

Coordination Compounds

basic concepts

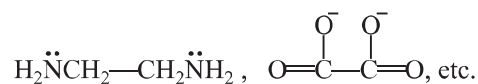
1. **Double Salts:** Double salts are the addition compounds which are stable in solid state but break up into constituent ions when dissolved in water or any other solvent. In these compounds the individual properties of constituent are not lost. Some common examples are:



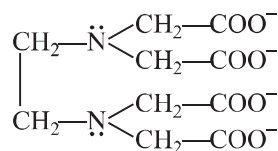
2. **Complex Ion:** An electrically charged species, carrying positive or negative charge, in which the central metal atom or ion is surrounded by fixed number of ions or molecules, *e.g.*, $[\text{Co}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, etc. The complex ion does not dissociate into simple ions in aqueous solutions.
3. **Coordination Compounds:** Coordination compounds are the compounds which contain complex ions, *e.g.*, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, 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.*, $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, 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 $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, 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.*, $\ddot{\text{N}}\text{H}_3$, $:\ddot{\text{C}}\ddot{\text{I}}:$, etc.

➤ **Bidentate ligands:** Contain two donor atoms, *e.g.*,

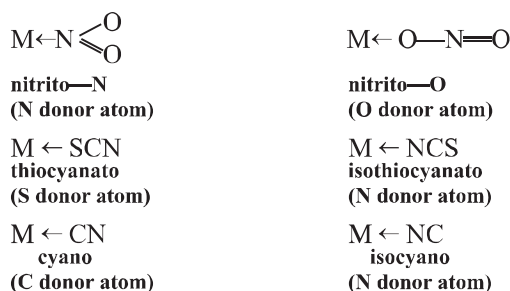


➤ **Polydentate ligands:** Contain several donor atoms, *e.g.*,



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:



- ➔ **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.

- 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 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^- .
- 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.

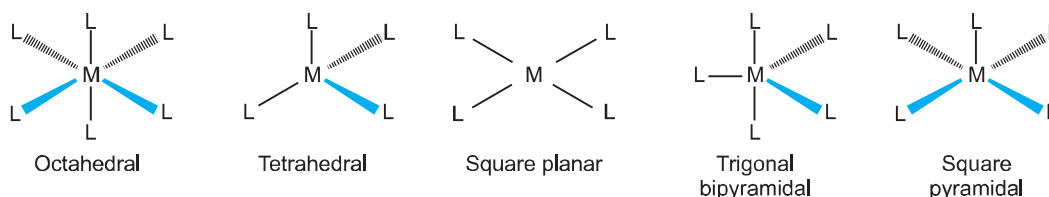


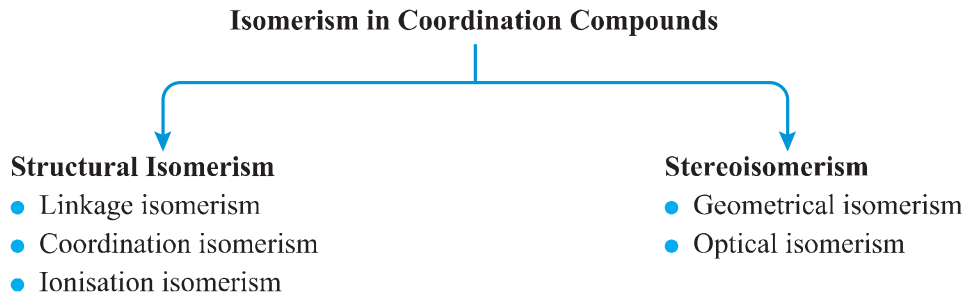
Fig. 9.1: Shapes of different coordination polyhedra.
M represents the central atom/ion and L, a unidentate ligand

- 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.
- 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., $[Co(NH_3)_4Cl_2]^+$.

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)

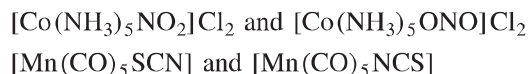
14. **Isomerism:** Two or more compounds having the same molecular formula but different arrangement of atoms and hence differ in one or more physical or chemical properties are called isomers and the phenomenon is called isomerism.



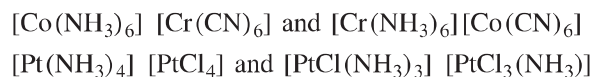
Structural isomers have different bonds. Stereoisomers have the same chemical formula and chemical bonds but differ in their spatial arrangements.

(a) Structural isomerism:

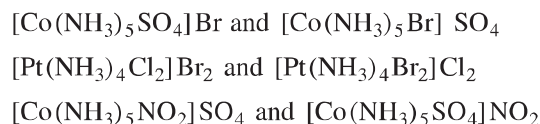
- (i) Linkage isomerism:** This type of isomerism arises due to the presence of an ambidentate ligand in a coordination compound. Some examples of linkage isomers are:



- (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

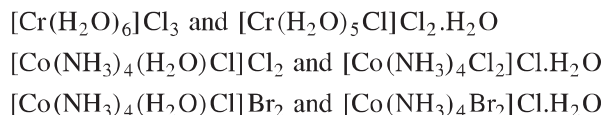


- (iii) Ionisation isomerism:** Ionisation isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. Some examples are:



- (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:



(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.

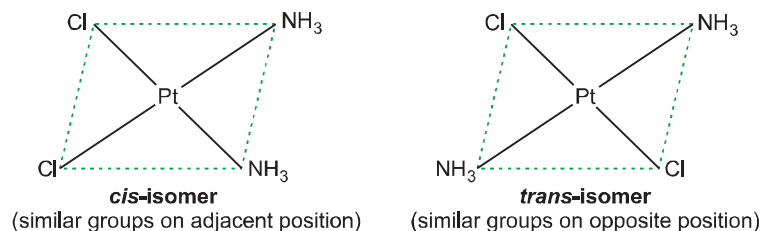
- **Isomerism in complexes with coordination number 4.**

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

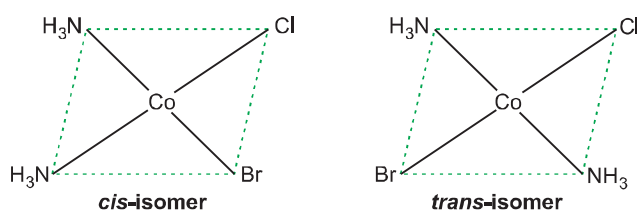
metal atom is same with respect to each other (adjacent). The square planar complexes on the other hand show this type of isomerism as given below:

- 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.

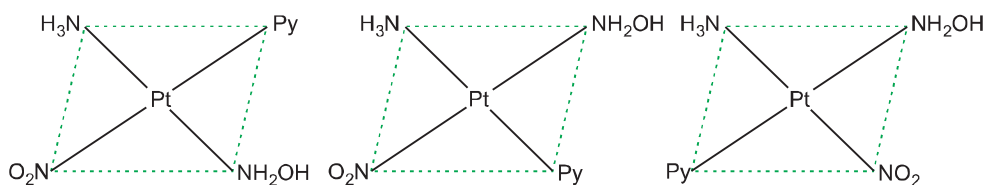
- **Type $[MA_2X_2]$:** $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2(NO_2)_2]$, $[Pt(Py)_2Cl_2]$



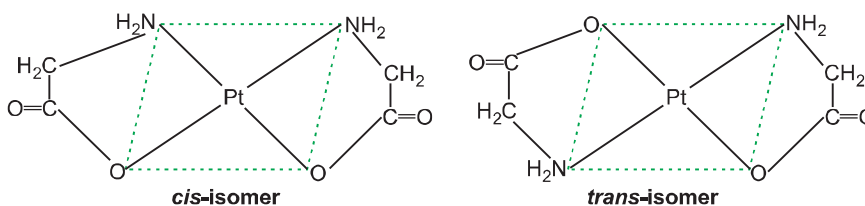
- **Type $[MA_2XY]$:** $[Co(NH_3)_2ClBr]$, $[Pt(Py)_2(NH_3)Cl]$



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



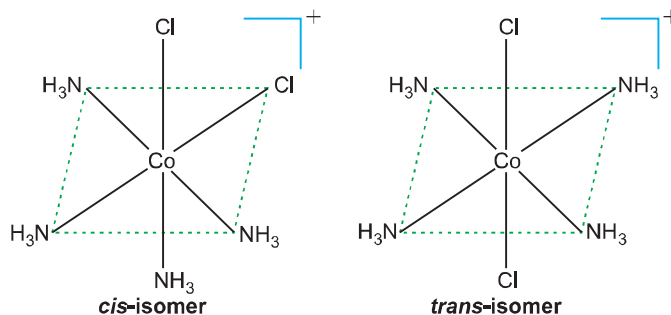
- **Type $[M(AB)_2]$:** $[Pt(gly)_2]$ where $gly = H_2NCH_2COO^-$



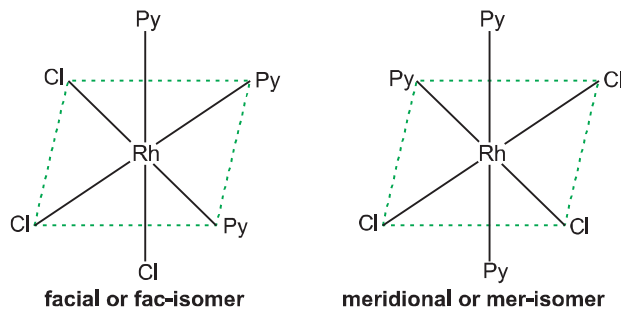
- **Isomerism in complexes with coordination number 6.**

- Octahedral complexes of the type $[MA_6]$ and $[MA_5X]$ are incapable of showing geometrical isomerism.

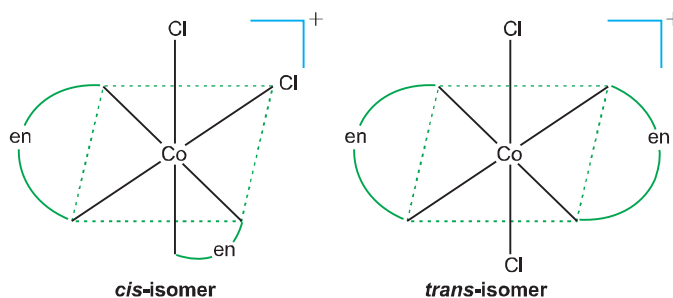
- **Type $[MA_4X_2]$ or $[MA_2X_4]$:** $[Co(NH_3)_4Cl_2]^+$, $[Cr(NH_3)_4Cl_2]^+$ ion



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



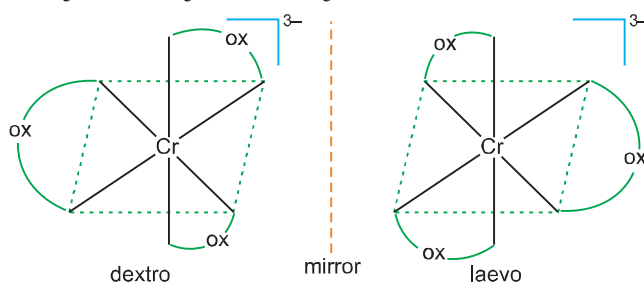
- **Type $[M(AA)_2X_2]$ or $[M(AA)_2XY]$:** $[Co(en)_2Cl_2]^+$, $[Ni(ox)_2Cl_2]^+$



(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*).

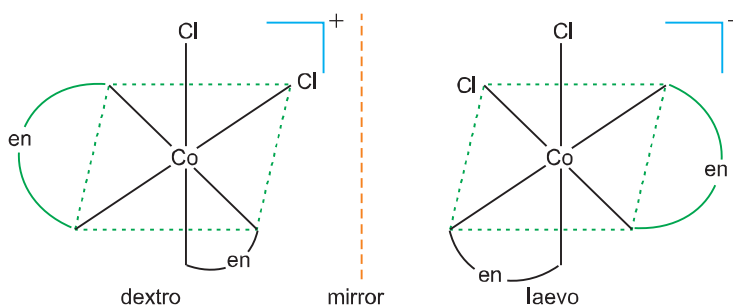
Optical isomerism is common in octahedral complexes involving bidentate ligands. Some examples of different types of octahedral complexes showing optical isomerism are given below:

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



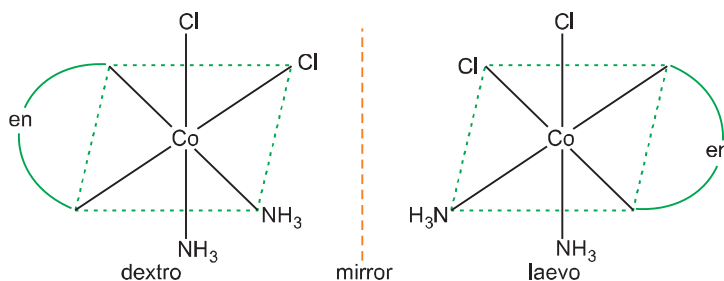
Optical isomers (*d* and *l*) of $[Cr(ox)_3]^{3-}$

- **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 $cis-[Co(en)_2Cl_2]^+$

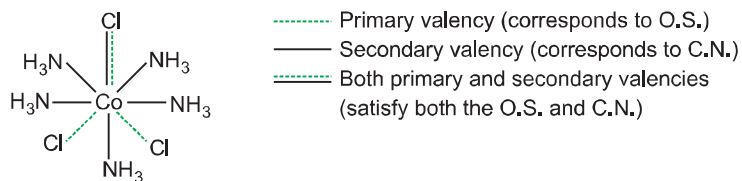
● **Type $[M(AA)X_2Y_2]$: $[Co(en)(NH_3)_2Cl_2]$**



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:

- In coordination compounds, metals show two types of valencies: primary and secondary.
- The primary valencies are normally ionisable and are satisfied by negative ions.
- 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

- 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:

- 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.
- 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

- 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.
- 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.
- 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
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Ti^{3+}	d^1	$d^2 sp^3$	Octahedral	1	Paramagnetic
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	V^{3+}	d^2	$d^2 sp^3$	Octahedral	2	Paramagnetic
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Cr^{3+}	d^3	$d^2 sp^3$	Octahedral	3	Paramagnetic
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Cr^{3+}	d^3	$d^2 sp^3$	Octahedral	3	Paramagnetic
$[\text{MnF}_6]^{3-}$	Mn^{3+}	d^4	$sp^3 d^2$	Octahedral	4	Paramagnetic
$[\text{Mn}(\text{CN})_6]^{3-}$	Mn^{3+}	d^4	$d^2 sp^3$	Octahedral	2	Paramagnetic
$[\text{MnCl}_4]^{2-}$	Mn^{2+}	d^5	sp^3	Tetrahedral	5	Paramagnetic
$[\text{FeF}_6]^{3-}$	Fe^{3+}	d^5	$sp^3 d^2$	Octahedral	5	Paramagnetic
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	Fe^{3+}	d^5	$sp^3 d^2$	Octahedral	5	Paramagnetic
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe^{3+}	d^5	$d^2 sp^3$	Octahedral	1	Paramagnetic
$[\text{Fe}(\text{CN})_6]^{4-}$	Fe^{2+}	d^6	$d^2 sp^3$	Octahedral	0	Diamagnetic
$[\text{FeCl}_4]^{2-}$	Fe^{2+}	d^6	sp^3	Tetrahedral	4	Paramagnetic
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Co^{3+}	d^6	$d^2 sp^3$	Octahedral	0	Diamagnetic
$[\text{CoF}_6]^{3-}$	Co^{3+}	d^6	$sp^3 d^2$	Octahedral	4	Paramagnetic
$[\text{Ni}(\text{CO})_4]$	Ni	$3d^8 4s^2$	sp^3	Tetrahedral	0	Diamagnetic
$[\text{Ni}(\text{CN})_4]^{2-}$	Ni^{2+}	d^8	dsp^2	Square planar	0	Diamagnetic
$[\text{NiCl}_4]^{2-}$	Ni^{2+}	d^8	sp^3	Tetrahedral	2	Paramagnetic
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	Ni^{2+}	d^8	$sp^3 d^2$	Octahedral	2	Paramagnetic
$[\text{CuCl}_4]^{2-}$	Cu^{2+}	d^9	sp^3	Tetrahedral	1	Paramagnetic
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	Zn^{2+}	d^{10}	sp^3	Tetrahedral	0	Diamagnetic
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	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_0 (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.

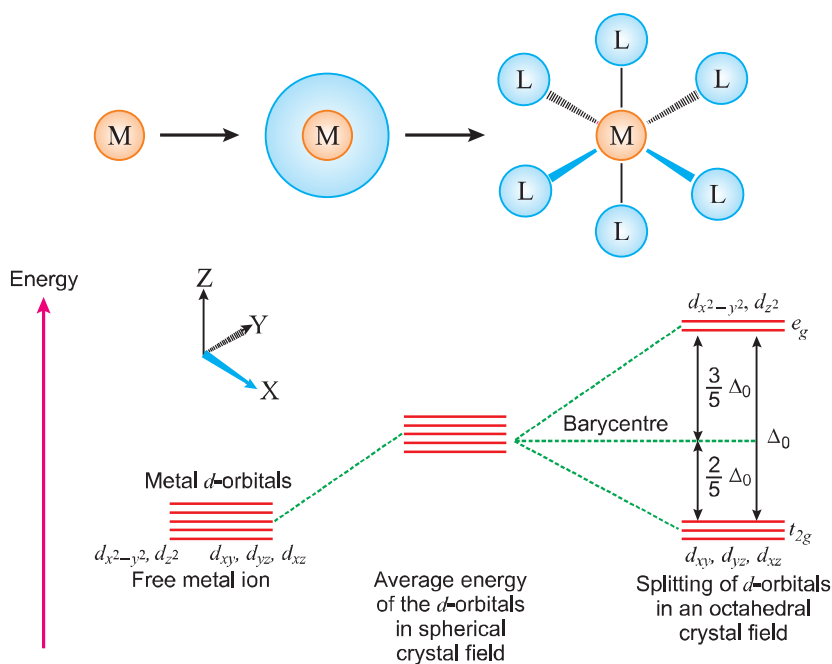
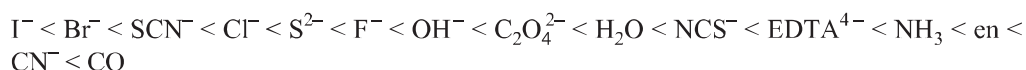


Fig. 9.2: d -orbital splitting in an octahedral crystal field

- 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.



- 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 $\Delta_0 > P$, 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.

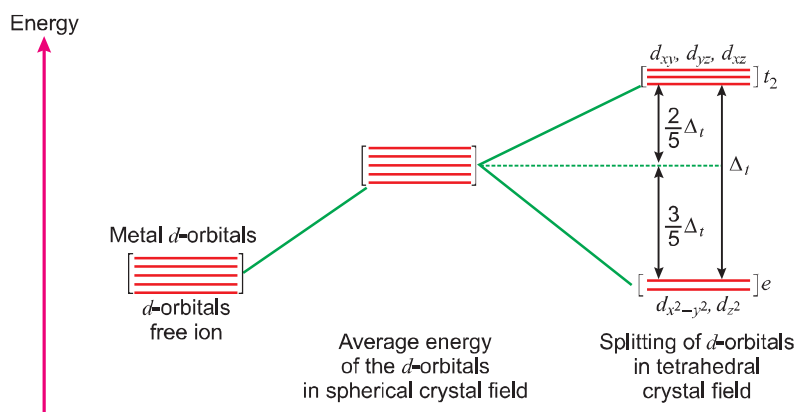


Fig. 9.3: d -orbital splitting in a tetrahedral crystal field

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 $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating renders it colourless. Similarly, anhydrous CuSO_4 is white, but $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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:

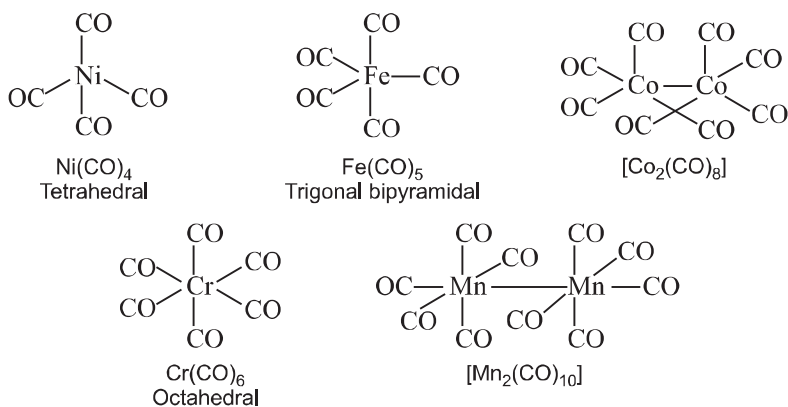


Fig. 9.4: Structures of some representative homoleptic metal carbonyls

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.

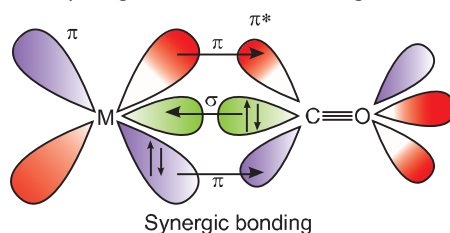
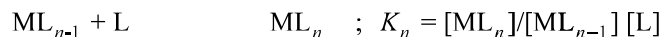
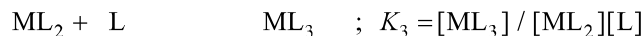
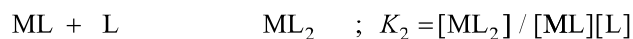


Fig. 9.5: Synergic bonding interactions in a carbonyl complex

- 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

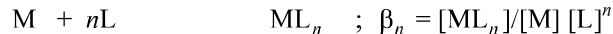


We can write stability constant as follows:



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:



The stepwise and overall stability constant are therefore as follows:

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

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

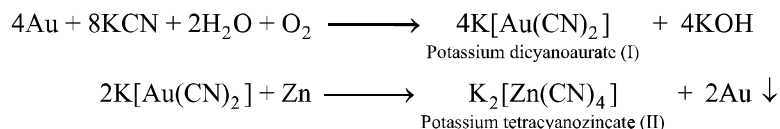
20. Factors Affecting the Stability of Complexes

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.

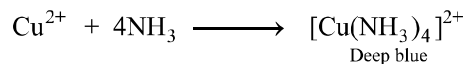


Purification of some metals can be achieved through complex formation. For example, in Mond's process, impure nickel is converted to $[\text{Ni}(\text{CO})_4]$, which is decomposed to yield pure nickel.

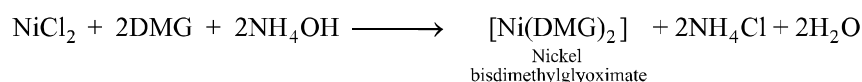
➤ **In analytical chemistry:** Complex formation is frequently encountered in qualitative and quantitative chemical analysis.

(i) Qualitative Analysis:

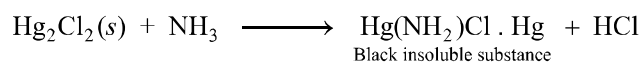
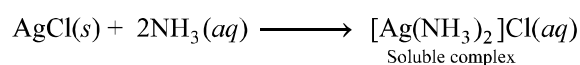
- Detection of Cu^{2+} is based on the formation of a blue tetraammine copper (II) ion.



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

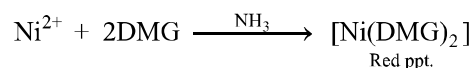


- The separation of Ag^+ and Hg^{2+} in group I is based on the fact that while AgCl dissolves in NH_3 , forming a soluble complex, Hg_2Cl_2 forms an insoluble black substance.



(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.



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*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, 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, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

- **In Catalysis:** Coordination compounds are used as catalysts for many industrial processes. For example, Wilkinson's catalyst, a rhodium complex having formula $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ 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 tetracyanonickelate(II)
- (iii) tris (ethane-1, 2-diamine) chromium(III) chloride
- (iv) amminebromidochloridonitrito-N-platinate(II)
- (v) dichloridobis(ethane-1, 2-diamine)platinum(IV) nitrate
- (vi) iron(III)hexacyanidoferrate(II)

- Ans.** (i) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ (ii) $\text{K}_2[\text{Ni}(\text{CN})_4]$
 (iii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ (iv) $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^-$
 (v) $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$ (vi) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

Q. 2. Write IUPAC names of the following coordination compounds:

- (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (iv) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
- (v) $\text{K}_2[\text{PdCl}_4]$ (vi) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$

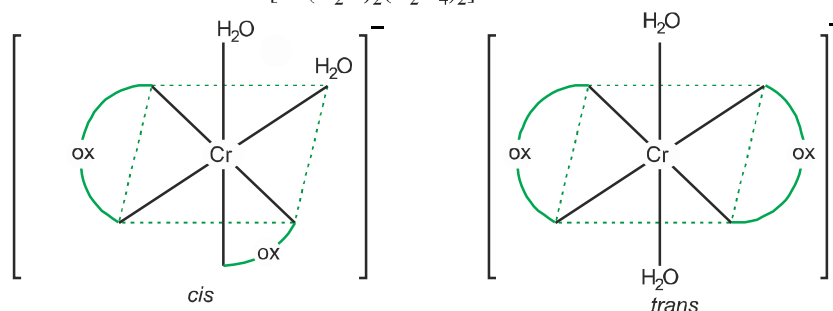
- Ans.** (i) hexaamminecobalt(III) chloride (ii) pentaamminechloridocobalt(III) chloride
 (iii) potassium hexacyanoferrate(III) (iv) potassium trioxalatoferrate(III)
 (v) potassium tetrachloridopalladate(II)
 (vi) diamminechlorido(methylamine)platinum (II) chloride

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

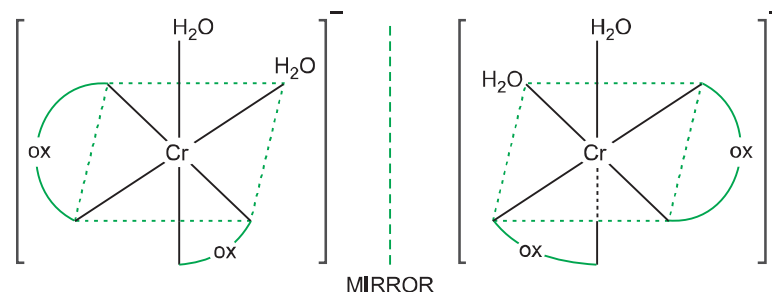
- (i) $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$ (ii) $[\text{Co}(\text{en})_3]\text{Cl}_3$
- (iii) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ (iv) $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$

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

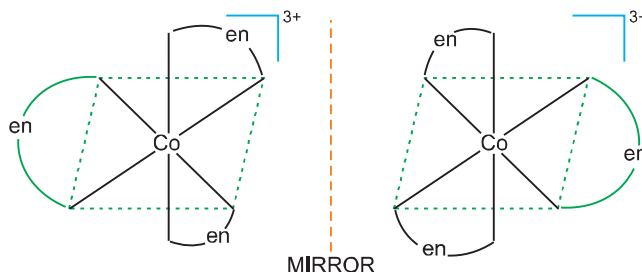
(a) Geometrical isomers of $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$:



(b) Optical isomers (*d-* and *l-*) of *cis*- $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$:



(ii) Two optical isomers can exist.



(iii) Ionisation isomers:

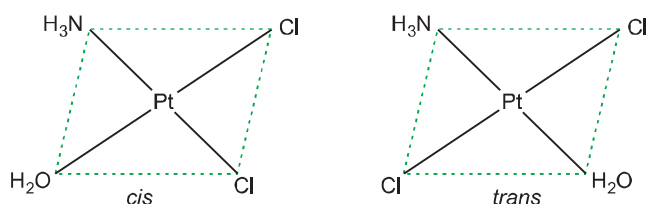


Linkage isomers:



MA_5X type complexes do not show geometrical and optical isomerism.

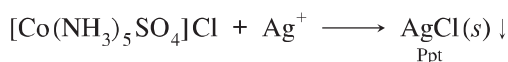
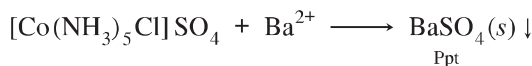
(iv) Geometrical isomers can exist.



Q. 4. Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionisation isomers.

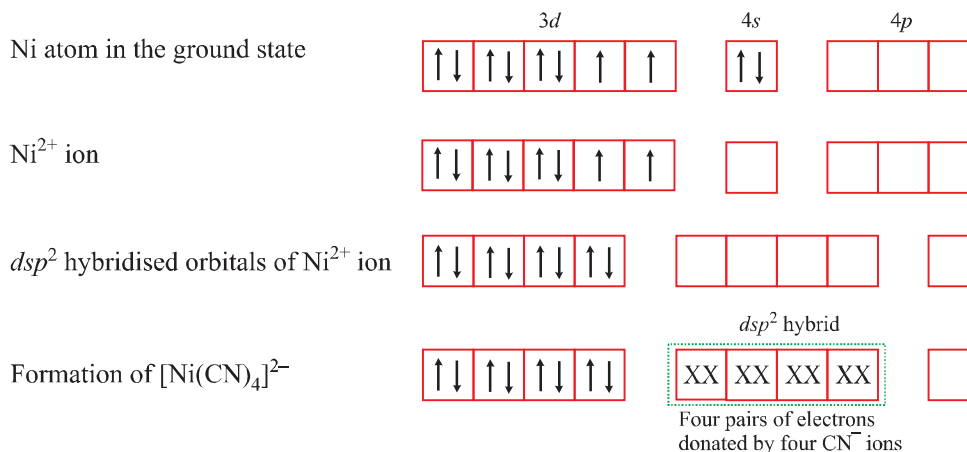
[CBSE 2019 (56/3/2)]

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



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

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



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

In $[\text{NiCl}_4]^{2-}$, 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. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?

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Ans. In $[\text{Ni}(\text{CO})_4]$, Ni is in zero oxidation state whereas in $[\text{NiCl}_4]^{2-}$ 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. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic. Explain.

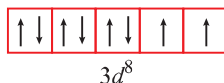
Ans. In presence of CN^- (a strong ligand), the $3d^5$ electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming an inner orbital complex. In the presence of H_2O (a weak ligand), $3d$ electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex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

Q. 8. Explain $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

Ans. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, 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 $[\text{Ni}(\text{NH}_3)_6]^{2+}$, 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 $[\text{Pt}(\text{CN})_4]^{2-}$ ion.

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



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

Q. 10. The hexaqua 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ solution in 1 : 1 molar ratio forms double salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ which ionises in the solution to give Fe^{2+} ions. Hence, it gives the test of Fe^{2+} ions.

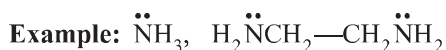
CuSO_4 solution mixed with aqueous ammonia in 1 : 4 molar ratio forms a complex, with the formula $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$. The complex ion, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ does not ionise to give Cu^{2+} ions. Hence, it does not give the test of Cu^{2+} ion.

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., $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, 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.



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, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ 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., $[\text{Cu}(\text{CN})_4]^{3-}$.

Heteroleptic Complex: The complex in which metal atom is bound to more than one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

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., $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ and $^-\text{OOC—COO}^-$.

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 $:\text{NO}_2^-$ or $:\text{ONO}^-$.

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

- | | |
|--|---|
| (i) $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$ | (ii) $[\text{CoBr}_2(\text{en})_2]^+$ |
| (iii) $[\text{PtCl}_4]^{2-}$ | (iv) $\text{K}_3[\text{Fe}(\text{CN})_6]$ |
| (v) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ | |

- 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 tetracyanonickelate(II) |
| (v) pentaamminenitrito-O-cobalt(III) | (vi) hexaamminecobalt(III) sulphate |

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- | | |
|---|-------------------------------|
| (vii) potassium tri(oxalato)chromate(III) | (viii) hexaammineplatinum(IV) |
| (ix) tetrabromidocuprate(II) | |
| (x) pentaamminenitrito-N-cobalt(III) | |

- Ans.**
- | | |
|---|--|
| (i) $[\text{Zn}(\text{OH})_4]^{2-}$ | (ii) $\text{K}_2[\text{PdCl}_4]$ |
| (iii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ | (iv) $\text{K}_2[\text{Ni}(\text{CN})_4]$ |
| (v) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ | (vi) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ |
| (vii) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ | (viii) $[\text{Pt}(\text{NH}_3)_6]^{4+}$ |
| (ix) $[\text{CuBr}_4]^{2-}$ | (x) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ |

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

- (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
 (iii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (iv) $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$
 (v) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (vi) $[\text{NiCl}_4]^{2-}$
 (vii) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ (viii) $[\text{Co}(\text{en})_3]^{3+}$
 (ix) $[\text{Ni}(\text{CO})_4]$

- Ans.** (i) hexaamminecobalt(III) chloride (ii) diamminechlorido(methylamine)platinum (II) chloride
 (iii) hexaaquatitanium(III) ion (iv) tetraamminechloridonitro-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.

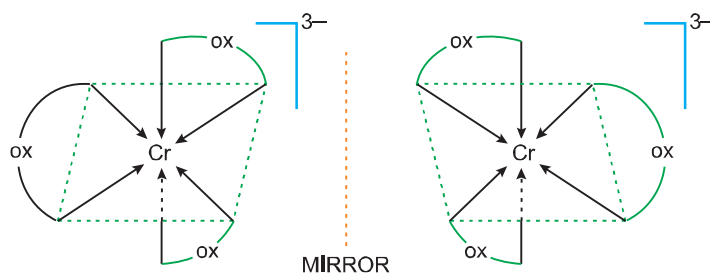
Q. 9. How many geometrical isomers are possible in the following coordination entities?

- (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (ii) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
Ans. (i) Nil (ii) Two (*cis* and *trans*)

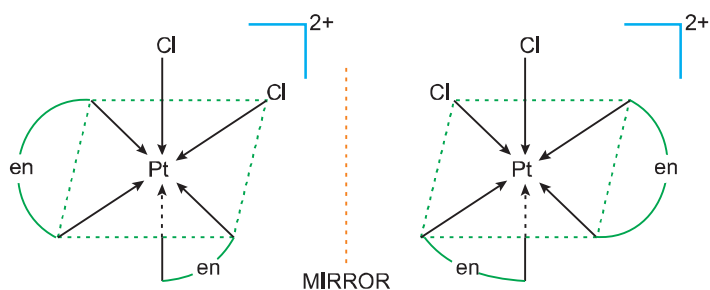
Q. 10. Draw the structures of optical isomers of

- (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (ii) $[\text{PtCl}_2(\text{en})_2]^{2+}$
 (iii) $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$

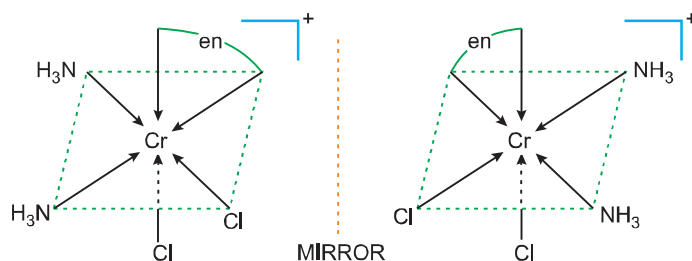
Ans. (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

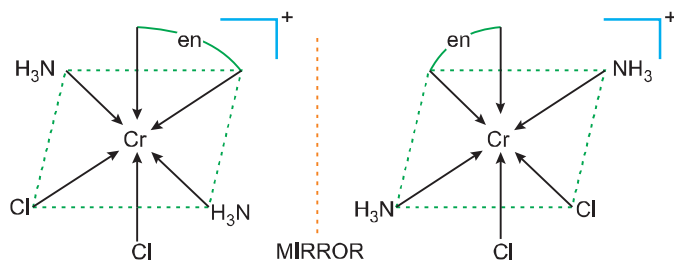


(ii) *cis*- $[\text{PtCl}_2(\text{en})_2]^{2+}$:



(iii) (a) *cis*- $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$

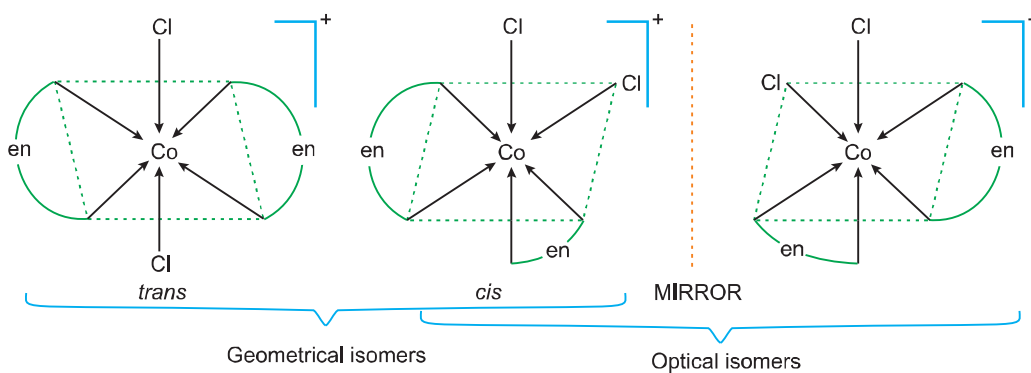




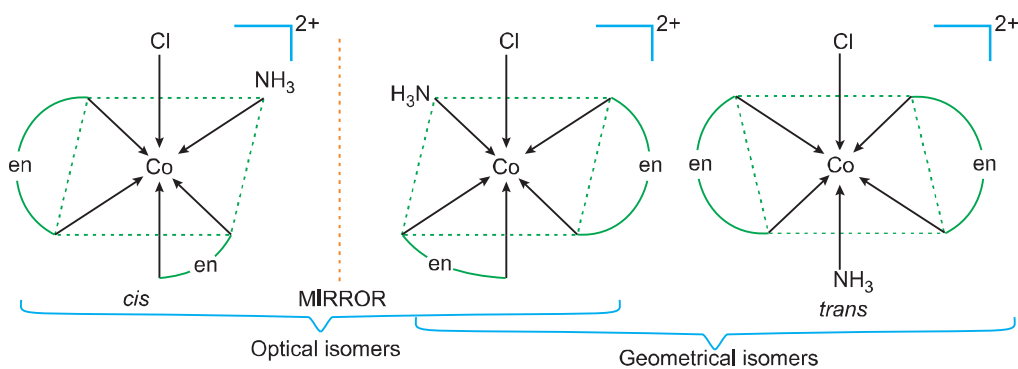
Q. 11. Draw all the isomers (geometrical and optical) of:



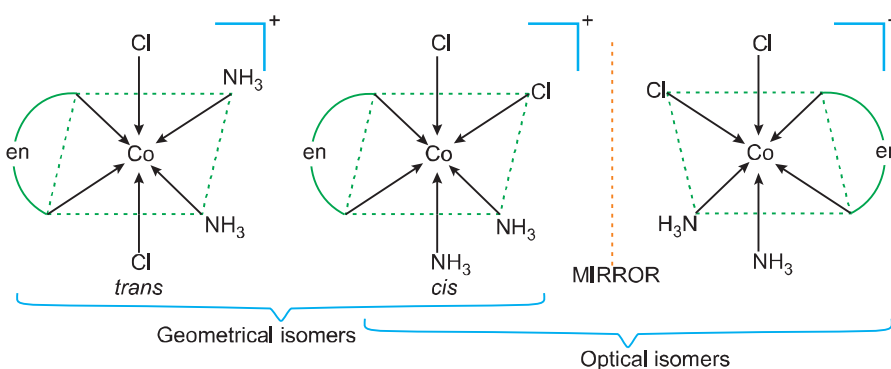
Ans. (i)



(ii)

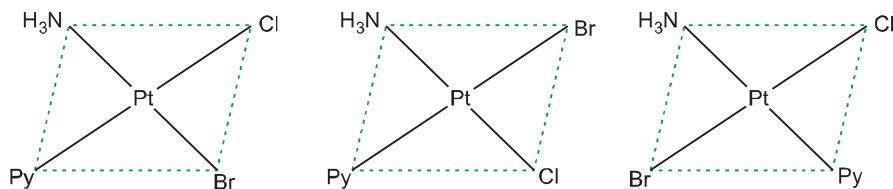


(iii)



Q. 12. Write all the geometrical isomers of $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$ and how many of these will exhibit optical isomerism?

Ans. Three isomers are possible as follows:

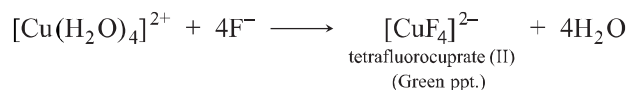


Isomers of this type do not show any optical isomerism. Optical isomerism rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

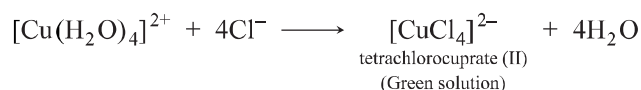
Q. 13. Aqueous copper sulphate solution (blue in colour) gives (i) a green precipitate with aqueous potassium fluoride, and (ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Ans. Aqueous copper sulphate exists as $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$. It is a labile complex. The blue colour of the solution is due to $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions.

(i) When KF is added, the weak H_2O ligands are replaced by F^- ligands forming $[\text{CuF}_4]^{2-}$ ions, which is a green precipitate.

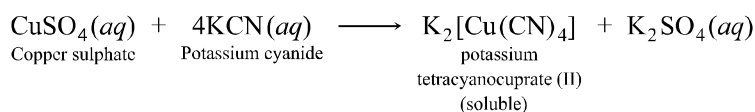


(ii) When KCl is added, Cl^- ligands replace the weak H_2O ligands forming $[\text{CuCl}_4]^{2-}$ ion, which has bright green colour.



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 $\text{H}_2\text{S}(\text{g})$ is passed through this solution?

Ans. $\text{K}_2[\text{Cu}(\text{CN})_4]$ is formed when excess of aqueous KCN is added to an aqueous solution of CuSO_4 .



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:



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

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

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

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

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.