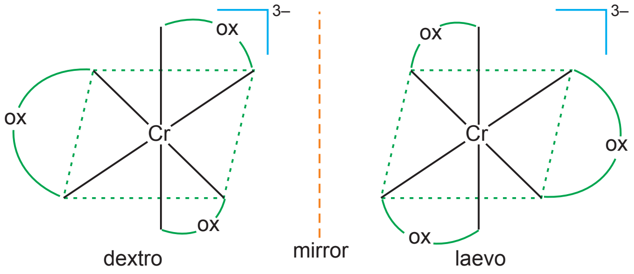


trans-isomer

(*ii*) Optical isomerism: This type of isomerism is exhibited by chiral molecules. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers and rotate the plane of polarised light equally but in opposite directions. The isomer which rotates the plane of polarised light towards left is called laevorotatory (*l*) while which rotates the plane towards right is called dextrorotatory (*d*).

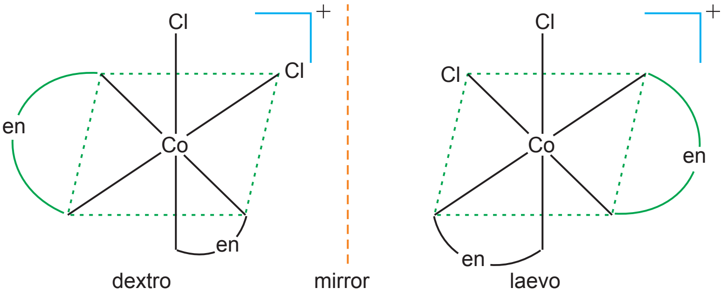
Optical isomerism is common in octahedral complexes involving bidentate ligands. Some examples of different types of octahedral complexes showing optical isomerism are given below:

- **Type $[M(AA)_3]$: $[Cr(ox)_3]^{3-}$, $[Co(en)_3]^{3+}$**



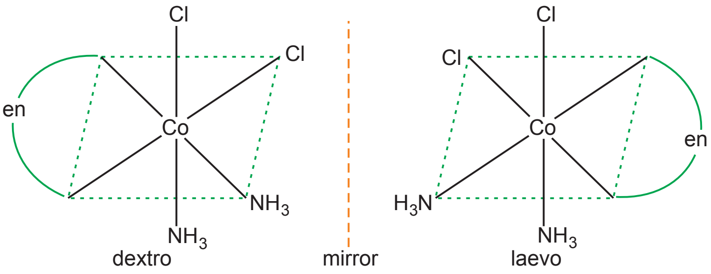
Optical isomers (*d* and *l*) of $[Cr(ox)_3]^{3-}$

- **Type $[M(AA)_2X_2]$ or $[M(AA)_2XY]$:** *cis*-$[Co(en)_2Cl_2]^+$, *cis*-$[Pt(en)_2Cl_2]^+$, *cis*-$[Cr(ox)_2Cl_2]^{3-}$, etc.



Optical isomers (*d* and *l*) of cis-$[Co(en)_2Cl_2]^+$

- **Type $[M(AA)X_2Y_2]$:** $[Co(en)(NH_3)_2Cl_2]$



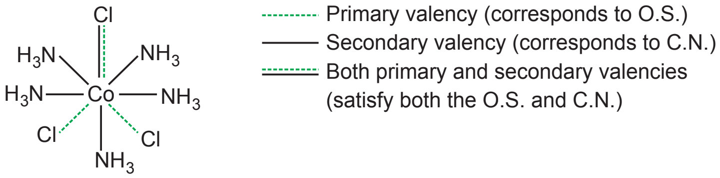
Optical isomers (d and l) of $[Co(en)(NH_3)_2Cl_2]$

15. Werner's Theory of Coordination Compounds: The main postulates of this theory are:

(*i*) In coordination compounds, metals show two types of valencies: primary and secondary.

(*ii*) The primary valencies are normally ionisable and are satisfied by negative ions.

(*iii*) The secondary valencies are non ionisable and are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.



Representation of $[CoCl(NH_3)_5]Cl_2$ on the basis of Werner's theory

(*iv*) The ions or groups bound by secondary linkage to the metal have characteristic spatial arrangements corresponding to different coordination number.

16. Bonding in Coordination Compounds

(*a*) **Valence bond theory:** The main features of the valence bond theory as applied to coordination compounds are as follows:

(*i*) The number of metal–ligand coordinate bonds which can be formed in case of given metal ion depends upon the number of vacant orbitals for bonding in metal ion and is known as the coordination number of metal ion.

(*ii*) The metal atom or ion under the influence of ligands uses its $(n-1)\,d$, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry.

Table 9.2: Number of Orbitals and Types of Hybridisations

Coordination Number	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	Octahedral
6	d^2sp^3	Octahedral

(*iii*) The empty hybrid orbitals of the central metal atom or ion overlap with the filled orbitals of the ligand containing the lone pair of electrons. In this way a metal–ligand coordinate bond is formed.

(*iv*) The inner orbital (low spin) or the outer orbital (high spin) complexes are formed depending upon whether the *d*-orbitals of inner shell or *d*-orbitals of outer shell are used in hybridisation.

(*v*) The complex will be diamagnetic if all electrons are paired. If unpaired electrons are present then the complex will be paramagnetic.

Table 9.3: Application of Valence Bond Theory to Some Complexes

Ion/Complex	Central Metal Ion	Configuration of Metal Ion	Hybridisation of Metal Ion Involved	Geometry of the Complex	Number of Unpaired Electrons	Magnetic Behaviour
$[Ti(H_2O)_6]^{3+}$	Ti^{3+}	d^1	d^2sp^3	Octahedral	1	Paramagnetic
$[V(H_2O)_6]^{3+}$	V^{3+}	d^2	d^2sp^3	Octahedral	2	Paramagnetic
$[Cr(H_2O)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	Octahedral	3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	Octahedral	3	Paramagnetic
$[MnF_6]^{3-}$	Mn^{3+}	d^4	sp^3d^2	Octahedral	4	Paramagnetic
$[Mn(CN)_6]^{3-}$	Mn^{3+}	d^4	d^2sp^3	Octahedral	2	Paramagnetic
$[MnCl_4]^{2-}$	Mn^{2+}	d^5	sp^3	Tetrahedral	5	Paramagnetic
$[FeF_6]^{3-}$	Fe^{3+}	d^5	sp^3d^2	Octahedral	5	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	d^5	sp^3d^2	Octahedral	5	Paramagnetic
$[Fe(CN)_6]^{3-}$	Fe^{3+}	d^5	d^2sp^3	Octahedral	1	Paramagnetic
$[Fe(CN)_6]^{4-}$	Fe^{2+}	d^6	d^2sp^3	Octahedral	0	Diamagnetic
$[FeCl_4]^{2-}$	Fe^{2+}	d^6	sp^3	Tetrahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$	Co^{3+}	d^6	d^2sp^3	Octahedral	0	Diamagnetic
$[CoF_6]^{3-}$	Co^{3+}	d^6	sp^3d^2	Octahedral	4	Paramagnetic
$[Ni(CO)_4]$	Ni	$3d^8 4s^2$	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(CN)_4]^{2-}$	Ni^{2+}	d^8	dsp^2	Square planar	0	Diamagnetic
$[NiCl_4]^{2-}$	Ni^{2+}	d^8	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	d^8	sp^3d^2	Octahedral	2	Paramagnetic
$[CuCl_4]^{2-}$	Cu^{2+}	d^9	sp^3	Tetrahedral	1	Paramagnetic
$[Zn(NH_3)_4]^{2+}$	Zn^{2+}	d^{10}	sp^3	Tetrahedral	0	Diamagnetic
$[Pt(NH_3)Cl_2]$	Pt^{2+}	d^8	dsp^2	Square planar	0	Diamagnetic

➡ Limitations of valence bond theory

(*i*) It involves a number of assumptions.

(*ii*) It does not give quantitative interpretation of magnetic data.

(*iii*) It does not distinguish between weak and strong ligands.

(*iv*) It does not explain the colour exhibited by complexes.

(*v*) It does not give an exact explanation of thermodynamic or kinetic stabilities of coordination compounds.

(*vi*) It does not make exact predictions regarding the tetrahedral and square planar structures of 4 – coordinated complexes.

(*b*) Crystal field theory

- According to crystal field theory, the bonding between central metal ion and ligand is purely electrostatic. Ligands are considered 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 orbitals. However, in a complex due to asymmetrical negative field of ligands, the *d*-orbitals are no more degenerate and split into two sets of orbitals. The pattern of splitting depends upon the nature of the crystal field.

- In an octahedral environment, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy as compared to average energy in the spherical crystal field. Thus, in an octahedral complex, the degeneracy of the five *d*-orbitals is partially removed due to ligand electron–metal electron repulsions to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.
- The splitting of the degenerate orbitals due to the presence of ligands in a definite geometry is known as crystal field splitting and the difference of energy between two sets of degenerate orbitals as a result of crystal field splitting is known as crystal field stabilisation energy (CFSE). It is usually denoted by symbol Δ_o (the subscript o stands for octahedral).

It is found that e_g orbitals are $\frac{3}{5}\Delta_0$ above the average energy level and t_{2g} orbitals are $\frac{2}{5}\Delta_0$ below the average energy level.

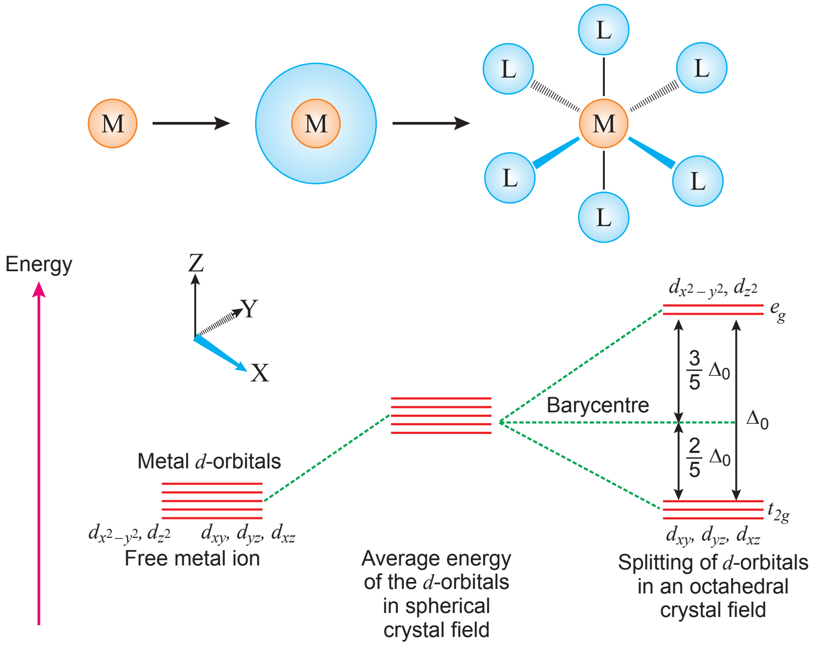


Fig. 9.2: *d*-orbital splitting in an octahedral crystal field

- The magnitude of Δ_0 depends upon the field produced by ligand and charge on the metal ion. The arrangement of ligands in a series in the order of increasing field strength is called spectrochemical series.

  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$
- In d^2 and d^3 coordination entities, the *d*-electrons occupy the t_{2g} orbitals singly in accordance with Hund's rule. For d^4 ions, the electronic distribution depends on crystal field stabilisation energy (Δ_0) and pairing energy (P). The two options are:
  (*i*) If $\Delta_0 < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.
  (*ii*) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Thus, ligands for which $\Delta_o > P$, are known as strong field ligands and form low spin complexes.

- In tetrahedral coordination entities, the *d*-orbitals splitting is inverted and is smaller as compared to the octahedral field splitting.

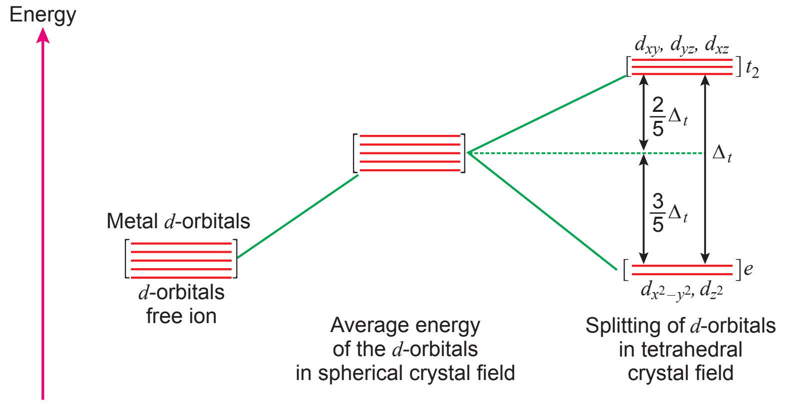


Fig. 9.3: d-orbital splitting in a tetrahedral crystal field

For the same metal, the same ligand and metal ligand distances, $\Delta_t = \frac{4}{9}\Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing, therefore, low spin configuration are rarely observed.

- **Colour in coordination compounds:** The crystal field theory attributes the colour of the coordination compounds to *d–d* transition of the electron from t_{2g} to e_g orbitals in octahedral complexes and from e_g to t_{2g} orbitals in tetrahedral complexes. In the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour.
- **Limitations of crystal field theory:**
  (*i*) As the ligands are considered as point charges, the anionic ligands should exert greater splitting effect. However, the anionic ligands are found at the low end of the spectrochemical series.
  (*ii*) It does not take into account the covalent character of metal ligand bond.

17. Metal Carbonyls: Metal carbonyls are the organometallic compounds in which carbon monoxide acts as the ligand. These compounds are formed by most of the transition metals. Structures of some metal carbonyls are given below:

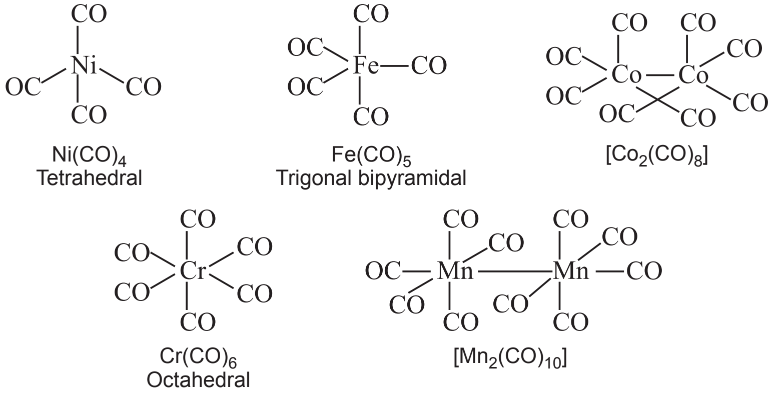


Fig. 9.4: Structures of some representative homoleptic metal carbonyls

18. Bonding in Metal Carbonyls: The metal–carbon bond in metal carbonyls have both σ and π character. The metal–carbon σ-bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The metal–carbon π-bond is formed by the donation of a pair of electrons from a filled *d*-orbital of metal into the vacant anti-bonding pi-molecular orbital (π^*) of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

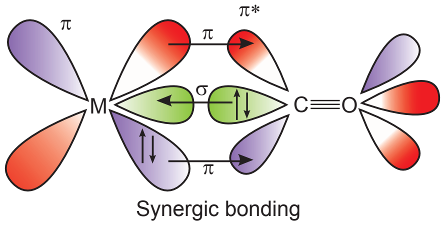


Fig. 9.5: Synergic bonding interactions in a carbonyl complex

19. Stability of Coordination Compounds:

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The stability of a complex ML_n is measured in terms of magnitude of (stability or formation) equilibrium constant. For a reaction of the type

$$M + nL \qquad\qquad ML_n$$

We can write stability constant as follows:

$$M + L \qquad\qquad ML \quad ; \ K_1 = [ML]/[M][L]$$

$$ML + L \qquad\qquad ML_2 \quad ; \ K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \qquad\qquad ML_3 \quad ; \ K_3 = [ML_3]/[ML_2][L]$$

....

$$ML_{n\text{-}1} + L \qquad\qquad ML_n \quad ; \ K_n = [ML_n]/[ML_{n-1}][L]$$

Where K_1, K_2, K_3 etc., are referred to as stepwise stability constants.

Alternatively, we can write the overall stability constant (β_n) as:

$$M + nL \qquad\qquad ML_n \quad ; \ \beta_n = [ML_n]/[M][L]^n$$

The stepwise and overall stability constant are therefore as follows:

$$\beta_n = K_1 \times K_2 \times K_3 \times \ldots \times K_n$$

➡ **Instability constant:** The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant.

20. Factors Affecting the Stability of Complexes

The stability of a complex depends upon

(*i*) **The nature of the central ion:** Greater the charge density (*i.e.*, charge/radius ratio) on the central metal ion, greater is the stability of the complex. For example, complexes of Fe^{3+} are more stable than Fe^{2+}. This is supported by the fact that the stability constant of $[Fe(CN)_6]^{3-}$ is 1.21×10^{31} and that of $[Fe(CN)_6]^{4-}$ is only 1.8×10^6.

(*ii*) **Nature of the ligand:** In general, more basic ligands have a tendency to donate the electron pairs to central metal ion more easily and hence the resulting complex is very stable. For example, the complexes involving F^- ions are more stable than those involving Cl^- ions or Br^- ions.

(*iii*) **Chelate effect:** When chelation occurs, entropy increases and therefore, the formation of the complex becomes more favourable. For example, chelate $[Cd(en)_4]^{2+}$ is 10,000 times more stable than the simple complex $[Cd(CH_3NH_2)_2]^{2+}$.

21. Applications of Coordination Compounds

➡ **In metallurgical separation:** Extraction of several metals from their ores involves complex formation. For example, silver and gold are extracted from their ores as cyanide complex.

$$4Au + 8KCN + 2H_2O + O_2 \longrightarrow \underset{\text{Potassium dicyanoaurate (I)}}{4K[Au(CN)_2]} + 4KOH$$

$$2K[Au(CN)_2] + Zn \longrightarrow \underset{\text{Potassium tetracyanozincate (II)}}{K_2[Zn(CN)_4]} + 2Au\downarrow$$

Purification of some metals can be achieved through complex formation. For example, in Mond's process, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- **In analytical chemistry:** Complex formation is frequently encountered in qualitative and quantitative chemical analysis.

(*i*) Qualitative Analysis:

- Detection of Cu^{2+} is based on the formation of a blue tetraammine copper (II) ion.

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}}$$

- Ni^{2+} is detected by the formation of a red complex with dimethyl glyoxime (DMG).

$$NiCl_2 + 2DMG + 2NH_4OH \longrightarrow \underset{\substack{\text{Nickel}\\ \text{bisdimethylglyoximate}}}{[Ni(DMG)_2]} + 2NH_4Cl + 2H_2O$$

- The separation of Ag^+ and Hg^{2+} in group I is based on the fact that while AgCl dissolves in NH_3, forming a soluble complex, Hg_2Cl_2 forms an insoluble black substance.

$$AgCl(s) + 2NH_3(aq) \longrightarrow \underset{\text{Soluble complex}}{[Ag(NH_3)_2]Cl(aq)}$$

$$Hg_2Cl_2(s) + NH_3 \longrightarrow \underset{\text{Black insoluble substance}}{Hg(NH_2)Cl \,.\, Hg} + HCl$$

(*ii*) Quantitative Analysis

Gravimetric estimation of Ni^{2+} is carried out by precipitating Ni^{2+} as red nickel dimethyl oxime complex in the presence of ammonia.

$$Ni^{2+} + 2DMG \xrightarrow{NH_3} \underset{\text{Red ppt.}}{[Ni(DMG)_2]}$$

EDTA is used in the complexometric determination of several metal ions such as Ca^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, etc.

- **In Medicinal Chemistry:**
  - The platinum complex, *cis*-$[Pt(NH_3)_2Cl_2]$, known as cisplatin is used in the treatment of cancer.
  - EDTA complex of calcium is used in the treatment of lead poisoning. Ca-EDTA is a weak complex; when it is administered, calcium in the complex is replaced by the lead present in the body and is eliminated with the urine.
  - The excess of copper and iron present in animal system are removed by the chelating ligands, D-penicillamine and desferrioxime B via the formation of complexes.
- **In Biological System:**
  - Haemoglobin, the red pigment of blood which acts as oxygen carrier is a complex of Fe^{2+} with porphyrin.
  - The pigment responsible for photosynthesis, chlorophyll, is a complex of Mg^{2+} with porphyrin.
  - Vitamin B_{12} (Cyanocobalamine), the antipernicious anaemia factor, is a complex of cobalt.
- **In the Estimation of Hardness of Water:** The hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- **In Photography:** In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- **In Catalysis:** Coordination compounds are used as catalysts for many industrial processes. For example, Wilkinson's catalyst, a rhodium complex having formula $[(Ph_3P)_3RhCl]$ is used for the selective hydrogenation of alkenes.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Write the formulas for the following coordination compounds:

(*i*) tetraamminediaquacobalt(III) chloride

(*ii*) potassium tetracyanidonickelate(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)hexacyanidoferrate(II)

Ans. (*i*) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (*ii*) $K_2[Ni(CN)_4]$

(*iii*) $[Cr(en)_3]Cl_3$ (*iv*) $[Pt(NH_3)BrCl(NO_2)]^-$

(*v*) $[PtCl_2(en)_2](NO_3)_2$ (*vi*) $Fe_4[Fe(CN)_6]_3$

Q. 2. Write 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*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$**

Ans. (*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

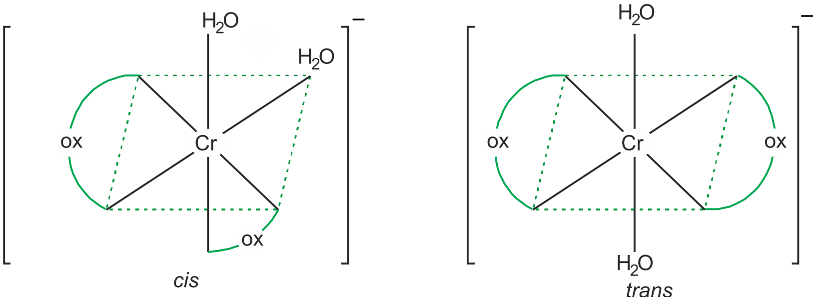
Q. 3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

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

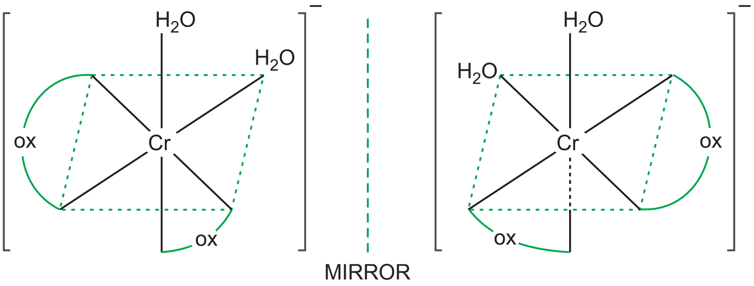
Ans. (*i*) Both geometrical (*cis–trans*) and optical isomers for *cis* can exist.

(*a*) Geometrical isomers of $K[Cr(H_2O)_2(C_2O_4)_2]$:

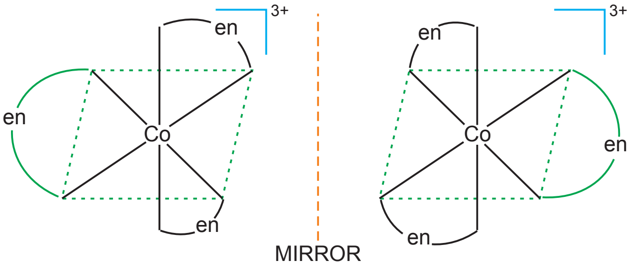


cis *trans*

(*b*) Optical isomers (*d*- and *l*-) of *cis*-$K[Cr(H_2O)_2(C_2O_4)_2]$:



(*ii*) Two optical isomers can exist.



(*iii*) Ionisation isomers:

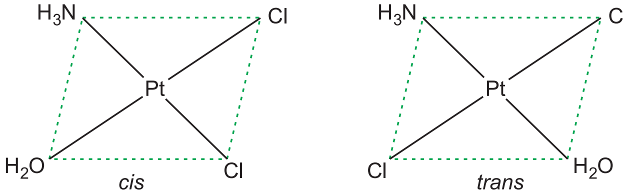
$[Co(NH_3)_5(NO_2)](NO_3)_2]$, $[Co(NH_3)_5(NO_3)](NO_2)(NO_3)]$

Linkage isomers:

$[Co(NH_3)_5(NO_2)](NO_3)_2]$, $[Co(NH_3)_5(ONO)](NO_3)_2]$

MA_5X type complexes do not show geometrical and optical isomerism.

(*iv*) Geometrical isomers can exist.



Q. 4. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

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Ans. The ionisation isomers dissolve in water to yield different ions and thus react differently with various reagents:

$$[Co(NH_3)_5Cl]SO_4 + Ba^{2+} \longrightarrow \underset{\text{Ppt}}{BaSO_4(s)\downarrow}$$

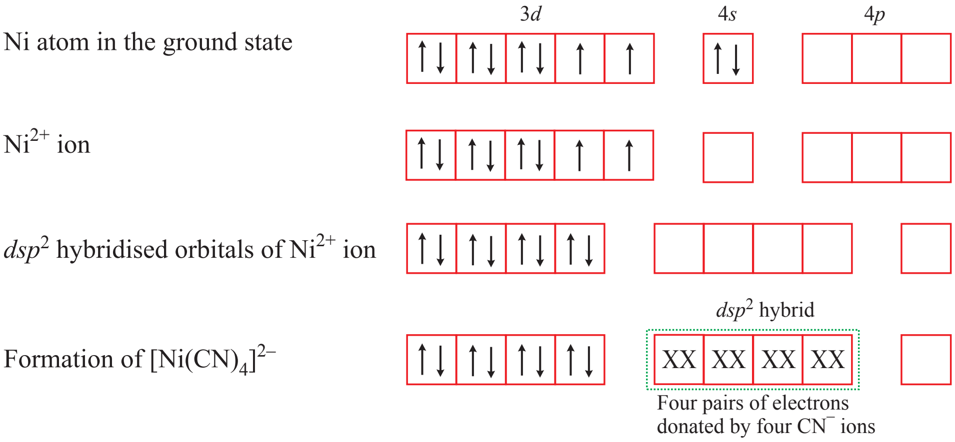
$$[Co(NH_3)_5SO_4]Cl + Ba^{2+} \longrightarrow \text{No reaction}$$

$$[Co(NH_3)_5Cl]SO_4 + Ag^{+} \longrightarrow \text{No reaction}$$

$$[Co(NH_3)_5SO_4]Cl + Ag^{+} \longrightarrow \underset{\text{Ppt}}{AgCl(s)\downarrow}$$

Q. 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.

Ans. Nickel in $[Ni(CN)_4]^{2-}$ is in the +2 oxidation state. The formation of $[Ni(CN)_4]^{2-}$ may be explained through hybridisation as follows:



Since no unpaired electrons is present, the square planar complex is diamagnetic.

In $[NiCl_4]^{2-}$, Cl^- is a weak field ligand. It is, therefore, unable to pair up the unpaired electrons of the $3d$ orbital. Hence, the hybridisation involved is sp^3 and the shape is tetrahedral. Since two electrons are unpaired, it is paramagnetic.

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

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Ans. In $[Ni(CO)_4]$, Ni is in zero oxidation state whereas in $[NiCl_4]^{2-}$ it is in +2 oxidation state. In the presence of strong ligand, CO, the unpaired *d*-electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

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

Ans. In presence of CN^- (a strong ligand), the $3d^5$ electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming an inner orbital complex. In the presence of H_2O (a weak ligand), $3d$ electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex containing five unpaired electrons. Hence, it is strongly paramagnetic.

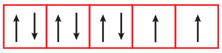
Q. 8. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Ans. In $[Co(NH_3)_6]^{3+}$, Co is in +3 oxidation state and has d^6 electrons. In the presence of NH_3, the $3d$ electrons pair up leaving two *d*-orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex.

In $[Ni(NH_3)_6]^{2+}$, Ni is in +2 oxidation state and has d^8 configuration. The hybridisation involved is sp^3d^2, forming the outer orbital complex.

Q. 9. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

Ans. In $[Pt(CN)_4]^{2-}$ ion, Pt is in +2 oxidation state, its electronic configuration is $5d^8$. It forms a square planner structure, it means the hybridisation is *dsp*^{2}.



$3d^8$

CN^- is a strong field ligand to pairing of unpaired electrons takes place. So, the number of unpaired electrons is 0.

Q. 10. The hexaaqua manganese(II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

Ans. Mn in the +2 state has the configuration $3d^5$. In the presence of H_2O a weak ligand, the distribution of these five electrons is $t_{2g}^3\, e_g^2$, *i.e.*, all the electrons remain unpaired. In the presence of CN^- a strong ligand, the distribution is $t_{2g}^5\, e_g^0$, *i.e.*, two t_{2g} orbitals contain paired electrons while the third t_{2g} orbital contains one unpaired electron.

NCERT Textbook Exercises

Q. 1. Explain the bonding in coordination compounds in terms of Werner's postulates.

Ans. Refer to Basic Concepts Point 15.

Q. 2. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why.

Ans. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio forms double salt $FeSO_4 . (NH_4)_2\, SO_4.6H_2O$ which ionises in the solution to give Fe^{2+} ions. Hence, it gives the test of Fe^{2+} ions.

$CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio forms a complex, with the formula $[Cu(NH_3)_4]SO_4$. The complex ion, $[Cu(NH_3)_4]^{2+}$ does not ionise to give Cu^{2+} ions. Hence, it does not give the test of Cu^{2+} ion.

Q. 3. Explain with two examples for each of the following:

Coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Ans. **Coordination Entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of molecules or ions (ligands), *e.g.*, $[Co(NH_3)_3Cl_3]$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, etc.

Ligands: Ligands are the atoms, molecules or ions which donate a pair of electrons to central metal atom or ion and form a coordinate bond with it.

Example: $\ddot{N}H_3$, $H_2\ddot{N}CH_2—CH_2\ddot{N}H_2$

Coordination Number (CN): The coordination number of a metal ion in a complex may be defined as the total number of ligand donor atoms to which the metal ion is directly bonded. For example, in the complex ions, $[Co(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$ the coordination numbers of both Co and Fe is 6.

Coordination Polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion is known as the coordination polyhedron around the central atom/ion. Tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal are common shapes of coordination polyhedra.

Homoleptic Complex: The complex in which metal atom is bound to only one kind of donor groups, *e.g.*, $[Cu(CN)_4]^{3-}$.

Heteroleptic Complex: The complex in which metal atom is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$.

Q. 4. What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.

Ans. A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, *e.g.*, Cl^- and NH_3.

A molecule or an ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called a bidentate ligand, *e.g.*, $NH_2—CH_2—CH_2—NH_2$ and $^-OOC—COO^-$.

A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called ambidentate ligand, *e.g.*, CN^- or NC^- and $:NO_2^-$ or $:ONO^-$.

Q. 5. Specify the oxidation numbers of the metals in the following coordination entities:

(*i*) $[Co(H_2O)(CN)(en)_2]^{2+}$ **(*ii*) $[CoBr_2(en)_2]^+$**

(*iii*) $[PtCl_4]^{2-}$ **(*iv*) $K_3[Fe(CN)_6]$**

(*v*) $[Cr(NH_3)_3Cl_3]$

Ans. (*i*) $x + (0) + (-1) + (0) = +2$ or $x = +3$

(*ii*) $x + 2(-1) + 0 = +1$ or $x = +3$

(*iii*) $x - 4 = -2$ or $x = +2$

(*iv*) $3(1) + x + 6(-1) = 0$ or $x = +3$

(*v*) $x + 0 + 3(-1) = 0$ or $x = +3$

Q. 6. Using IUPAC norms, write the formulae of the following:

(*i*) tetrahydroxozincate(II) **(*ii*) potassium tetrachloridopalladate(II)**

(*iii*) diamminedichloridoplatinum(II) **(*iv*) potassium tetracyanidonickelate(II)**

(*v*) pentaamminenitrito-O-cobalt(III) **(*vi*) hexaamminecobalt(III) sulphate**

[*CBSE 2019 (56/1/1)*]

(*vii*) potassium tri(oxalato)chromate(III) **(*viii*) hexaammineplatinum(IV)**

(*ix*) tetrabromidocuprate(II)

(*x*) pentaamminenitrito-N-cobalt(III)

Ans. (*i*) $[Zn(OH)_4]^{2-}$ (*ii*) $K_2[PdCl_4]$

(*iii*) $[Pt(NH_3)_2Cl_2]$ (*iv*) $K_2[Ni(CN)_4]$

(*v*) $[Co(NH_3)_5(ONO)]^{2+}$ (*vi*) $[Co(NH_3)_6]_2(SO_4)_3$

(*vii*) $K_3[Cr(C_2O_4)_3]$ (*viii*) $[Pt(NH_3)_6]^{4+}$

(*ix*) $[CuBr_4]^{2-}$ (*x*) $[Co(NH_3)_5(NO_2)]^{2+}$

Q. 7. Using IUPAC norms, write the systematic names of the following:

(*i*) $[Co(NH_3)_6]Cl_3$ **(*ii*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$**
(*iii*) $[Ti(H_2O)_6]^{3+}$ **(*iv*) $[Co(NH_3)_4Cl(NO_2)]Cl$**
(*v*) $[Mn(H_2O)_6]^{2+}$ **(*vi*) $[NiCl_4]^{2-}$**
(*vii*) $[Ni(NH_3)_6]Cl_2$ **(*viii*) $[Co(en)_3]^{3+}$**
(*ix*) $[Ni(CO)_4]$

Ans. (*i*) hexaamminecobalt(III) chloride (*ii*) diamminechlorido(methylamine)platinum (II) chloride
(*iii*) hexaaquatitanium(III) ion (*iv*) tetraamminechloridonitrito-N-cobalt(III) chloride
(*v*) hexaaquamanganese(II) ion (*vi*) tetrachloridonickelate(II)
(*vii*) hexaamminenickel(II) chloride (*viii*) tris (ethane-1, 2-diamine) cobalt(III) ion
(*ix*) tetracarbonylnickel (0)

Q. 8. List various types of isomerism possible for coordination compounds, giving an example of each.

Ans. Refer to Basic Concepts Point 14.

Q. 9. How many geometrical isomers are possible in the following coordination entities?

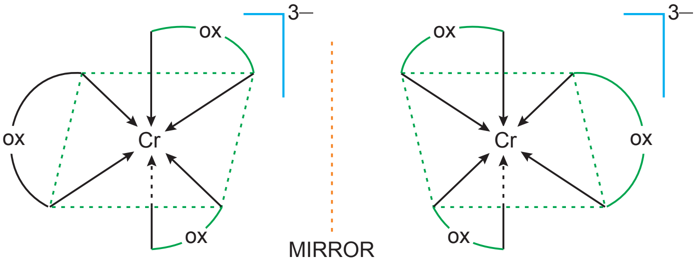
(*i*) $[Cr(C_2O_4)_3]^{3-}$ **(*ii*) $[Co(NH_3)_3Cl_3]$**

Ans. (*i*) Nil (*ii*) Two (*cis* and *trans*)

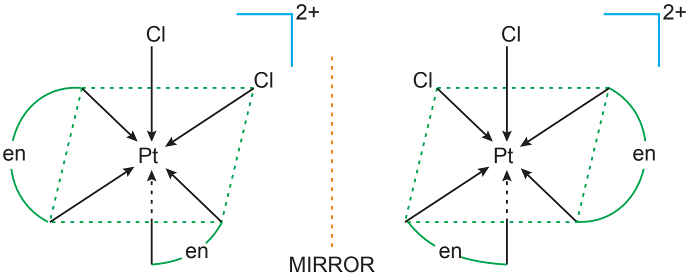
Q. 10. Draw the structures of optical isomers of

(*i*) $[Cr(C_2O_4)_3]^{3-}$ **(*ii*) $[PtCl_2(en)_2]^{2+}$**
(*iii*) $[Cr(NH_3)_2Cl_2(en)]^{+}$

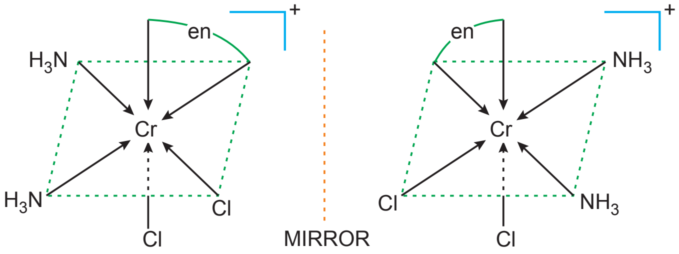
Ans. (*i*) $[Cr(C_2O_4)_3]^{3-}$



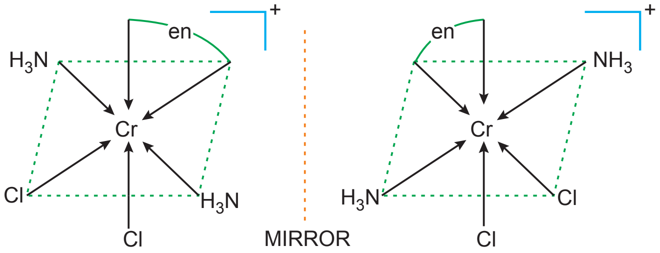
(*ii*) *cis*-$[PtCl_2(en)_2]^{2+}$:



(*iii*) (*a*) *cis*-$[Cr(NH_3)_2Cl_2(en)]^{+}$



(*b*) *trans*-$[Cr(NH_3)_2Cl_2(en)]^+$



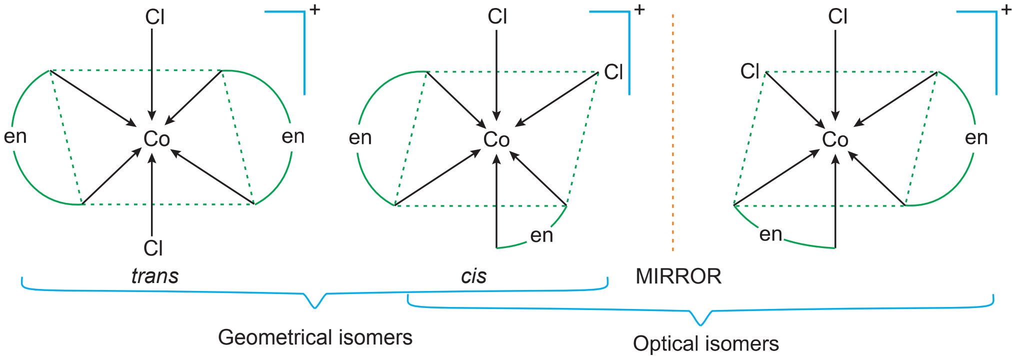
Q. 11. Draw all the isomers (geometrical and optical) of:

(*i*) $[CoCl_2(en)_2]^+$

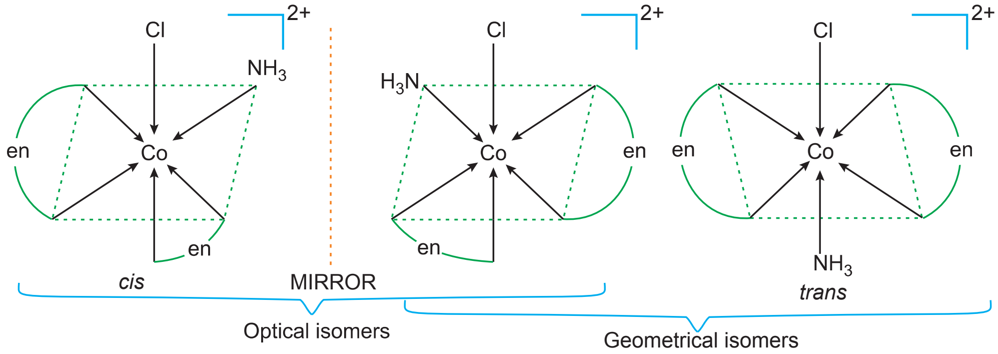
(*ii*) $[Co(NH_3)Cl(en)_2]^{2+}$

(*iii*) $[Co(NH_3)_2Cl_2(en)]^+$

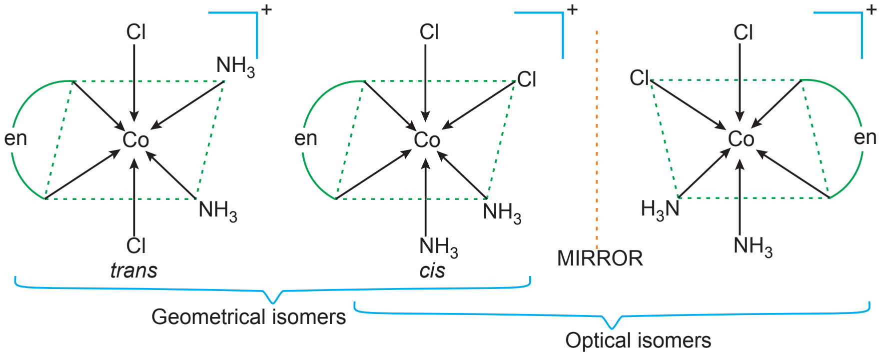
Ans. (*i*)



(*ii*)

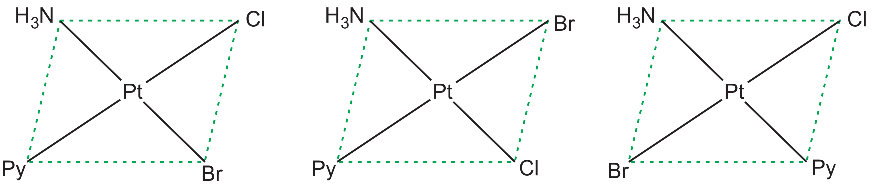


(*iii*)



Q. 12. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomerism?

Ans. Three isomers are possible as follows:



Isomers of this type do not show any optical isomerism. Optical isomerism rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

Q. 13. Aqueous copper sulphate solution (blue in colour) gives (*i*) a green precipitate with aqueous potassium fluoride, and (*ii*) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Ans. Aqueous copper sulphate exists as $[Cu(H_2O)_4]SO_4$. It is a labile complex. The blue colour of the solution is due to $[Cu(H_2O)_4]^{2+}$ ions.

(*i*) When KF is added, the weak H_2O ligands are replaced by F^- ligands forming $[CuF_4]^{2-}$ ions, which is a green precipitate.

$$[Cu(H_2O)_4]^{2+} + 4F^- \longrightarrow \underset{\substack{\text{tetrafluorocuprate (II)} \\ \text{(Green ppt.)}}}{[CuF_4]^{2-}} + 4H_2O$$

(*ii*) When KCl is added, Cl^- ligands replace the weak H_2O ligands forming $[CuCl_4]^{2-}$ ion, which has bright green colour.

$$[Cu(H_2O)_4]^{2+} + 4Cl^- \longrightarrow \underset{\substack{\text{tetrachlorocuprate (II)} \\ \text{(Green solution)}}}{[CuCl_4]^{2-}} + 4H_2O$$

Q. 14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

Ans. $K_2[Cu(CN)_4]$ is formed when excess of aqueous KCN is added to an aqueous solution of $CuSO_4$.

$$\underset{\text{Copper sulphate}}{CuSO_4(aq)} + \underset{\text{Potassium cyanide}}{4KCN(aq)} \longrightarrow \underset{\substack{\text{potassium} \\ \text{tetracyanocuprate (II)} \\ \text{(soluble)}}}{K_2[Cu(CN)_4]} + K_2SO_4(aq)$$

As CN^- ions are strong ligands the complex is very stable. It is not replaced by S^{2-} ions when H_2S gas is passed through the solution and thus no precipitate of CuS is obtained.

Q. 15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(*i*) $[Fe(CN)_6]^{4-}$ **(*ii*) $[FeF_6]^{3-}$**

(*iii*) $[Co(C_2O_4)_3]^{3-}$ **(*iv*) $[CoF_6]^{3-}$** **[*CBSE 2020 (56/2/1)*]**

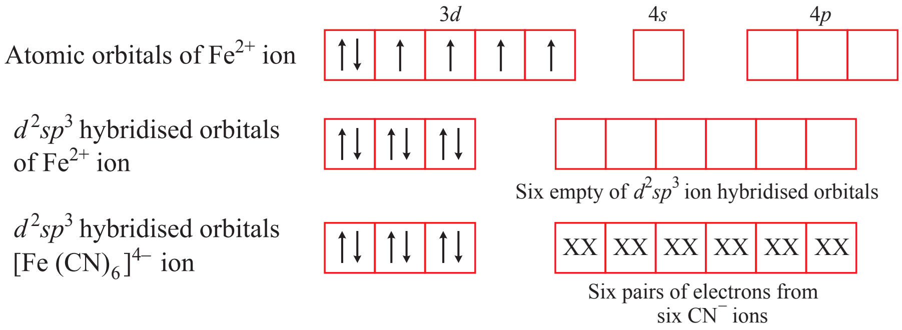
Ans. **(*i*) $[Fe(CN)_6]^{4-}$:** d^2sp^3, octahedral, diamagnetic.

In this complex ion, the oxidation state of iron is +2.

Electronic configuration of Fe = [Ar] $3d^6\,4s^2$

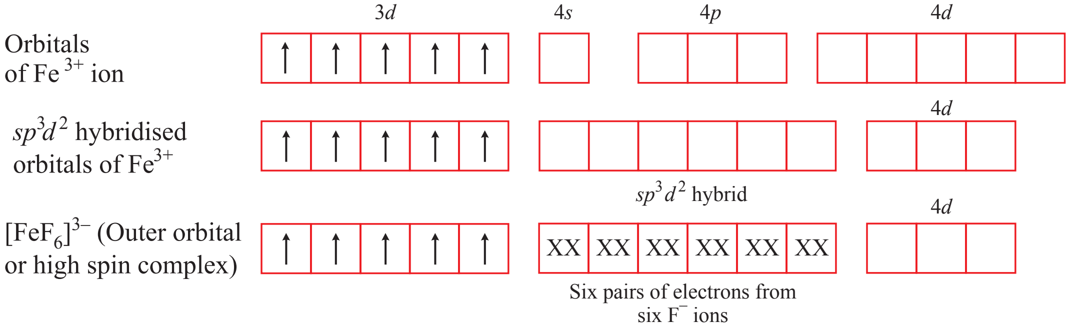
Electronic configuration of Fe^{2+} = [Ar] $3d^6$

To accommodate six pairs of electrons from six cyanide ions, the iron(II) ion must make available six empty orbitals. This can be achieved by the following hybridization scheme wherein electrons in the *d*-subshell have been paired up as CN^- ions are strong field ligands.



Thus, six pairs of electrons from six cyanide ions occupy the six hybridized orbitals of iron (II) ion. At the same time, we find no orbital which contains unpaired electron. Hence, $[Fe(CN)_6]^{4-}$ is octahedral and shows diamagnetism.

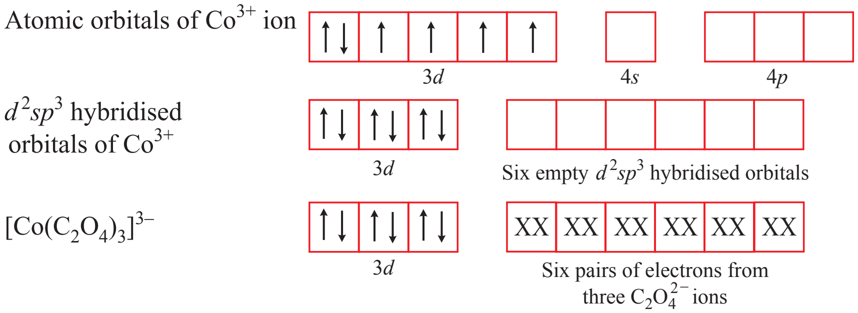
(*ii*) $[FeF_6]^{3-}$



Number of unpaired electrons (n) = 5

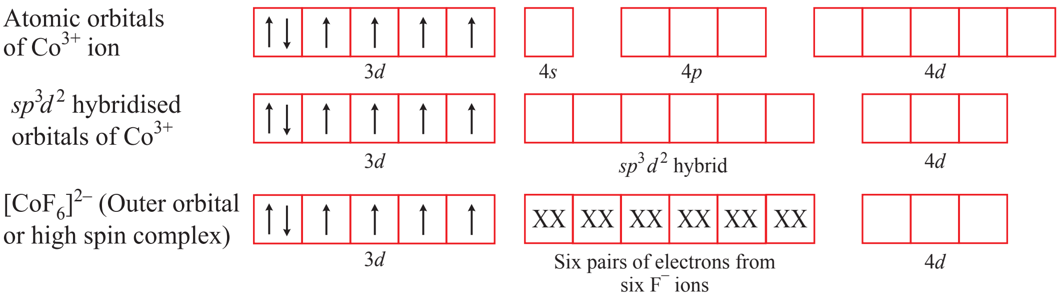
Magnetic moment (μ) = $\sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM

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



This complex is inner-orbital complex. It is an octahedral complex with d^2sp^3 hybridisation. As there is no orbital which contains unpaired electron, the complex is diamagnetic.

(*iv*) $[CoF_6]^{3-}$



sp^3d^2 hybridisation leads to octahedral geometry. Paramagnetic, as there are four unpaired electrons.

Q. 16. Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.

Ans. Refer to Basic Concepts Point 16 (Fig. 9.2).

Q. 17. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

Ans. The arrangement of ligands in order of their increasing field strengths, *i.e.*, increasing crystal field splitting energy (CFSE) values is called spectrochemical series.

The ligands with a small value of CFSE (Δ_0) are called weak field ligands whereas those with a large value of CFSE are called strong field ligands.

Q. 18. What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of *d*-orbitals in a coordination entity?

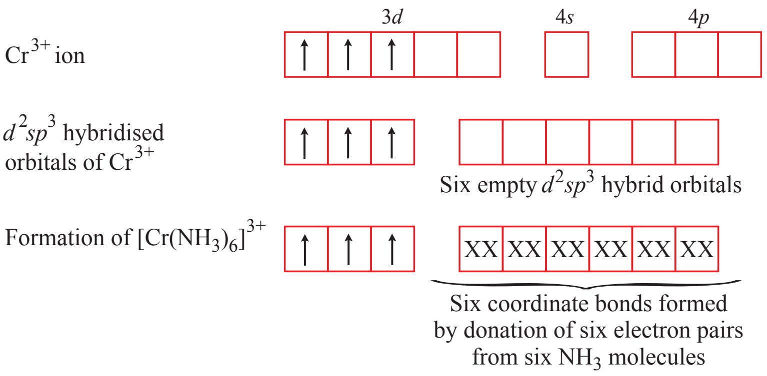
Ans. When ligands approach a transition metal ion, the *d*-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy (Δ_0) in case of octahedral field.

If $\Delta_0 < P$ (pairing energy), the 4th electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\, e_g^1$, thereby forming high spin complexes. Such ligands for which $\Delta_0 < P$ are called weak field ligands.

If $\Delta_0 > P$, the 4th electron pairs up in one of the t_{2g} orbitals giving the configuration $t_{2g}^4\, e_g^0$, thus forming low spin complexes. Such ligands for which $\Delta_0 > P$ are called strong field ligands.

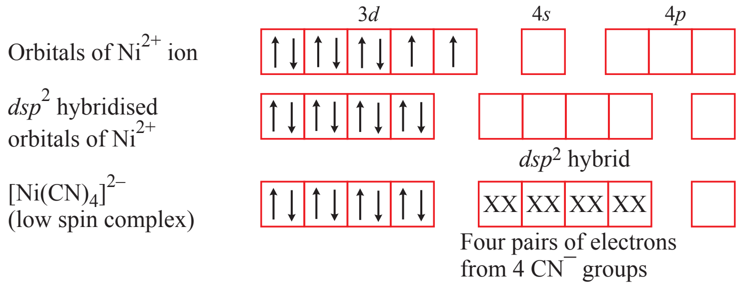
Q. 19. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why.

Ans. (*i*) **Formation of $[Cr(NH_3)_6]^{3+}$:** The oxidation state of chromium in $[Cr(NH_3)_6]^{3+}$ ion is +3. The hybridisation scheme is as shown in figure given below.



Cr^{3+} ion provides six empty orbitals to accommodate six pairs of electrons from six molecules of ammonia. The resulting complex $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridisation and is hence octahedral. The presence of three unpaired electrons in the complex explains its paramagnetic behaviour.

(*ii*) **Formation of $[Ni(CN)_4]^{2-}$:** In $[Ni(CN)_4]^{2-}$ nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in the diagram given here:



The complex $[Ni(CN)_4]^{2-}$ involves dsp^2 hybridisation and hence square planar.

Each of the dsp^2 hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

Q. 20. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Ans. In $[Ni(H_2O)_6]^{2+}$, Ni is in +2 state with the configuration $3d^8$, *i.e.*, it has two unpaired electrons which do not pair up in the presence of the weak H_2O ligand. So, it is coloured. The *d–d* transition absorbs red light and the complementary light emitted is green.

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

Q. 21. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

Ans. In both the complexes, Fe is in +2 oxidation state with d^6 configuration. As the ligands CN and H_2O possess different crystal field splitting energy (Δ_0), they absorb different components of visible light for *d-d* transition. Hence, the transmitted colours are different in dilute solutions.

Q. 22. Discuss the nature of bonding in metal carbonyls.

Ans. Refer to Basic Concepts Point 18.

Q. 23. Give the oxidation state, *d* orbital occupation and coordination number of the central metal ion in the following complexes:

(*i*) $K_3[Co(C_2O_4)_3]$ **(*ii*) *cis*-$[Cr(en)_2Cl_2]Cl$**

(*iii*) $(NH_4)_2[CoF_4]$ **(*iv*) $[Mn(H_2O)_6]SO_4$**

Ans. Let *x* be the oxidation state of central metal ion.

S.No.	Complex	Oxidation state	Coordination Number	*d*-orbital occupation
(*i*)	$K_3[Co(C_2O_4)_3]$	$3 \times 1 + x + (-2) \times 3 = +3$	6 (as $C_2O_4^{2-}$ is didentate)	$Co^{3+} = 3d^6 = t_{2g}^6\, e_g^0$
(*ii*)	*cis*-$[Cr(en)_2Cl_2]Cl$	$x + 0 \times 2 + (-2) \times 1 + (-1) \times 1 = +3$	6 (en is didentate)	$Cr^{3+} = 3d^3 = t_{2g}^3$
(*iii*)	$(NH_4)_2[CoF_4]$	$2 \times 1 + x + (-1) \times 4 = +2$	4	$Co^{2+} = 3d^7 = e_g^4\, t_{2g}^3$
(*iv*)	$[Mn(H_2O)_6]SO_4$	$x + 0 \times 6 + (-2) \times 1 = +2$	6	$Mn^{2+} = 3d^5 = t_{2g}^3\, e_g^2$

Q. 24. 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:

(*i*) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ **(*ii*) $[Co(NH_3)_5Cl]Cl_2$**

(*iii*) $[CrCl_3(py)_3]$ **(*iv*) $Cs[FeCl_4]$** **(*v*) $K_4[Mn(CN)_6]$**

Ans. (*i*) potassiumdiaquadioxalatochromate(III)trihydrate.

Coordination number = 6 ; Shape = Octahedral

Oxidation state of Cr : $x + 0 + 2\,(-2) = -1,\ x = +3$

EC of $Cr^{3+} = 3d^3 = t_{2g}^3 e_g^0$; Unpaired electrons ($n$) = 3.

Magnetic moment $(\mu) = \sqrt{n(n+2)} = \sqrt{3 \times 5} = \sqrt{15}\ \text{BM} = 3.87\ \text{BM}$

(*ii*) pentaamminechloridocobalt (III) chloride

Coordination number of Co = 6; Shape = Octahedral

Oxidation state of Co: $x + 0 - 1 = +2$ or $x = +3$

EC of $Co^{3+} = 3d^6 = t_{2g}^6\, e_g^0$

$n = 0,\ \mu = 0.$

(*iii*) trichloridotripyridinechromium (III)

Coordination number of Cr = 6; Shape = Octahedral

Oxidation state of Cr : $x - 3 + 0 = 0,\ x = +3$

EC of $Cr^{3+} = 3d^3 = t_{2g}^3\, e_g^0$

$n = 3,\ \mu = 3.87$ BM

(*iv*) caesiumtetrachloridoferrate (III)

Coordination number of Fe = 4 ; Shape = Tetrahedral

Oxidation state of Fe: $x - 4 = -1$ or $x = +3$

$$\text{EC of Fe}^{3+} = 3d^5 = e_g^2\, t_{2g}^3$$

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

(*v*) potassiumhexacyanomanganate (II)

Coordination number of Mn = 6; Shape = Octahedral

Oxidation state of Mn : $x - 6 = -4,\ x = +2$

$$\text{EC of Mn}^{2+} = 3d^5 = t_{2g}^5\, e_g^0$$

$$n = 1,\ \mu = \sqrt{1\,(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

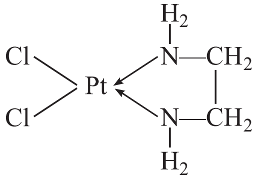
Q. 25. Explain the violet colour of the complex $[\mathrm{Ti(H_2O)_6}]^{3+}$ on the basis of crystal field theory.

Ans. In $[\mathrm{Ti(H_2O)_6}]^{3+}$, Ti is in +3 oxidation state with d^1 configuration. Therefore, the complex appears violet due to the transition of electron from t_{2g} level to the e_g level, *e.g.*,

$$(t_{2g}^1\, e_g^0 \longrightarrow t_{2g}^0\, e_g^1)$$

Q. 26. What is meant by chelate effect? Give an example. **[*CBSE 2020 (56/2/1)*]**

Ans. When a bidentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six-membered ring is formed, the effect is called chelate effect. Example, $[\mathrm{PtCl_2(en)}]$.



Q. 27. Discuss briefly giving an example in each case, the role of coordination compounds in:

(*i*) biological systems
(*ii*) medicinal chemistry
(*iii*) analytical chemistry
(*iv*) extraction/metallurgy of metals

Ans. Refer to Basic Concepts Point 21.

Q. 28. How many ions are produced from the complex, $[\mathrm{Co(NH_3)_6]Cl_2}$ in solution?

(*i*) 6
(*ii*) 4
(*iii*) 3
(*iv*) 2

Ans. The correct option is (*iii*).

Coordination number of cobalt = 6. It ionises in the solution as:

$[\mathrm{Co(NH_3)_6]Cl_2} \xrightarrow{aq} [\mathrm{Co(NH_3)_6}]^{2+} + 2\mathrm{Cl}^-$. Hence, three ions are produced.

Q. 29. Amongst the following ions which one has the highest magnetic moment value?

(*i*) $[\mathrm{Cr(H_2O)_6}]^{3+}$
(*ii*) $[\mathrm{Fe(H_2O)_6}]^{2+}$
(*iii*) $[\mathrm{Zn(H_2O)_6}]^{2+}$

Ans. The oxidation states are: Cr (III), Fe (II) and Zn (II).

EC of $\mathrm{Cr}^{3+} = 3d^3$, unpaired electrons = 3

EC of $\mathrm{Fe}^{2+} = 3d^6$, unpaired electrons = 4

EC of $\mathrm{Zn}^{2+} = 3d^{10}$, unpaired electrons = 0

As $\mu = \sqrt{n\,(n+2)}$, therefore, (*ii*) has the highest magnetic moment.

Q. 30. The oxidation number of cobalt in $K[Co(CO)_4]$ is:

(*i*) +1 **(*ii*) +3**

(*iii*) – 1 **(*iv*) – 3**

Ans. $K^+[Co(CO)_4]^{-1}$

$\therefore \quad 1 + x + 0 = 0, x = -1$

Therefore, (*iii*) is the correct option.

Q. 31. Amongst the following, the most stable complex is:

(*i*) $[Fe(H_2O)_6]^{3+}$ **(*ii*) $[Fe(NH_3)_6]^{3+}$**

(*iii*) $[Fe(C_2O_4)_3]^{3-}$ **(*iv*) $[FeCl_6]^{3-}$**

Ans. In each of the given complex, Fe is in +3 state. As $C_2O_4^{2-}$ is bidentate chelating ligand, it forms chelate rings and therefore, (*iii*) is the most stable complex.

Q. 32. What will be the correct order for the wavelengths of absorption in the visible region for the following: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

Ans. As metal ion is fixed, the increasing CFSE values of the ligands from the spectrochemical series are in the order:

$$H_2O < NH_3 < NO_2^-$$

Hence, the energies absorbed for excitation will be in the order:

$$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$$

As $E = \frac{hc}{\lambda}$, therefore, the wavelengths absorbed will be in the opposite order,

$$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Which of the following has highest molar conductivity?

(*a*) potassiumhexacyanoferrate (II) (*b*) hexaaquachromium(III)chloride

(*c*) tetraamminedichloridocobalt (III)chloride (*d*) diamminechlorido platinum (II)

2. When 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to *[NCERT Exemplar]*

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

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

3. When 1 mol $CrCl_3.6H_2O$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained. The formula of the complex is: *[NCERT Exemplar]*

(*a*) $[CrCl_3(H_2O)_3].3H_2O$ (*b*) $[CrCl_2(H_2O)_4]Cl.2H_2O$

(*c*) $[CrCl(H_2O)_5]Cl_2.H_2O$ (*d*) $[Cr(H_2O)_6]Cl_3$

4. Which of the following species is not expected to be a ligand? *[NCERT Exemplar]*

(*a*) NO (*b*) NH_4^+

(*c*) $NH_2CH_2CH_2NH_2$ (*d*) CO

5. 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? *[NCERT Exemplar]*

(*a*) Thiosulphato (*b*) Oxalato

(*c*) Glycinato (*d*) Ethane-1,2-diamine

6. Which of the following is π-acid ligand?

(*a*) NH_3 (*b*) CO

(*c*) F^- (*d*) ethylenediammine

7. **The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?** [*NCERT Exemplar*]

(*a*) $[Fe(CO)_5]$
(*b*) $[Fe(CN)_6]^{3-}$
(*c*) $[Fe(C_2O_4)_3]^{3-}$
(*d*) $[Fe(H_2O)_6]^{3+}$

8. **The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is** [*NCERT Exemplar*]

(*a*) diamminedichloridoplatinum (II)
(*b*) diamminedichloridoplatinum (IV)
(*c*) diamminedichloridoplatinum (0)
(*d*) dichloridodiammineplatinum (IV)

9. **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** [*NCERT Exemplar*]

(*a*) linkage isomers
(*b*) coordination isomers
(*c*) ionisation isomers
(*d*) geometrical isomers

10. **Indicate the complex ion which shows geometrical isomerism.** [*NCERT Exemplar*]

(*a*) $[Cr(H_2O)_4Cl_2]^+$
(*b*) $[Pt(NH_3)_3Cl]$
(*c*) $[Co(NH_3)_6]^{3+}$
(*d*) $[CO(CN)_5(NC)]^{3-}$

11. **The geometry of $Ni(CO)_4$ and $[Ni(PPh_3)_2Cl_2]$ are**

(*a*) both square planar
(*b*) tetrahedral and square planar, respectively
(*c*) both tetrahedral
(*d*) square planar and tetrahedral, respectively

12. **Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?** [*NCERT Exemplar*]

(*a*) $[Co(NH_3)_6]^{3+}$
(*b*) $[Mn(CN)_6]^{3-}$
(*c*) $[Fe(CN)_6]^{4-}$
(*d*) $[Fe(CN)_6]^{3-}$

13. **Atomic number of Mn, Fe, Co and Ni are 25, 26 27 and 28 respectively. Which of the following outer orbital octahedral complexes have same number of unpaired electrons?** [*NCERT Exemplar*]

(*a*) $[MnCl_6]^{3-}$
(*b*) $[FeF_6]^{3-}$
(*c*) $[CoF_6]^{3-}$
(*d*) $[Ni(NH_3)_6]^{2+}$

14. **Crystal field stabilization energy for high spin d^4 octahedral complex is**

(*a*) $-1.6\ \Delta_0 + P$
(*b*) $-1.80\ \Delta_0$
(*c*) $-1.2\ \Delta_0$
(*d*) $-0.6\ \Delta_0$

15. **The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be** [*NCERT Exemplar*]

(*a*) 18,000 cm^{-1}
(*b*) 16,000 cm^{-1}
(*c*) 8,000 cm^{-1}
(*d*) 20,000 cm^{-1}

16. **In spectrochemical series, chlorine is above water, *i.e*, $Cl > H_2O$. This is due to**

(*a*) large size of Cl than H_2O
(*b*) Good π-acceptor properties of Cl
(*c*) Strong σ-donor and good π-acceptor properties of Cl
(*d*) Good π-donor properties of Cl

17. **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, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$** [*NCERT Exemplar*]

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

18. **Which of the following statement is correct?**

(*a*) Higher CFSE favours formation of high spin complex
(*b*) Lower CFSE favours formation of low spin complex
(*c*) t_{2g} orbital are three fold degenerate whereas e_g orbitals are two fold degenerate.
(*d*) A particular metal ion in a particular oxidation state can form either diamagnetic complexes only or paramagnetic complexes only.

19. Which of the following is an organometallic compound?

(*a*) $Ti(C_2H_4)_4$ (*b*) $Ti(OC_2H_5)$ (*c*) $Ti(OCOCH_3)_4$ (*d*) $Ti(OC_6H_5)$

20. Ziegler-Natta catalyst is $TiCl_4$ dissolved in

(*a*) triethylaluminium (*b*) ether (*c*) water (*d*) ammonia

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*b*) **7.** (*c*) **8.** (*a*) **9.** (*a*) **10.** (*a*)
11. (*c*) **12.** (*a*), (*c*) **13.** (*a*),(*c*) **14.** (*d*) **15.** (*c*) **16.** (*d*) **17.** (*c*) **18.** (*c*) **19.** (*a*) **20.** (*a*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

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

1. **Assertion (*A*)** : Oxalate ion is a bidentate ligand.
   Reason (*R*) : Oxalate ion has two donor atoms.
2. **Assertion (*A*)** : Linkage isomerism arises in coordination compounds containing ambidentate ligand.
   Reason (*R*) : Ambidentate ligand has two different donor atoms.
3. **Assertion (*A*)** : Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
   Reason (*R*) : Geometrical isomerism is not shown by complexes of coordination number 6.
4. **Assertion (*A*)** : $[Ni(CN)_4]^{2-}$ is square planar and diamagnetic.
   Reason (*R*) : It has no unpaired electrons due to presence of strong ligand.
5. **Assertion (*A*)** : $[Ni(CO)_4]$ has square planar geometry while $[Ni(CN)_4]^{2-}$ has tetrahedral geometry.
   Reason (*R*) : Geometry of any complex depends upon the nature of ligands attached.
6. **Assertion (*A*)** : $[FeF_6]^{3-}$ is a low spin complex.
   Reason (*R*) : Low spin complexes have lesser number of unpaired electrons.
7. **Assertion (*A*)** : ($[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   Reason (*R*) : Because it has d^2sp^3 type hybridisation.
8. **Assertion (*A*)** : $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.
   Reason (*R*) : Unpaired electrons are present in their *d*-orbitals.
9. **Assertion (*A*)** : F^- ion is a weak ligand and forms outer orbital complex.
   Reason (*R*) : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.
10. **Assertion (*A*)** : Toxic metal ions are removed by the chelating ligands.
    Reason (*R*) : Chelate complexes tend to be more stable.

Answers

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

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Coordination compounds are the compounds in which the central metal atom is linked to a number of ions or neutral molecules by coordinate bonds and the donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it are called ligands. Coordination number is the number of atoms or ions immediately surrounding a central atom in a complex or a crystal.

Coordination number of Ni^{2+} is 4 and it forms two complexes A and B as given below:

$$NiCl_2 + KCN \longrightarrow A\text{ (Cyano complex)}$$

$$NiCl_2 + \text{conc. } HCl \longrightarrow B\text{ (Chloro complex)}$$

1. Write the IUPAC name of complex A.

Ans. Potassium tetracyanonickelate(II).

2. Write the formula of the complex B.

Ans. $K_2[NiCl_4]$

3. Predict the magnetic nature of A.

Ans. Diamagnetic.

4. Write the state of hybridization of the complex B.

Ans. sp^3.

5. What will be the shape of the complex A?

Ans. Square planar.

PASSAGE–2

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. Formation of coordination compounds is largely used in analytical chemistry for the qualitative detection and quantitative estimation of metal ions. Coordination compounds also find several important applications in the field of medicine. Several coordination compounds are also used as antidote to poisoning caused by the ingestion of poisonous metals by human beings.

1. Which complexing material is added to vegetable oils to remove the ill effects of undesired metal ions?

Ans. EDTA

2. How would you detect the presence of nickel in a food sample?

Ans. With the help of dimethylglyoxime which forms a red complex with Ni^{2+} ions.

3. What is chelate therapy?

Ans. Chelate therapy is used for the removal of excess of metal ions present in toxic amounts in the body.

4. Which complex is used in the treatment of cancer?

Ans. Cisplatin

5. Name a vitamin which is a complex of cobalt.

Ans. Vitamin B_{12}

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Very Short Answer Questions [1 mark]

Q. 1. A coordination compound with the molecular formula $CrCl_3.4H_2O$ precipitates AgCl with $AgNO_3$ solution. Its molar conductivity is found to be equivalent to two ions. What is the structural formula and name of the compound? **[*HOTS*]**

Ans. $[Cr(H_2O)_4Cl_2]Cl$; tetraaquadichloridochromium(III) chloride

Q. 2. Arrange the following complexes in the order of increasing electrical conductivity: [*HOTS*]
$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$

Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

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

Ans. $[Co(en)_3]^{3+}$ is more stable complex because of chelation.

Q. 4. Why is CO a stronger ligand than Cl^-? [*CBSE (F) 2011*]

Ans. CO is a stronger ligand than Cl^- as it is a π-acceptor ligand.

Q. 5. Square planar complexes with coordination number of four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?

Ans. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the ligands attached to the central metal atom are same with respect to each other.

Q. 6. How many isomers are there for octahedral complex $[CoCl_2(en)(NH_3)_2]^+$? [*NCERT Exemplar*]

Ans. There will be three isomers: *cis* and *trans* isomers. *Cis* will also show optical isomerism.

Q. 7. A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex. [*NCERT Exemplar*] [*HOTS*]

Ans. An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure, *e.g.*, *cis*-$[Pt(en)_2Cl_2]^{2+}$ or *cis*-$[Cr(en)_2Cl_2]^+$.

Q. 8. Give IUPAC name of linkage isomer of $[Co(NH_3)_5(NO_2)]^{2+}$. [*HOTS*]

Ans. The linkage isomer is $[Co(NH_3)_5(ONO)]^{2+}$. Its IUPAC name is pentaaminenitrito-O-cobalt (III) ion.

Q. 9. What type of isomerism is shown by the following complex: [*CBSE (F) 2014*]
$[Co(NH_3)_6]$ $[Cr(CN)_6]$

Ans. Coordination isomerism

Q. 10. Write IUPAC name of coordination isomer of $[Co(NH_3)_6]$ $[Cr(CN)_6]$. [*HOTS*]

Ans. The coordination isomer is $[Cr(NH_3)_6]$ $[Co(CN)_6]$, hexaamminechromium(III) hexacyanidocobaltate(III).

Q. 11. What type of isomerism is exhibited by the following complex: [*CBSE (F) 2014*]
$[Co(NH_3)_5SO_4]Cl$

Ans. Ionisation isomerism

Q. 12. What is spectrochemical series?

Ans. The series in which ligands are arranged in the order of increasing field strength is called spectrochemical series. The order is

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

Q. 13. Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (*i*) strong field ligand, and (*ii*) weak field ligand.
(Atomic no. of Fe = 26) [*CBSE 2019 (56/3/2)*]

Ans. (*i*) $t_{2g}^5 e_g^0$

(*ii*) $t_{2g}^3 e_g^2$

Q. 14. Why are low spin tetrahedral complexes not formed? [*NCERT Exemplar*]

Ans. Because for tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy.

Q. 15. Do we call metal carbonyls as organometallics? Why?

Ans. Yes, metal carbonyls are called organometallics because C atom of CO is linked to the metal atom. In fact, the metal–carbon bonds have both σ and π character.

Short Answer Questions–I [2 marks]

Q. 1. **(*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 ***[CBSE (F) 2017]***

Ans. (*i*) *cis*-diamminedichloridoplatinum (II) and *trans*-diamminedichloridoplatinum (II)

(*ii*) $[Co(NH_3)_4(H_2O)Cl](NO_3)_2$

Q. 2. **Using IUPAC norms write the formulae for the following:**

(*i*) tris(ethane-1, 2-diamine) chromium (III) chloride

(*ii*) potassium tetrahydroxozincate(II) ***[CBSE (AI) 2017]***

Ans. (*i*) $[Cr(en)_3]Cl_3$ (*ii*) $K_2[Zn(OH)_4]$

Q. 3. **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. ***[HOTS] [CBSE Delhi 2016; 2019 (56/4/3)]***

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

(*ii*) pentaaquachloridochromium (III) chloride monohydrate.

Q. 4. **When a coordination compound $PtCl_4.6NH_3$ is mixed with $AgNO_3$, 4 moles of AgCl are precipitated per mole of the compound. Write**

(*i*) structural formula of the complex.

(*ii*) IUPAC name of the complex. ***[CBSE East 2016] [HOTS]***

Ans. (*i*) $[Pt(NH_3)_6]Cl_4$

(*ii*) hexaammineplatinum (IV) chloride

Q. 5. **A chloride of fourth group cation in qualitative analysis gives a green coloured complex [*A*] in aqueous solution which when treated with ethane-1, 2-diamine (en) gives pale-yellow solution [*B*] which on subsequent addition of ethane-1, 2-diamine turns to blue/purple [*C*] and finally to violet [*D*]. Write the structures of complexes [*A*], [*B*], [*C*] and [*D*].** ***[CBSE Sample Paper 2017]***

Ans. $A = [Ni(H_2O)_6]^{2+}$ $B = [Ni(H_2O)_4 (en)]^{2+}$

$C = [Ni(H_2O)_2(en)_2]^{2+}$ $D = [Ni(en)_3]^{2+}$

Q. 6. **Using IUPAC norms, write the formulae for the following complexes:** ***[CBSE 2019 (56/2/1)]***

(*i*) hexaaquachromium (III) chloride

(*ii*) sodium trioxalatoferrate (III)

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

(*ii*) $Na_3[Fe(C_2O_4)_3]$

Q. 7. **Write IUPAC name of the complex $[Co(en)_2(NO_2)Cl]^+$. What type of structural isomerism is shown by this complex?** ***[CBSE 2019 (56/2/1)]***

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

This complex shows linkage isomerism.

Q. 8. **Why do compounds having similar geometry have different magnetic moment?** ***[NCERT Exemplar]***

Ans. It is due to the presence of weak and strong ligands in complexes, if CFSE is high, the complex will show low value of magnetic moment and vice versa, *e.g.*, $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic and the latter is diamagnetic.

Q. 9. **Give the formula of each of the following coordination entities:**

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

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

Write the name and magnetic behaviour of each of the above coordination entities.

(At. nos. Co = 27, Ni = 28) ***[CBSE Delhi 2012]***

Ans. (*i*) $[Co(NH_3)Cl(en)_2]^{2+}$: amminechloridobis (ethane-1, 2-diamine)-cobalt(III) ion

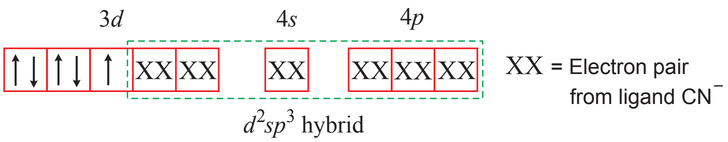
Magnetic behaviour : Diamagnetic

(*ii*) $[Ni(H_2O)_2(ox)_2]^{2-}$: diaquadioxalatonickelate (II)

Magnetic behaviour : Paramagnetic

Q. 10. For the complex $[Fe(CN)_6]^{3-}$, write the hybridisation type, magnetic character and spin nature of the complex. (At. Number : Fe = 26). ***[CBSE Delhi 2016]***

Ans. $[Fe(CN)_6]^{3-}$, $Fe^{3+}(3d^5)$



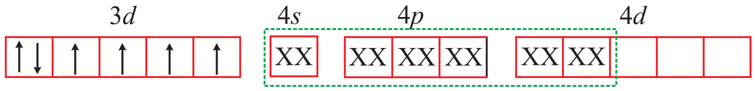
- d^2sp^3 hybridisation
- Paramagnetic in nature and low spin complex.

Q. 11. Write the state of hybridisation, shape and IUPAC name of the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) ***[CBSE (F) 2014]***

OR

Write IUPAC name and hybridisation of the complex: $[CoF_6]^{3-}$. (Atomic number of Co = 27) ***[CBSE 2020 (56/4/2)]***

Ans. $[CoF_6]^{3-}$: hexafluoridocobaltate (III); $Co^{3+} = [Ar]3d^6$

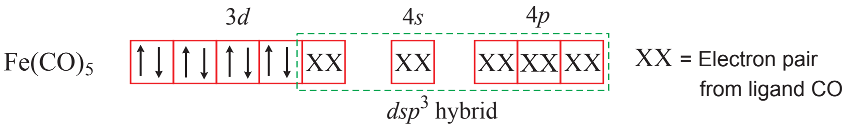


XX = Electron pair from ligand F⁻

Hybridisation = sp^3d^2, Shape = Octahedral

Q. 12. For the complex $[Fe(CO)_5]$, write the hybridization, magnetic character and spin of the complex. (At. number: Fe = 26) ***[CBSE (F) 2016]***

Ans. Fe([Ar] $3d^6$ $4s^2$)



Hybridisation	dsp^3
Magnetic character	Diamagnetic
Spin of the complex	Low spin complex or inner orbital complex

Q. 13. 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. ***[NCERT Exemplar]***

Ans. $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons. This difference is due to the presence of strong CN^- and weak ligand H_2O in these complexes.

Q. 14. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when

(i)* $\Delta_0 > P$** ***(ii)* $\Delta_0 < P$** ***[CBSE (AI) 2013]

Ans. The difference of energy between two sets of degenerate orbitals after crystal field splitting is known as crystal field splitting energy.

(*i*) $t_{2g}^4 e_g^0$ (*ii*) $t_{2g}^3 e_g^1$

Q. 15. The π-complexes are known for transition metals only. Why?

Ans. Transition metals have vacant *d*-orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing π-electrons, *e.g.*, C_6H_6, $CH_2{=}CH_2$, etc. Thus, $d\pi - p\pi$ bonding is possible.

Q. 16. On the basis of crystal field theory explain why Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands. [*NCERT Exemplar*]

Ans. With weak field ligands, $\Delta_0 < P$, the electronic configuration of Co(III) will be $t_{2g}^4\, e_g^2$ and it has 4 unpaired electrons and is paramagnetic. With strong field ligands, $\Delta_0 > P$ the electronic configuration will be $t_{2g}^6\, e_g^0$. It has no unpaired electrons and is diamagnetic.

Q. 17. What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex? [*NCERT Exemplar*]

Ans. When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

Short Answer Questions–II [3 marks]

Q. 1. Explain with two examples each of the following:
- **(*i*) Coordination polyhedron**
- **(*ii*) Homoleptic complex** [*CBSE 2019 (56/2/3)*]
- **(*iii*) Heteroleptic complex**

Ans. Refer to NCERT Textbook Exercises, Q. 3.

Q. 2. Write the correct formulae for the following coordination compounds:
- **(*i*) $CrCl_3.6H_2O$ (violet with 3 chloride ions precipitated as AgCl)**
- **(*ii*) $CrCl_3.6H_2O$ (light green colour, with 2 chloride ions precipitated as AgCl)**
- **(*iii*) $CrCl_3.6H_2O$ (dark green colour, with 1 chloride ion precipitated as AgCl)**

[*CBSE Sample Paper 2017*]

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

(*ii*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$

(*iii*) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Q. 3. Using valence bond theory, predict the hybridisation and magnetic character of the following:

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

[Atomic number: Co = 27, Ni = 28] [*CBSE 2019 (56/5/2)*]

Ans. (*i*) sp^3d^2, paramagnetic

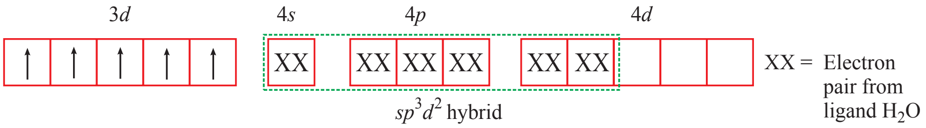
(*ii*) dsp^2, diamagnetic

Q. 4. (*i*) For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridisation, 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.

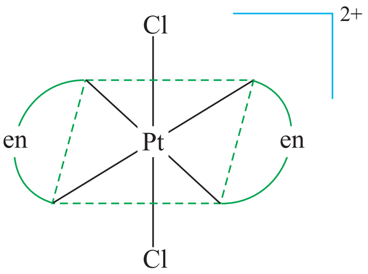
[*CBSE Central 2016*]

Ans. (*i*) $Fe^{3+}([Ar]3d^5)$



Hybridisation	sp^3d^2
Magnetic character	Paramagnetic
Spin of the complex	High spin complex

(*ii*)



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

Q. 5. Write the name, the structure and the magnetic behaviour of each one of the following complexes:

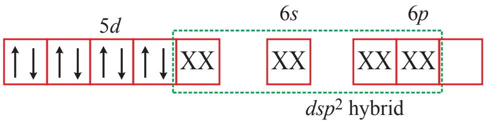
(*i*) $[Pt(NH_3)_2Cl(NO_2)]$

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

(*iii*) $[Ni(CO)_4]$

(At. nos. Co = 27, Ni = 28, Pt = 78) **[*CBSE Delhi 2012, 2020 (56/2/1)*]**

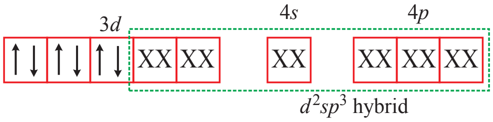
Ans. (*i*) $[Pt(NH_3)_2ClNO_2]$: diamminechloridonitrito-N-platinum (II); $Pt^{2+} = 5d^8$



XX = Electron pair from ligands NH_3, Cl^- and NO_2

Structure = Square planar; Magnetic behaviour : Diamagnetic

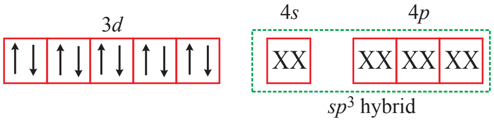
(*ii*) $[Co(NH_3)_4Cl_2]Cl$: tetraamminedichloridocobalt (III) chloride; $Co^{3+} = 3d^6$



XX = Electron pair from ligands NH_3, Cl^- and NO_2

Structure = Octahedral; Magnetic behaviour : Diamagnetic

(*iii*) $[Ni(CO)_4]$: tetracarbonyl nickel(0); $Ni = 3d^8\ 4s^2$



XX = Electron pair from ligand CO

Structure = Tetrahedral; Magnetic behaviour : Diamagnetic

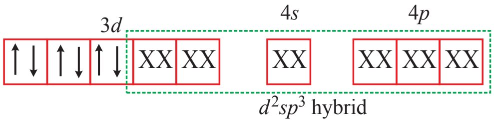
Q. 6. Name the following coordination entities and describe their structures:

(*i*) $[Fe(CN)_6]^{4-}$ **(*ii*) $[Cr(NH_3)_4Cl_2]^+$**

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

(Atomic Numbers: Fe = 26, Cr = 24, Ni = 28) **[*CBSE (AI) 2012*]**

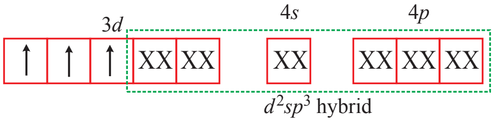
Ans. (*i*) $[Fe(CN)_6]^{4-}$ = hexacyanoferrate (II) ion; $Fe^{2+}(3d^6)$



XX = Electron pair from the CN^- ion

d^2sp^3 hybridisation in $[Fe(CN)_6]^{4-}$ leads to octahedral structure.

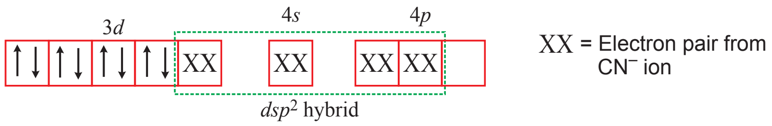
(*ii*) $[Cr(NH_3)_4Cl_2]^+$ = tetraamminedichloridochromium (III) ion; $Cr^{3+}(3d^3)$



XX = Electron pair from NH_3 molecule and Cl^- ion

d^2sp^3 hybridisation in $[Cr(NH_3)_4Cl_2]^+$ leads to octahedral structure.

(*iii*) $[Ni(CN)_4]^{2-}$ = tetracyanonickelate(II)ion; Ni^{2+} $(3d^8)$



dsp^2 hybridisation in $[Ni(CN)_4]^{2-}$ leads to square planar structure.

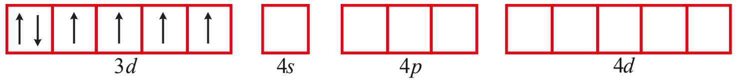
Q. 7. Describe for any two of the following complex ions, the type of hybridisation, shape and magnetic property:

(*i*) $[Fe(H_2O)_6]^{2+}$ **(*ii*) $[Co(NH_3)_6]^{3+}$**

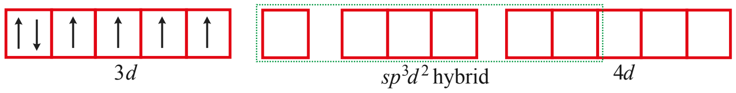
(*iii*) $[NiCl_4]^{2-}$

(At. Nos. Fe = 26, Co = 27, Ni = 28)

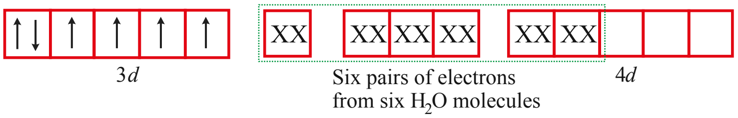
Ans. (*i*) Atomic orbitals of Fe^{2+} ion



sp^3d^2 hybridised orbitals of Fe^{2+} ion



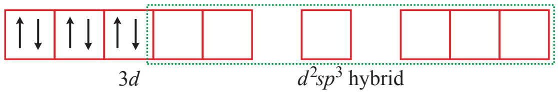
Formation of $[Fe(H_2O)_6]^{2+}$



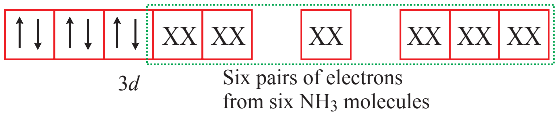
Octahedral because of sp^3d^2 hybridisation. Paramagnetic, as there are four unpaired electrons present in the complex ion.

(*ii*) Atomic orbitals of Co (III) ion

d^2sp^3 hybridised orbitals of Co (III) ion

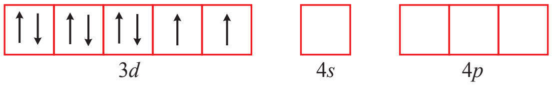


Formation of $[Co(NH_3)_6]^{3+}$

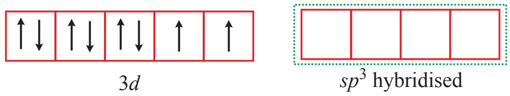


d^2sp^3 hybridisation leads to octahedral geometry. Diamagnetic, as there is no unpaired electron present in the complex.

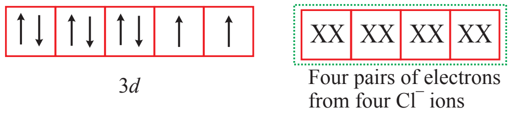
(*iii*) Atomic orbitals of Ni (II) ion



sp^3 hybridised orbitals of Ni (II)



Formation of $[NiCl_4]^{2-}$



sp^3 hybridisation leads to tetrahedral geometry. Paramagnetic, as there are two unpaired electrons.

(*any two*)

Q. 8. $Fe^{3+} \xrightarrow[\text{excess}]{SCN^-} A \xrightarrow[\text{excess}]{F^-} B$

What are A and B? Give IUPAC names of A and B. Find spin only magnetic moment of B. [*HOTS*]

Ans. A = $[Fe(SCN)_3]$, B = $[FeF_6]^{3-}$

trithiocyanato iron(III) hexafluoridoferrate(III)

EC of Fe(III) = d^5,

Unpaired electrons $(n) = 5$

Spin only magnetic moment of B $= \sqrt{n(n+2)}$

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

$=$ **5.916 BM**

Q. 9. Write the name, stereochemistry and magnetic behaviour of the following:

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

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

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

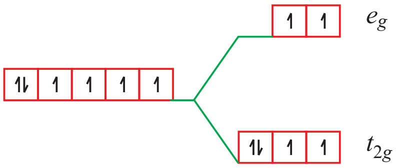
(*iii*) $K_2[Ni(CN)_4]$ [*CBSE Delhi 2011*]

Ans.

S. No.	Name of the complex	Hybridisation of metal ion involved	Geometry of complex	Magnetic behaviour
(*i*)	potassiumhexacyanomanganate (II)	d^2sp^3	Octahedral	Paramagnetic
(*ii*)	pentaamminechloridocobalt (III) chloride	d^2sp^3	Octahedral	Diamagnetic
(*iii*)	potassiumtetracyanonickelate (II)	dsp^2	Square planar	Diamagnetic

Q. 10. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the $[Fe(H_2O)_6]^{2+}$. [*NCERT Exemplar*]

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



i.e., $t_{2g}^4\, e_g^2$

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

Number of unpaired electrons (n) = 4

Magnetic moment (μ) $= \sqrt{4(4+2)} = \sqrt{24} =$ **4.9 BM**

Q. 11. (*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 $\Delta_0 > P$.

(*iii*) Write the hybridisation and shape of $[CoF_6]^{3-}$.

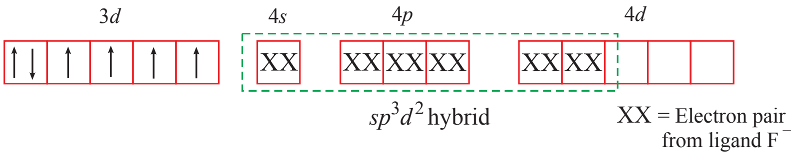
(Atomic number of Co = 27) [*CBSE Allahabad 2015*]

Ans. (*i*) Hydration isomerism is shown by complex $[Cr(H_2O)_6]Cl_3$.

(*ii*) If $\Delta_0 > P$, electronic configuration becomes $t_{2g}^4\, e_g^0$.

(*iii*) Co^{3+} : $3d^6\, 4s^0$

$[CoF_6]^{3-}$:
(outer orbital complex)



Hybridisation = sp^3d^2; Shape = Octahedral

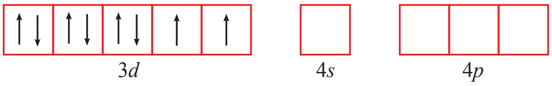
Q. 12. Explain the following: [*HOTS*]

(*i*) Low spin octahedral complexes of nickel are not known.

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

(*iii*) CO is a stronger complexing reagent than NH_3.

Ans. (*i*) Orbitals of Ni^{2+}



For the formation of low spin complex, electrons present in 3*d* electrons of Ni^{2+} should pair up. This will produce only one empty *d* orbital. Hence, d^2sp^3 hybridisation in nickel is not possible to form low spin octahedral complex.

(*ii*) With the electronic configuration $3d^7 4s^0$, Co^{2+} has three unpaired electrons. H_2O being a weak ligand, the unpaired electrons present in 3*d* orbitals of Co (II) do not pair up. In the presence of strong ligands, two unpaired electrons in 3*d* orbitals pair up and the third unpaired electron shifts to higher energy orbital from where it can be easily lost and hence shows an oxidation state of III.

(*iii*) CO has empty π-orbitals which overlap with filled *d*-orbitals (t_{2g} orbitals) of transition metals and form π-bonds by back bonding. These π-interactions increase the value of crystal field stabilisation energy (Δ_0).

As NH_3 cannot form π bonds by back bonding, therefore, CO is stronger ligand than NH_3.

Q. 13. Give the electronic configuration of the **[*HOTS*]**

(*i*) *d*-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.

(*ii*) Why is this complex coloured? Explain on the basis of distribution of electrons in the *d*-orbitals.

(*iii*) How does the colour change on heating $[Ti(H_2O)_6]^{3+}$ ion?

Ans. (*i*) In $[Ti(H_2O)_6]^{3+}$ ion, Ti is in +3 oxidation state. There is one electron in *d*-orbital and the electronic configuration is $t_{2g}^1 e_g^0$.

(*ii*) Due to *d*-*d* transition, the electron present in t_{2g} absorbs green and yellow radiation of white light for excitation to e_g and the configuration becomes e_g^1. The complementary colour is purple.

(*iii*) On heating, H_2O is lost. In the absence of ligand, crystal field splitting does not occur hence the substance becomes colourless.

Long Answer Questions [5 marks]

Q. 1. (*i*) (*a*) What type of isomerism is shown by the complex $[Co(NH_3)_6]\,[Cr(CN)_6]$?

(*b*) 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)

(*c*) Write the IUPAC name of the following complex: $[Co(NH_3)_5\,(CO_3)]Cl$. [*CBSE Delhi 2017*]

(*ii*) Differentiate between weak field and strong field coordination entity.

Ans. (*i*) (*a*) Coordination isomerism.

(*b*) In $[Ni(H_2O)_6]^{2+}$, Ni is in + 2 oxidation state with the configuration $3d^8\,4s^0$, *i.e.*, it has two unpaired electrons which do not pair up in the presence of weak H_2O ligand. The *d*–*d* transition absorbs red light and the complementary green light is emitted.

On the other hand, in $[Ni(CN)_4]^{2-}$, Ni is again in +2 oxidation state with the electronic configuration $3d^8$. In the presence of strong CN^- ligand the two unpaired electrons in the 3*d* orbitals pair up. As there is no unpaired electron in $[Ni(CN)_4]^{2-}$ therefore the complex is colourless.

(*c*) Pentaamminecarbonatocobalt(III)chloride

(*ii*)

S.No.	Weak field coordination entity	Strong field coordination entity
(*i*)	They are formed when the crystal field stabilisation energy (Δ_o) in octahedral complexes is less than the energy required for an electron pairing in a single orbital (P).	They are formed when the crystal field stabilisation energy (Δ_o) is greater than the P.
(*ii*)	They are also called high spin complexes.	They are called low spin complexes.
(*iii*)	They are mostly paramagnetic in nature.	They are mostly diamagnetic or less paramagnetic than weak field.
(*iv*)	Never formed by CN^- ligands.	Formed by CN^- like ligands.

Q. 2. A metal ion M^{n+} having d^4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_0 > P$: **[*HOTS*]**

- **(*i*) Explain orbital splitting during this complex formation.**
- **(*ii*) Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.**
- **(*iii*) What type of hybridisation will M^{n+} ion have?**
- **(*iv*) Name the type of isomerism exhibited by this complex.**

Ans. (*i*) As $\Delta_0 > P$ pairing will occur in the t_{2g} orbitals and e_g orbitals will remain vacant.

(*ii*) $t_{2g}^4\ e_g^0$

(*iii*) As there are three bidentate ligands to combine therefore hybridisation will be d^2sp^3.

(*iv*) Optical isomerism.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. Which of the following compounds can show optical isomerism?

(*a*) *trans*-$[Co(en)_2Cl_2]Br$ (*b*) $[Co(en)_3]Cl_3$

(*c*) *trans*-$[Co(NH_3)_4Cl_2]Cl$ (*d*) $[(NH_3)_5Cl]Cl_2$

2. Which one will give the test for Fe^{3+} in solution?

(*a*) $[Fe(CN)_6]^{3-}$ (*b*) $[Fe(CN)_6]^{2-}$

(*c*) $(NH_4)_2SO_4.FeSO_4.6H_2O$ (*d*) $Fe_2(SO_4)_3$

3. Ethylene diammine is a

(*a*) monodentate ligand (*b*) bidentate ligand

(*c*) hexadentate ligand (*d*) tridentate ligand

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.* (3 × 1 = 3)

4. Assertion (*A*) : Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ is not a coordination compound.
Reason (*R*) : The aqueous solution of this salt gives the test of Fe^{2+}, NH_4^+ and SO_4^{2-} ions.

5. Assertion (*A*) : The tetrahedral complexes can show geometrical isomerism.
Reason (*R*) : This is because all the four ligands lie at the same distance from central metal atom in a tetrahedral geometry.

6. Assertion (*A*) : The complex $[Fe(H_2O)_6]^{2+}$ is paramagnetic in nature.
Reason (*R*) : It consists of two unpaired electrons.

Answer the following questions:

7. Write IUPAC name of linkage isomer of $[Cr(H_2O)_5SCN]^{2+}$. **(1)**

8. Name a complex used in treatment of cancer. **(1)**

9. An octahedral complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio 1 : 4, 0.1 m solution of this complex was found to freeze at 0.372°C. What is the formula of the complex? Given that molal depression constant (K_f) for water = 1.86°C/m. **(2)**

10. (*i*) What is meant by denticity of a ligand?
    (*ii*) Which compound is used to estimate the hardness of water volumetrically? **(2)**

11. Using valence bond theory explain the $[Co(NH_3)_6]^{3+}$ in relation to the terms given below:
    (*i*) Type of hybridisation
    (*ii*) Inner or outer orbital complex
    (*iii*) Magnetic behaviour
    (*iv*) Spin only magnetic moment value. **(2)**

12. $CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why? **(2)**

13. Give the name, the stereochemistry and the magnetic behaviour of the following complexes:
    (*i*) $[Co(NH_3)_5Cl]Cl_2$
    (*ii*) $K_2[Ni(CN)_4]$ **(3)**

14. (*i*) What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?
    (*ii*) Write the formula of pentamminechloridoplatinum (IV).
    (*iii*) Arrange following complex ions in increasing order of crystal field splitting energy (Δ_0):
    $[Cr(Cl)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$ **(3)**

15. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following:
    $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$ **(3)**

16. $CoSO_4Cl.5NH_3$ 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 $AgNO_3$. Answer the following questions:
    (*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'. **(5)**

Answers

1. (*b*) **2.** (*d*) **3.** (*b*) **4.** (*b*) **5.** (*d*) **6.** (*c*)