9

Coordination Compounds

Facts that Matter

Important Terms

- **Coordination compounds:** Coordination compounds are the compounds in which a central metal atom or ion is linked to a number of ions or neutral molecules by coordinate bonds or the one which contain complex ions.
  Examples: $K_4[Fe(CN)_6]$; $[Cu(NH_3)_4]SO_4$; $Ni(CO)_4$
- **The main postulates of Werner's theory of coordination compounds:**
  (*i*) In coordination compounds metals show two types of linkages or valencies—Primary and Secondary.
  (*ii*) The primary valencies are 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 valence is equal to the coordination number and is fixed for a metal.
  (*iv*) The ions or groups bounded by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
- **Coordination entity:** A coordination entity is a compound having a central metal ion/atom bonded with fixed number of ions or molecules and exist as a single entity. It is written within the square brackets [metal ion/atom and ligands].
- **Central metal atom/ion:** In a coordination entity, the metal ion/atom which is bonded to a fixed number of ions/molecules (ligands) is called central metal ion/atom.
- **Ligands:** The ions or molecules bonded with the central metal ion/atom with coordinate bond are called ligands. They are of different types: monodentate or unidentate ligands.
  (*i*) **Mondendate ligands:** They are bonded with the central metal ion through one site(bond). Examples are H_2O, NH_3, CN^-.
  (*ii*) **Ambidentate ligands:** They are unidentate ligands but they can donate the electron through two different atoms but at a time only through one atom.
  Example: CN^- can donate the electron through C as well as through N atom, NO_2^- can donate the electron through O as well as through N atom.
  (*iii*) **Didentate ligands:** These type of ligands are bonded with metal ion through two site/form two coordinate bonds. Example are (COO^-), Ethylenediamine.
  (*iv*) **Polydentate ligands:** These ligands can form more than two coordinate bonds with the central metal ion/atom. Example: EDTA
  (*v*) **Chelating ligands:** Didentate or polydentate ligands which can form a closed ring structure around the central metal ion are called chelating ligands. Example: Oxalate ion, Ethylenediamine, etc.

- **Coordination number:** Coordination number of a metal ion is equal to the number of coordinate bonds that ligands can form with metal ion. Coordination number of a metal ion is
  - = the no. of monodentate ligands
  - = 2 × no. of didentate ligands
  - = 3 × no. of tridentate ligands
- **Coordinate sphere:** In a coordination compound, [ ] known as coordination sphere, as the species within [ ] are bonded through coordinate bonds.
- **Oxidation number of metal ion:** It is equal to the charge on the metal ion in the complex or coordination compounds. It is represented in parentheses.
- **Chelate compound:** The coordination compound formed by chelating ligands with the central metal ion is called chelate compound. Chelate compounds are more stable than normal coordination compounds.
- **Difference between a double salt and a complex:** Both double salts as well as complexes are formed by the combination of two or more stable compounds in a stoichiometric ratio. However, double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$ do not dissociate into Fe^{2+} and CN^- ions.

Double Salt	Coordination Compound
It gives the test of all the ions present in the composition of the salt.	It does not give the test of all the ions present in the composition of the salt.

- **Homoleptic complexes:** Complexes in which a metal is bonded to only one kind of donor group. **Example:** $[Co(NH_3)_6]^{3+}$.
- **Heteroleptic complexes:** Complexes in which a metal is bonded to more than one kind of donor groups. **Example:** $[Co(NH_3)_4Cl_2]^+$.
- **Naming of Mononuclear Coordination Compounds:** The principle of additive nomenclature is followed while naming the coordination compounds. The following rules are used:
  - (*i*) The cation is named first in both positively and negatively charged coordination entities.
  - (*ii*) The ligands are named in an alphabetical order before the name of the central atom/ion.
  - (*iii*) The name of the anionic ligands ends in –o, while those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. These are placed within the enclosing mark( ).
  - (*iv*) The prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands includes a numerical prefix, then the terms, bis, tris, tetrakis are used, for the ligand to which they refers as being placed in the parenthesis.
  - (*v*) Oxidation state of the metal in the cation, anion, or neutral coordination entity is indicated by roman numeral in the parentheses.
  - (*vi*) If the complex ion is a cation, the metal is same as the element.
  - (*vii*) The neutral complex molecule is named similar to that of the complex cation.

- **Names of Some Common Ligands**

Negative Ligands		Charge	Neutral Ligands		Charge
CN^-	Cyano	–1	NH_3	Ammine	0
Cl^-	Chlorido	–1	H_2O	Aqua/aquo	0
Br^-	Bromido	–1	NO	Nitrosyl	0
F^-	Fluorido	–1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	–2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	–2	$CH_2–NH_2$	(1, 2-Ethane	0
NH_2^-	Amido	–1	|		
NH^{2-}	Imido	–2	CH_2NH_2	diamine)	
ONO^-	Nitrito	–1			
NO_2^-	Nitro	–1	**Positive Ligands**		
NO_3^-	Nitrato	–1	$NH_2—NH_3^+$	Hydrazinium	+1
SCN^-	Thiocyanato	–1	NO^+	Nitrosonium	+1
NCS^-	Isothiocyanato	–1	NO_2^+	Nitronium	+1
$CH_2(NH_2)COO^-$	Glycinato	–1			
OH^-	Hydroxo	–1			

- **Isomerism in Coordination Compounds:** Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism. Coordination compounds show two main types of isomerism—

  (*a*) Structural Isomerism (*b*) Stereoisomerism

  (*a*) **Structural Isomerism:** It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types:

  (*i*) **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers: $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

  (*ii*) **Hydrate or solvate isomerism:** This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2H_2O$ (grey-green).

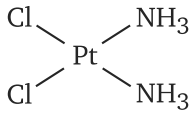
  (*iii*) **Linkage Isomerism:** Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by the complexes containing the thiocyanate ligand, NCS, which may bind through the nitrogen to give M-NCS or through sulphur to give M-SCN.

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

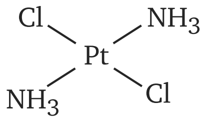
  (*b*) **Stereoisomerism:** Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangements. They are of two kinds:

  (*i*) Geometrical isomerism (*ii*) Optical isomerism.

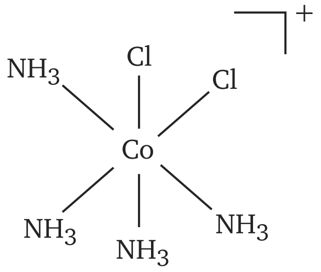
(*i*) **Geometrical isomerism:** This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_{-2}]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer [MABXL]–Where A, B, X, L are unidentates ligands.



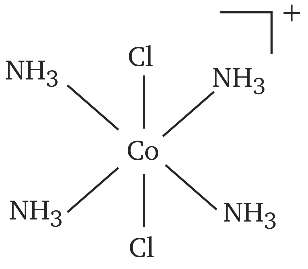
cis



trans

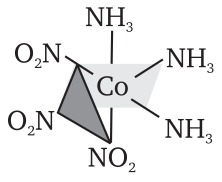


cis

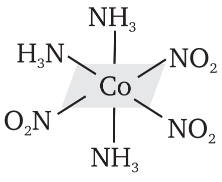


trans

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

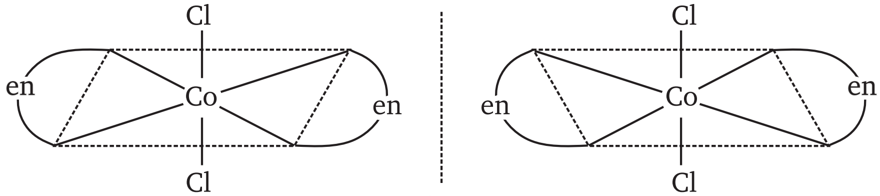


fac–



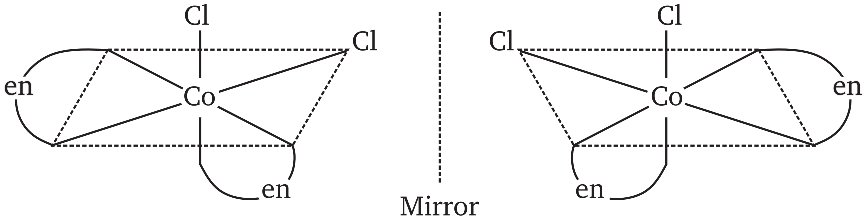
mer–

(*ii*) **Optical Isomerism:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral molecules. The two forms are called *dextro*(d) and *laevo*(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type $[CoCl_2(en)_2]^{2+}$, only the cis-isomer shows optical activity.



Mirror

Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



Mirror

Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

- **Types of Hybridisation**

Coordination Number	Type of Hybridisation	Acquired Geometry
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

- **Crystal Field Theory**
  1. The metal-ligand bond is ionic, arising purely from electrostatic interactions between the metal ion and the ligand.
  2. Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
  3. In an isolated gaseous metal atom or ion the five *d*-orbitals are degenerate.
  4. Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal/ion.
  5. In a complex the negative field becomes asymmetrical and results in splitting of the *d*-orbitals.

(A) Crystal Field Splitting in Octahedral Coordination Entities:

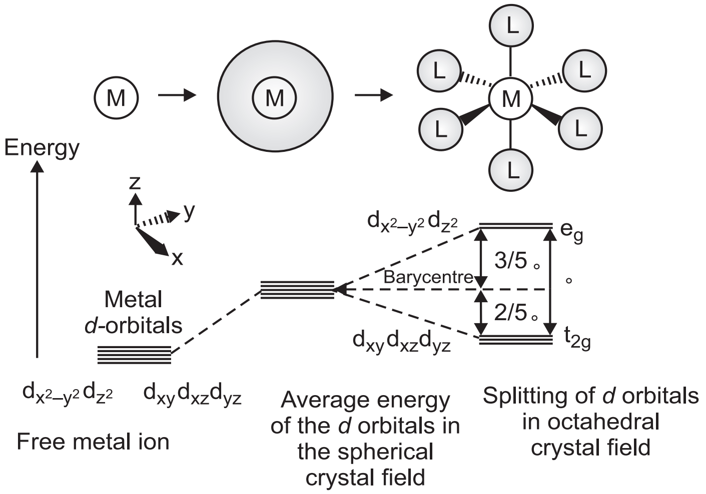


Fig 9.1: *d* orbital splitting in an octahedral crystal field

For d^4 ions, two possible patterns of electron distribution arise:

(*i*) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t^3_{2g}e^1_g$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

(*ii*) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t^4_{2g}e^0_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

(B) Crystal Field Splitting in Tetrahedral Coordination Entities:

1. The four surrounding ligands approaches the central metal atom/ion along the plane between the axes.

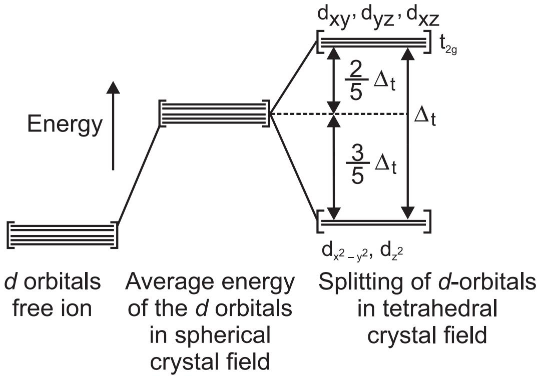
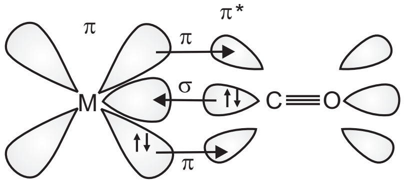


Fig 9.2: *d* orbital splitting in a tetrahedral crystal field

2. The t_{2g} orbitals are raised in energy (2/5) Δ_t.
3. The two e_g orbitals are lowered in energy $(3/5)\Delta_t$.
4. The splitting is smaller as compared to octahedral field splitting, $\Delta_t = (4/9)\Delta_o$.
5. Pairing of electrons is rare and thus complexes generally high spin configurations.

- **Bonding in Metal Carbonyls:** The metal-carbon bond in metal carbonyls possess both σ and π character. The M-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of the metal into the vacant antibonding π* orbital of carbon monoxide. The metal to the ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

Stability of Coordination Compounds

The extent of dissociation and hence the thermodynamic stability of the complex ion depends upon the strength of the metal-ligand bond. Stronger is the metal ligand bond, lesser is the dissociation in the solution and hence greater is the stability.

If we talk about the formation of a complex ion in the solution. The equilibrium constant for this reaction is therefore called the stability constant.

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$\text{stability constant, } \beta = \frac{\left[Cu\left(NH_3\right)_4\right]^{2+}}{\left[Cu^{2+}\right]\left[NH_3\right]^4}$$

Stability constant is the reciprocal of the instability constant or the dissociation constant.

$$\beta = \frac{1}{K_i}$$

Where K_i is called the instability constant or dissociation constant.

Importance and Application of Coordination Compounds

(*i*) Coordination compounds are of great importance. These compounds constitute the minerals, plants and are also present in animals. These play important functions. Examples of such reagents include EDTA, DMG (dimethyl glyoxime) α-nitroso-β-naphthol, cupron etc.

(*ii*) The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

(*iii*) Some important extraction process of metals, like those of silver and gold make use of complex formation.

(*iv*) Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$ which is decomposed to yield pure Nickel.

(*v*) The pigment responsible for photosynthesis is chlorophyll which is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier, is also a coordination compound of iron. Vitamin B_{12}, (cyanocobalamine) the pernicious anaemia factor, is a coordination compound of cobalt.

(*vi*) Coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase.

(*vii*) Coordination compounds are used as catalysts for many industrial processes.

(*viii*) Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$.

(*ix*) 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 $[Ag(S_2O_3)_2]^{3-}$.

(*x*) EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours.

NCERT IN-TEXT QUESTIONS SOLVED

9.1. Write the formulae 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*) Dichlorobis(ethane –1, 2-diamine)platinum(IV)nitrate.
(*vi*) Iron(III) hexacyanoferrate(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*) $Fe_4[Fe(CN)_6]_3$.

9.2. Write the IUPAC names of the following:

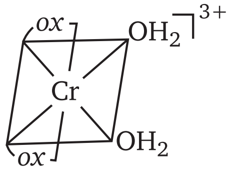
(*i*) $[Co(NH_3)_6]Cl_3$ (*ii*) $[Co(NH_3)_5Cl]Cl_2$ (*iii*) $K_3[Fe(CN)_6]$
(*iv*) $K_3[Fe(C_2O_4)_3]$ (*v*) $K_2[PdCl_4]$ (*vi*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

Ans. (*i*) Hexaamine cobalt (III) chloride
(*ii*) Pentaamine chloridocobalt (III) chloride
(*iii*) Potassium hexacyanoferrate (III)
(*iv*) Potassium trioxalatoferrate (III)
(*v*) Potassium tetrachlorido palladate (II)
(*vi*) Diamminechlorido (methylamine) platinum (II) chloride.

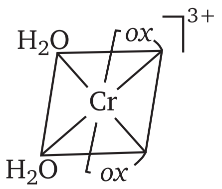
9.3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

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

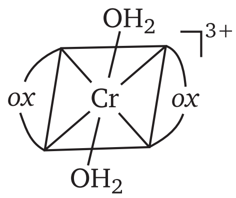
Ans. (*i*) Both geometrical (*cis, trans*) and optical isomer for *cis*-form.



cis d(+)-form

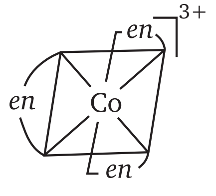


cis l(–)-form

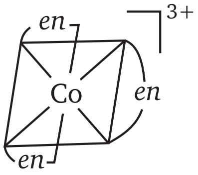


trans-form

(*ii*) Two optical isomers can exist.



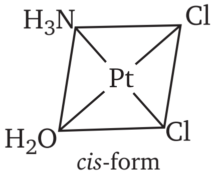
d(+)-form



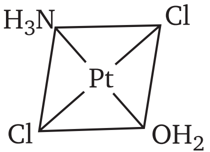
l (–)-form

(*iii*) Linkage isomers $[Co(NH_3)_5ONO](NO_3)_2$ and $[Co(NH_3)_5NO_2](NO_3)_2$.

(*iv*) Geometrical isomerism.



cis-form



trans-form

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

Ans. When they are dissolved in water, they will give different ions in the solution which can be tested by adding $AgNO_3$ solution and $BaCl_2$ solution. When Cl^- ions are the counter ions, a white precipitate will be obtained with $AgNO_3$ solution. If SO_4^{2-} ions are the counter ions, a white precipitate will be obtained with $BaCl_2$ solution.

$$[Co(NH_3)_5Cl]SO_4(aq) + BaCl_2(aq) \rightarrow \underset{\text{ppt}}{BaSO_4(s)}\downarrow$$

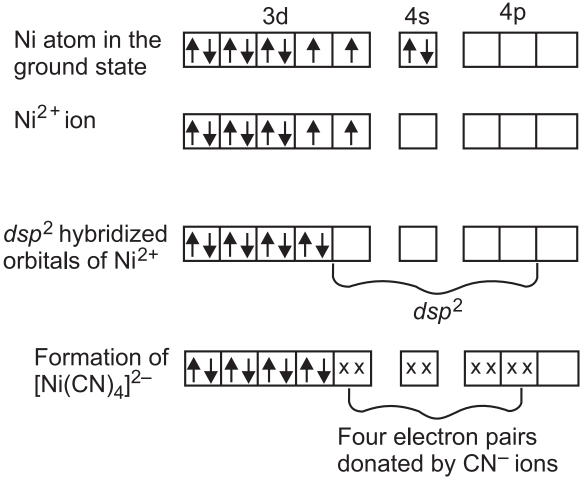
$$[Co(NH_3)_5Cl]SO_4(aq) + AgNO_3 \rightarrow \text{No reaction}$$

$$[Co(NH_3)_5SO_4]Cl(aq) + BaCl_2(aq) \rightarrow \text{No reaction}$$

$$[Co(NH_3)_5SO_4]Cl(aq) + AgNO_3(aq) \rightarrow \underset{\text{ppt}}{AgCl(s)}\downarrow$$

9.5. 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, *i.e.* nickel is present as Ni^{2+} ion.



dsp^2 – hybrid orbitals

– Diamagnetic

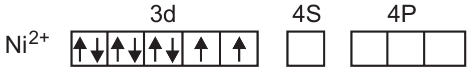
CN^- is a strong ligand as it approaches the metal ion, So the electrons should get paired up.

In $[NiCl_4]^{2-}$, Cl^- provides a weak ligand field. It is therefore unable to pair up the unpaired electrons of the 3*d* orbital.

Hence the hybridisation is sp^3 and it is paramagnetic.

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

Ans. In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state with electronic configuration = $3d^8 4s^0$.



Cl^- is a weak ligand. It cannot pair up the electrons in 3*d* orbitals. Hence, it is paramagnetic. In $[Ni(CO)_4]$, Ni is in zero oxidation state and its configuration is $-3d^8 4s^2$.

In the presence of CO ligand the 4*s* electrons shift to 3*d* orbital to pair up the 3*d* electrons. Thus, there is no unpaired electron present. Hence it is diamagnetic.

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

Ans. In both the complexes, Fe is in +3 oxidation state with the configuration $3d^5$. CN^- is a strong field ligand. In its presence, 3*d* electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming inner orbital complex. H_2O is a weak ligand. In its presence 3*d* 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.

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

Ans. In $[Co(NH_3)_6]^{3+}$, oxidation state of Co = +3

Electronic configuration = $3d^6$

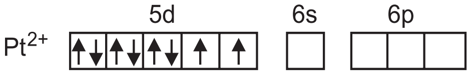
In presence of NH_3, 3*d* electrons pair up leaving two *d*-orbitals empty. Hence, the hybridisation is d^2sp^3 forming an inner orbital complex.

In $[Ni(NH_3)_6]^{2+}$

Oxidation state = +2, Electronic Configuration = $3d^8$. In the presence of NH_3, 3*d* electrons do not pair up. The hybridisation involved is sp^3d^2 and it forms an outer orbital complex.

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

Ans. Electronic Configuration of P*t* = $5d^9 6s^1$



For square planar shape, hybridisation = dsp^2

Hence, the unpaired electron in 5*d*-orbital pair up to make one *d*-orbital empty for dsp^2 hybridisation. Thus, there is no unpaired electron.

9.10. The hexaqua manganese(II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electrons. Explain using crystal field theory.

Ans. Mn in +2 state has the configuration $3d^5$.

In the presence of H_2O as a ligand, the distribution of these five electrons is $t_{2g}^3\ eg^2$, *i.e.* all the electrons remain unpaired. In presence of CN^- as ligand the distribution is $t_{2g}^5\ eg^0$, *i.e.* two t_{2g} orbitals contains paired electrons. While the third t_{2g} orbital contains one unpaired electron.

9.11. Calculate the overall complex dissociation equilibrium constant for $Cu(NH_3)_4^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

Ans. Overall stability constant

$$(\beta_4) = 2.1 \times 10^{13}$$

Overall dissociation constant is the reciprocal of overall stability constant.

Hence, overall dissociation constant.

$$K = \frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}} = 4.7 \times 10^{-14}.$$

NCERT TEXTBOOK QUESTIONS SOLVED

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

Ans. The main postulates of Werner's theory of coordination compounds are:

(*i*) In coordination compounds, metal show two types of linkages (valencies)—primary and secondary.

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

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

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

9.2. $FeSO_4$ 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. $FeSO_4.(NH_4)_2\ SO_4.6H_2O$ is a double salt. It dissociates into aqueous solution forming Fe^{2+}, NH_4^+ and SO_4^{2-} ions. $[Cu(NH_3)_4]^{2+}$ is a complex ion which does not dissociate to give Cu^{2+} in aqueous solution.

9.3. Explain with two examples each of the following: Coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic complexes.

Ans. **Coordination entity:** This entity usually constitutes a central metal atom or ion, to which are attached a fixed number of other atoms or ions or groups by coordinate bond. Examples are $[Ni(CO)_4]$, $[COCl_3(NH_3)_3]$. etc.

Ligands: It is an ion having at least one lone pair of electrons and are capable of forming a coordinate bond with the central metal atom/ion in the coordination entity. Examples are: Cl^-, $(OH)^-$, $(CN)^-$, etc.

Coordination number: The total number of coordinate bonds with which central metal atom/ion is linked to ligands in the coordination entity is called the coordination number of the central metal atom/ion.

Coordination polyhedron: The spatial arrangement of the ligands which are directly attached to the central metal atom/ion defines a coordination polyhedron about the central metal atom/ion.

Examples are: $[Co(NH_3)_6]^{3+}$ is octahedral,
$[Ni(CO)_4]$ is tetrahedral.

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

Complexes in which a metal is bound to more than one kind of donor groups are called hetroleptic complexes. Example $[Co(NH_3)_4Cl_2]^+$.

9.4. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

Ans. **Unidentate ligand:** When a ligand is bound to a metal ion through a single donor atom, for eg. with Cl^-, H_2O. then ligand is said to be unidentate.

Didentate ligand: When a ligand is bound through two donor atoms then the ligand is said to be didentate.

Example: $C_2O_4^{2-}$ (Oxalate)
$H_2NCH_2 — CH_2NH_2$ (ethane–2–diammine)

Ambidentate ligand: Ligand which can ligate through two different atoms is called ambidentate ligand.

Examples: — NO_2^- and SCN^-.

9.5. 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*) $[Cr(NH_3)_3Cl_3]$

(*v*) $K_3[Fe(CN)_6]$

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

or $x = +3$

(*ii*) $x - 4 = -2$

or $x = +2$

(*iii*) $x + 0 + 3(-1) = 0$

$x - 3 = 0$

$x = +3$

(*iv*) $x + 2\,(-1) + 0 = +1$

or $x = +3$

(*v*) $x + 6\,(-1) = -3$

or $x = +3$

9.6. Using IUPAC norms write the formulae for the following:

(*i*) Tetrahydroxozincate(II) (*ii*) Potassium tetrachloridopalladate(II)

(*iii*) Diamminedichlorido platinum(II) (*iv*) Potassium tetracyanonickelate(II)

(*v*) Pentaamminenitrito–O–cobalt(III) (*vi*) Hexaamminecobalt(III) sulphate

(*vii*) Potassium tri(oxalato)chromate(III) (*viii*) Hexaamine platinum(IV)

(*ix*) Tetrabromidocuprate(II) (*x*) Pentaamminenitrito–N–cobalt(III)

Ans. (*i*) $[Zn(OH)_4]^{2-}$ (*ii*) $K_2[PdCl_4]$ (*iii*) $[PtCl(NH_3)_2Cl]$

(*iv*) $K_2[Ni(CN)_4]$ (*v*) $[Co(NH_3)_5(ONO)]^{2+}$ (*vi*) $[Co(NH_3)_6(SO_4)_3]$

(*vii*) $K_3[Cr(C_2O_4)_3]$ (*viii*) $[Pt(NH_3)_6]^{4+}$ (*ix*) $[CuBr_4]^{2-}$

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

9.7. 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*) Hexaammine cobalt(III) chloride

(*ii*) Diammine dichlorido (methylamine) platinum(II) chloride

(*iii*) Hexaaqua titatium(III) ion

(*iv*) Tetraammine chloridonitrito–N–Cobalt(III) chloride

(*v*) Hexaaquamanganese(II) ion

(*vi*) Tetrachloridonickelate(II) ion (*vii*) Hexaammine nickel(II) chloride

(*viii*) Tris (ethane –1, 2–diamine) cobalt(III) ion (*ix*) Tetracarbonyl nickel (O)

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

Ans. Two principal types of isomerism are known among coordination compounds:

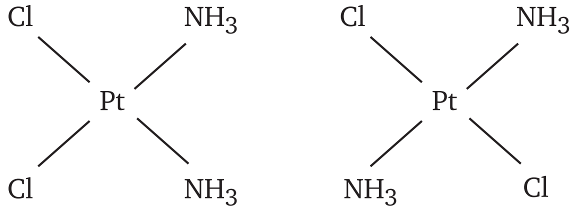
(A) Stereoisomerism, (B) Structural isomerism

Each of which can be further sub-divided as:

(A) Stereoisomerism

(*i*) *Geometrical isomerism.* Type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

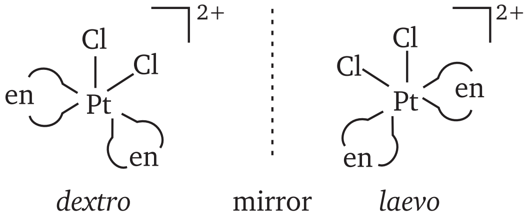
Example: Pt $[(NH_3)_2 Cl_2]$



Geometrical isomers (cis & trans)

(*ii*) *Optical isomerism.* Common is octahedral complexes involving didentate ligands.

Example: $[Pt\ Cl_2\ (en)_2]^{2+}$



Optical isomers (*d* and *l*) of *cis*- $[PtCl_2(en)_2]^{2+}$

(B) Structural isomerism

(*i*) *Linkage isomerism*.

Example: $[Co(NH_3)_5(NO_2)]Cl_2$

(*ii*) *Coordination isomerism* .

Example: $[Co(NH_3)_6]$ $[Cr(CN)_6]$

(*iii*) *Ionisation isomerism*.

Example: $[Co(NH_3)_5SO_4]Br$ $[Co(NH_3)_5\ Br]SO_4$

(*iv*) *Solvate isomerism.*

Example: $[Cr(H_2O)_6]Cl_3$ (violet) its solvate isomer
$[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ (grey–green)

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

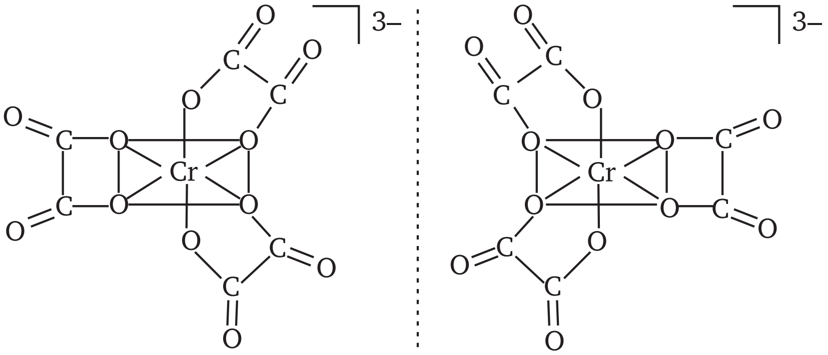
(*i*) $[Cr(C_2O_4)_3]^{3-}$ (*ii*) $[Co(NH_3)_3Cl_3]$

Ans. (*i*) Nil (*ii*) Two (*fac* and *mer*)

9.10. Draw the structures of optical isomers of:

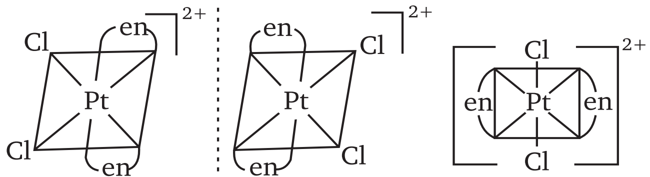
(*i*) $[Cr(C_2O_4)_3]^{3-}$ (*ii*) $[PtCl_2(en)_2]^{2+}$ (*iii*) $[Cr(NH_3)_2Cl_2(en)]^+$

Ans. (*i*)



Optical isomers of $[Cr(C_2O_4)_3]^{3-}$

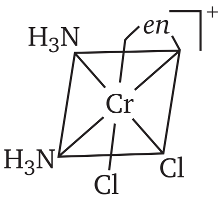
(*ii*)



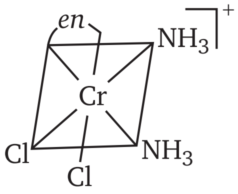
cis-l(–) | cis-d(+) | trans-isomer (meso form)

Optical isomers of $[PtCl_2(en)_2]^{2+}$

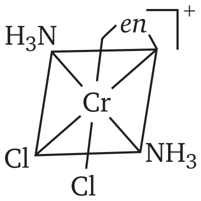
(*iii*) *cis* and *trans*-forms, both show optical isomerism.



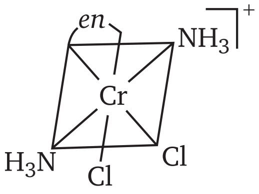
cis-d(+)



cis-l(–)



trans-d(+)



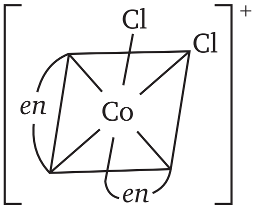
trans-l(–)

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

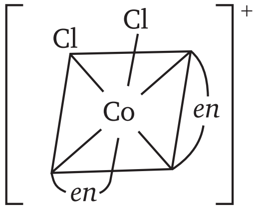
(*i*) $[CoCl_2(en)_2]^+$ (*ii*) $[Co(NH_3)Cl(en)_2]^{2+}$

(*iii*) $[Co(NH_3)_2Cl_2(en)]^+$ [*AI CBSE* 2014]

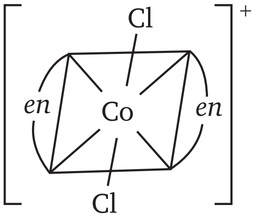
Ans. (*i*)



d(+)

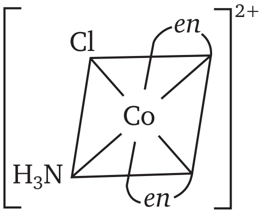


l (–)

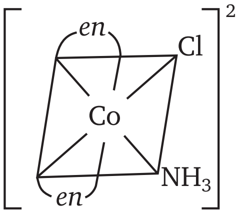


trans-$[CoCl_2(en)_2]^+$ (meso form)

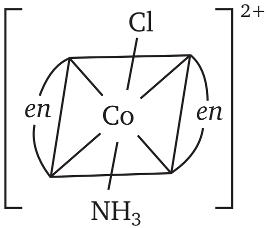
(*ii*) Optical isomers of *cis*-$[CoCl_2(en)_2]^+$



cis-d(+)

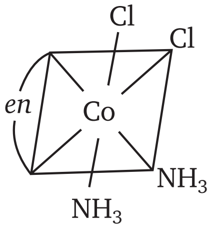


cis-l(–)

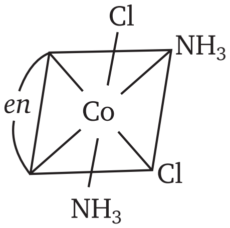


trans-$[Co(NH_3)Cl(en)_2]^{2+}$ (meso form) (*iii*) Optical isomers of cis-$[Co(NH_3)Cl(en)_2]^{2+}$

(*a*)

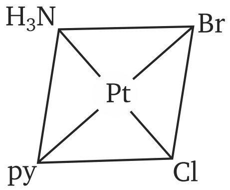


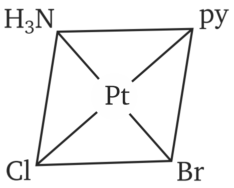
(*b*)

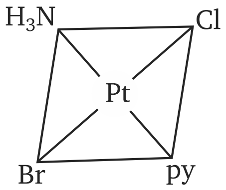


9.12. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(Py)]$ and how many of these will exhibit optical isomers?

Ans.







None of them will not show optical isomerism. Optical isomerism only rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

9.13. 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 $CuSO_4$ solution exists as $[Cu(H_2O)_4]SO_4$ which has blue colour 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.

$$[Cu(H_2O)_4]^{2+} + 4F^- \rightarrow \underset{\text{Green ppt}}{[CuF_4]^-} + 4H_2O$$

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

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

9.14. 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. $2CuSO_4 + 10KCN \rightarrow 2K_3[Cu(CN)_4] + 2\ K_2SO_4 + (CN)_2$

Thus, coordination entity formed = $[Cu(CN)_4]^{3-}$

As CN^- is a strong ligand, thus the complex ion is highly stable and it does not dissociate to give Cu^{2+} ions. Hence, no precipitate with H_2S is formed.

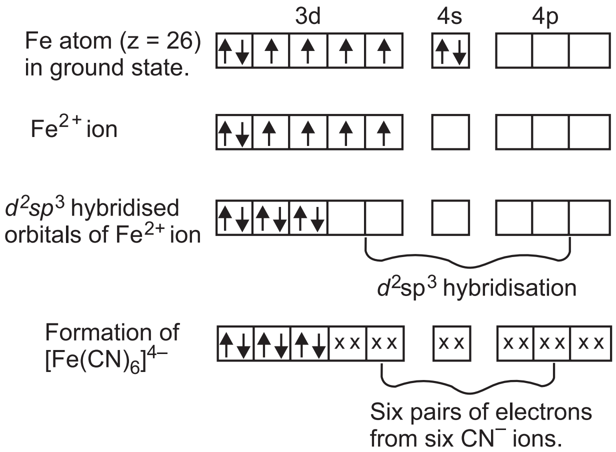
9.15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

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

(*iii*) $[Co(C_2O_4)_3]^{3-}$ (*iv*) $[CoF_6]^{3-}$

Ans. (*i*) In $[Fe(CN)_6]^{4-}$

oxidation state of Fe = +2



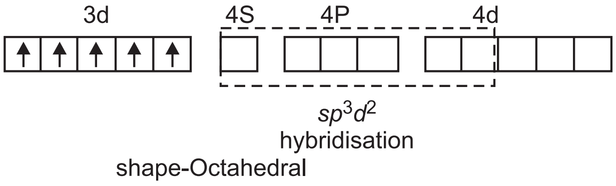
It has octahedral shape and it is diamagnetic.

(*ii*) In $[FeF_6]^{3-}$: [Ar]$4s^2 3d^6$

Fe^{3+} : [Ar] $4s^0 3d^5$

F^- is a weak ligand, it does not cause pairing of electrons.

$[FeF_6]^{3-}$:

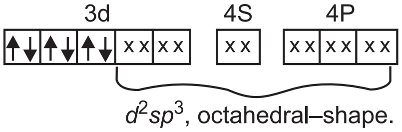


(*iii*) $[Co(C_2O_4)_3]^{3-}$:

Co(27): [Ar] $4s^2$ $3d^7$

Co^{3+} : [Ar] $4s^0$ $3d^6$

$C_2O_4^{2-}$ is a strong field ligand which causes pairing of electrons.

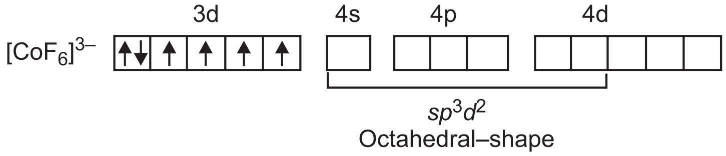


(*iv*) $[CoF_6]^{3-}$

Co(27) – [Ar] $4s^2$ $3d^7$

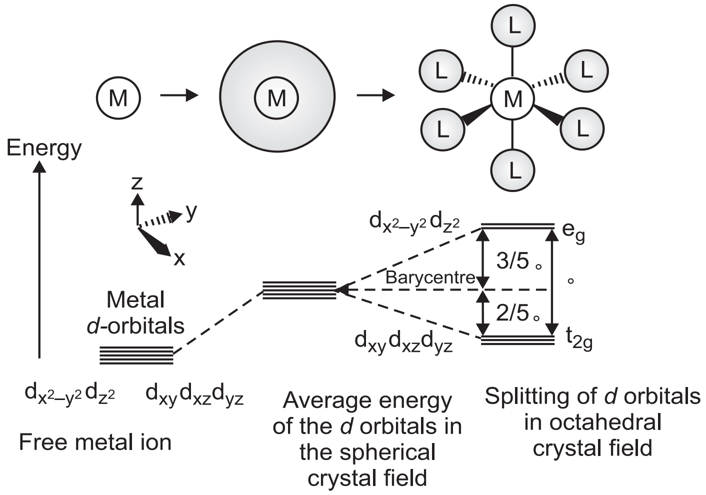
Co^{3+} – [Ar] $4s^0$ $3d^6$

F^- is a weak field ligand and it does not cause pairing of electrons.



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

Ans.



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

Ans. **Spectrochemical series:** The arrangement of ligands in the order of their increasing field strength the increasing crystal field splitting energy (CFSE) values is called spectrochemical series.

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

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

Ans. When ligands approaches a transition metal ion, the *d*-orbitals splits up into two sets—one with lower energy and other with higher energy. The difference of energy between the two set of orbitals is called crystal field splitting energy (Δ_o for octahedral field).

If $\Delta_0 < P$ (pairing energy) then the 4th electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g^{\ 1}$, thus forming high spin complexes.

Such ligands for which $\Delta_o < P$ are called weak field ligands.

If $\Delta_o > P$, the 4th electron gets paired up in one of the t_{2g} orbitals giving the configuration $t_{2g}^{\ 4}\ e_g^{\ 0}$ thereby forming low spin complexes.

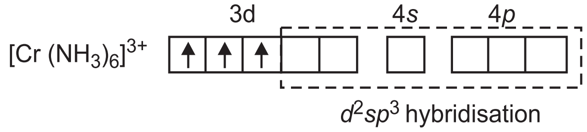
Such ligands for which $\Delta_o > P$ are called strong field ligands.

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

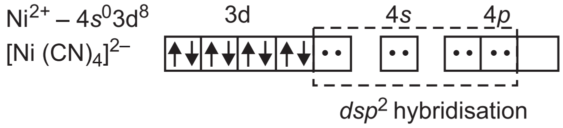
$Cr(24)$: [Ar] $4s^1 3d^5$

$Cr^{3+}(24)$: [Ar] $4s^0\ 3d^3$

Ans.



It is paramagnetic due to the presence of unpaired electrons.



It has a square planar structure, and it is diamagnetic due to the absence of unpaired electrons.

9.20. 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 oxidation state with the configuration $3d^8$, *i.e.* it has two unpaired electrons which do not pair up in the presence of weak H_2O ligand. Hence, 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 oxidation state with the configuration $3d^8$ but in the presence of strong CN^- ligand, the two unpaired electrons in the 3*d* orbitals pair up. Thus, there is no unpaired electron present. Hence it is colourless.

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

Ans. In both the complexes, Fe is in +2 oxidation state with the configuration $3d^6$, *i.e.* it has four unpaired electrons.

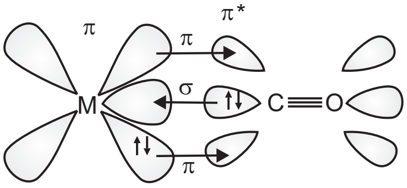
As the ligands H_2O and CN^- possess different crystal field splitting energy (Δ_0), therefore they absorb different components of the visible light (VIBGYOR) for *d–d* transition. Hence, the transmitted colours are different.

9.22. Discuss the nature of bonding in metal carbonyls.

Ans. (*i*) The metal-carbon bond in metal carbonyls possess both s & p character.

(*ii*) The M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.

(*iii*) The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of the metal into the vacant antibonding π* orbital of carbon monoxide.



Synergic bonding

(*iv*) The metal to ligand bonding creates a synergic effect, which strengthens the bond between CO & the metal.

9.23. 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. (*i*) Oxidation state of $K_3[Co(C_2O_4)_3]^{3-}$

or $x - 6 = -3$ coordination no. = – 6

or $x = +3$

d-orbital occupation of $Co^{3+} = 3d^6 = t_{2g}{}^6\ e_g{}^0$

No. of unpaired electrons = 0

(*ii*) *cis*–$[Cr(en)_2Cl_2]^+\ Cl^-$

Oxidation State $x = +3$ coordination no. = –6

$Cr^{3+} = 3d^3$

$= t_{2g}{}^3$ no. of unpaired electrons = 3

(*iii*) $(NH_4)_2[CoF_4]$

$x - 4 = -2$ coordination no. = 4

$x = +2$

$Co^{2+} = 3d^7$

$= e^4t_2^3$ no. of unpaired electrons = 3 (*iv*) $[Mn(H_2O)_6]^{2+}SO_4^{2-}$

Oxidation State $x = +2$ coordination no. = 6

$Mn^{2+} = 3d^5$

$= t_{2g}^3 e_g^2$ no. of unpaired electrons = 5.

9.24. 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*) $K[Cr(H_2O)_2(C_2O_4)_2]\cdot 3H_2O$ (*ii*) $[Co(NH_3)_5Cl]Cl_2$ (*iii*) $CrCl_3(py)_3$

(*iv*) $Cs[FeCl_4]$ (*v*) $K_4[Mn(CN)_6]$

Ans. (*i*) Potassium diaquabis(oxalato)chromate(III) trihydrate.

Coordination no. = 6

Shape = Octahedral

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

or $x - 4 = -1$

or $x = +3$

Electronic configuration of $Cr^{3+} = 3d^3 = t_{2g}{}^3 e_g{}^0$

No. of Unpaired electrons (n) = 3

Magnetic moment (μ) $= \sqrt{n\,(n+2)} = \sqrt{3\,(5)} = \sqrt{15}$ BM = 3.87 BM

(*ii*) Pentaaminechloro cobalt(III) chloride:

Coordination no. of Co = 6

shape = octahedral

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

or $x = +3$

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

$n = 0$

Magnetic moment (μ) = 0

(*iii*) Trichlorotripyridine chromium(III)

Coordination no. of Cr = 6 shape = octahedral

Oxidation state of Cr =

$x - 3 + 0 = 0$

$x = +3$

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

$n = 3$

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

(*iv*) Caesium tetrachloroferrate(III)

Coordination no. of Fe = 4 shape = tetrahedral

Oxidation state of Fe: $x - 4 = -1$

$x = +3$

Electronic configuration of $Fe^{3+} = 3d^5 = e^2 t_2^3$

$n = 5$

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

(*v*) Potassium hexacyanomanganate (II)

Coordination no. of Mn = 6   Shape = octahedral
Oxidation state of Mn: $x - 6 = -4$
$x = +2$
Electronic configuration of $Mn^{2+} = 3d^5 = t_{2g}^{5}e_g^{0}$
$n = 1$

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

9.25. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

Ans. The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant for the association, quantitatively expresses the stability.

Factors which govern the stability of a complex are:

(*i*) Smaller the size of cation, greater will be the stability of complex, e.g. Fe^{3+} ion forms more stable complex than Fe^{2+}.
(*ii*) Greater the charge on the central metal ion, more stable will be the complex.
(*iii*) Stronger the ligand, more stable will be the complex formed, e.g. CN^- forms more stable complex than NH_3.

9.26. What is meant by chelate effect? Give an example.

Ans. The complexes which are formed by chelating ligands like ethylene diamine (en), EDTA, etc. are more stable than those formed by monodentate ligands such as H_2O or NH_3. This enhanced stability of the complexes containing chelating ligand is called chelate effect.

The number of such ligating groups is called the denticity of the ligand.

Example: $[PtCl_2(en)]$

9.27. 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. (*i*) *Biological systems*: Chlorophyll is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as an oxygen carrier is a coordination compound of iron.

Vitamin B_{12}, cyanocobalamin the antipernicious anaemia factor is a coordination compound of cobalt.

(*ii*) *Medicinal chemistry*: EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibits the growth of tumours. For example : *cis*-platin and related compounds.

(*iii*) *Analytical chemistry*: Hardness of water is estimated by simple titration with Na_2EDTA.

DMG, EDTA are also used in qualitative and quantitative analysis.

(*iv*) *Extraction and metallurgy*: In the purification of metal.

For example, Nickel is converted to $[Ni(CO)_4]$ which is decomposed to yield pure nickel.

9.28. How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in a solution?
(*i*) 6   (*ii*) 4   (*iii*) 3   (*iv*) 2

Ans. $[Co(NH_3)_6]Cl_2 \longrightarrow [Co(NH_3)_6]^{2+} + 2Cl^-$
(*iii*) 3.

9.29. Amongst the following ions which one has the highest magnetic moment value?
(*i*) $[Cr(H_2O)_6]^{3+}$ (*ii*) $[Fe(H_2O)_6]^{2+}$
(*iii*) $[Zn(H_2O)_6]^{2+}$

Ans. The oxidation states of Cr is + 3, Fe is +2 and that of Zn is also +2.

Electronic configuration of $Cr^{3+} = 3d^3$, no. of unpaired electrons = 3 (inner orbital complex)

Electronic configuration of Fe^{2+}, $= 3d^6$ no. of complex unpaired electrons = 4 (outer orbital complex)

Electronic configuration of $Zn^{2+} = 3d^{10}$, no. of unpaired electrons = 0 (inner orbital complex)

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

∴ (*ii*)has the highest magnetic moment

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

(*i*) +1 (*ii*) +3 (*iii*) –1 (*iv*) –3

Ans.
$$x + 0 = -1$$
$$x = -1$$

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

9.31. 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 oxidation state.

So, the most stable complex is:

(*iii*) $[Fe(C_2O_4)_3]^{3-}$, As $C_2O_4^{2-}$ is didentate chelating ligand, which forms chelate ring and hence is the most stable complex.

9.32. 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 field strengths (CFSE) values of the ligands form the spectrochemical series are in order:

$$H_2O < NH_3 < NO_2^-$$

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

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

The order of wavelength absorbed will be opposite of it.

Since $$E = \frac{hc}{\lambda}$$

ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

(1 *Mark*)

Q1. Why does a tetrahedral complex of the type $[MA_2B_2]$ do not show geometrical isomerism? [*CBSE* 2009]

Ans. This is because Unidentate ligands are equidistant from each other.

Q2. Write a neutral molecule in which the central atom is sp^3d^2 hybridised. [*AI* 2009]

Ans. $K_3[CoF_6]$

Q3. Name the following complex using IUPAC norms:

$[Co(en)_2(ONO)Cl]Cl$ [*AI* 2003]

Ans. Chlorobis(ethylene diammine) nitro cobalt(III) chloride.

Q4. What is an 'ambidentate group'? Give an example. [*AI* 2003]

Ans. It is the group of atoms which can combine at either of its ends. For example, –CN group.

Q5. What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

Ans. Six.

Q6. Give the names of two complexes which are used in medicines. [*CBSE* 2005 *C*]

Ans. (*i*) EDTA, is used in the treatment of lead poisoning.

(*ii*) *cis*-platin $[Pt(NH_3)_2Cl_2]$, is used in the treatment of cancer.

Q7. Write the IUPAC name of the complex:

$Na_3[Cr(OH)_2F_4]$

[*CBSE* 2003]

Ans. Sodium tetrafluoridodihydroxy chromate(III)

Q8. Write the IUPAC name of $[Ni(H_2O)_6]\ (Cl)_2$ [*Foreign* 2003]

Ans. Hexaqua nickel(II) chloride.

Q9. Name an ionisation isomer of

$[Cr(H_2O)_5Br]SO_4$

Ans. The ionisation isomer is:

$[Cr(H_2O)_5SO_4]Br$

Q10. Define 'Ligand'. Give an example.

Ans. Ligand is an atom or a group of atoms which is either negatively charged or has lone pair of electrons and form co-ordinate bond with the central metal atom or ion, *e.g.* H_2O.

Q11. Write the formula of copper hexacyanoferrate(II).

Ans. $Cu_2[Fe(CN)_6]$

Q12. Write the IUPAC name of $[Pt(NH_3)_2\ Cl_4]^{2-}$

Ans. Diammine tetrachlorido platinum (II).

Q13. Give IUPAC name of the linkage isomer of $[(NH_3)_3Pt(NO_2)]Cl$.

Ans. The linkage isomer is $[Pt(ONO)(NH_3)_3]Cl$

IUPAC Name — triaminenitrito-O-platinum (II) chloride.

Q14. How many moles of AgCl will be precipitated when excess of $AgNO_3$ is added to one molar solution of $[CrCl(H_2O)_5]Cl_2$?

Ans. 2 moles of AgCl will be precipitated.

Q15. Write the IUPAC name of $[Ag(NH_3)_2]Cl$.

Ans. Diamine silver(I) chloride.

Q16. In the geometry of a complex compound the molecule is trigonal bipyramidal. What is the hybridisation of the central atom?

Ans. dsp^3 or sp^3d.

Q17. Write the IUPAC name of $[Cu(NH_3)_4]\ SO_4$.

Ans. Tetraamine copper(II) sulphate.

Q18. If the geometry of $[PtCl_4]^{2-}$ is square planar, which orbital of Pt are involved in the bonding?

Ans. dsp^2 hybridisation is taking place, involving 5*d*, 6*s* and 6*p* orbitals.

Q19. Give the chemical formula of potassium trioxalatoferrate(III).

Ans. $K_3[Fe(C_2O_4)_3]$

Q20. Give the chemical formula of pentaamminechloro cobalt(III) chloride.

Ans. $[Co(NH_3)_5Cl]Cl_2$

Q21. What is the oxidation state of Ni in $[Ni(CO)_4]$?

Ans. Oxidation state of Ni = 0

Q22. Give the chemical formula of hexaamine platinum(IV) chloride.

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

Q23. Give an example of chelate complex.

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

Q24. How many coordination sites are there in ethylene diamine?

Ans. 2 coordination sites are there.

Q25. Write the IUPAC name of $K_3[Fe(C_2O_4)_3]$.

Ans. Potassium trioxalato ferrate(III).

Q26. What is the shape of $[Cr(NH_3)_6]^{3+}$ complex ion?

Ans. Octahedral

Q27. What is the charge on the metal atom in a complex ion?

$[Co(NH_3)_3(H_2O)_2Cl]^{2+}$

Ans. Co has +3 charge in the complex ion.

Q28. Name the metal present in haemoglobin.

Ans. Fe

Q29. Name the type of isomerism that occurs in complexes in which both cation and anion are complex ions.

Ans. Coordination isomerism

Q30. Name the hybridisation, the orbitals involved and the shape of the complex:

Ans. Hybridisation = dsp^2

Orbitals involved are 3*d*, 4*s* and 4*p*; and Shape = square planner.

Q31. Give an example of hexadentate ligand.

Ans. Ethylenediammine tetraacetate.

Q32. Name the compound used for measuring the hardness of water, *i.e.* for the estimation of Ca^{2+} and Mg^{2+} ions.

Ans. EDTA (Ethylene diammine tetraacetate).

Q33. What does stability constant indicate?

Ans. Stability constant indicates the stability of the complexes in solution and the strength of the ligand for a particular metal ion.

Q34. Define coordination number.

Ans. Coordination number is the number of co-ordinate bonds formed by the ligands with the central metal atom.

Q35. Give the geometry and magnetic character of $[NiCl_4]^{2-}$.

Ans. Tetrahedral, paramagnetic.

Q36. What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

Ans. Six.

Q37. What are t_{2g} and e_g orbitals?

Ans. In a free transition metal ion, all the five *d*-orbitals are degenerate, when it forms a complex, the degeneracy is split. In an octahedral field, three *d*-orbitals having lower energy are called t_{2g} orbitals and the remaining two *d*-orbitals of higher energy are called e_g orbitals.

Q38. What is crystal field splitting energy?

Ans. The difference of energy between two sets of *d*-orbitals after splitting is called crystal field splitting energy or crystal field stabilisation energy (CFSE).

Q39. Name a complex used in the treatment of cancer.

Ans. *cis*- Platin, $[Pt(NH_3)_2Cl_2]$.

Q40. Write the formula of potassium trioxalato aluminate(III).

Ans. $K_3[Al(C_2O_4)_3]$

Q41. What is the solution in which photographic film is washed? What reaction takes place?

Ans. $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Q42. What is the most common coordination numbers encountered in coordination compounds?

Ans. 4 and 6.

Q43. Write the IUPAC name of

$$[Co(NH_3)_3ONO]Cl_2$$

Ans. Hexaammine nitritocobalt (III) chloride.

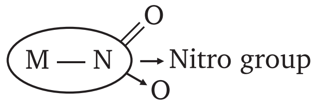
Q44. What type of hybrid orbital is associated with Ni atom in $[Ni(CN)_4]^{2-}$?

Ans. (*dsp*^{2})

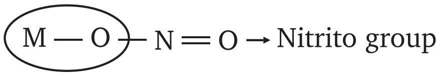
Q45. What are ambidentate ligands? Give two examples for each.

Ans. Ambidentate ligands are the ligands that can attach themselves to the central metal atom through two different atoms. For example:

(*a*)



(The donor atom is N)



(The donor atom is oxygen)

II. Short Answer Type Questions

(2 *or* 3 *Marks*)

Q1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $A_0 > P$.

(*i*) Draw the diagram showing *d* orbitals splitting during this complex formation.

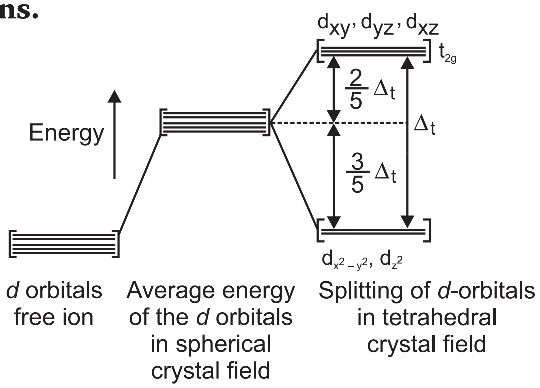
(*ii*) Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.

(*iii*) What type of hybridisation will M^{n+} ion have?

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

[*CBSE Sample Paper*-I, 2009]

Ans.



(*ii*) $t_{2g}^4 e_g^0$ (*iii*) d^2sp^3

(*iv*) Optical isomerism

Q2. (*a*) Give the IUPAC name of $[CrCl_2(H_2O)_4]Cl$.

(*b*) Give the number of unpaired electrons in the following complex ions: $[FeF_6]^{4-}$ and $[Fe(CN)_6]^{4-}$

(*c*) Name the isomerism exhibited by the following pair of coordination compounds.

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

Give one chemical test to distinguish between these two compounds.

[*CBSE Sample Paper* II 2009]

Ans. (*a*) Tetraaquadichloro chromium(III) chloride.

(*b*) $[FeF_6]^{4-}$ has four unpaired electrons as F^- is a weak field ligand.

$[Fe(CN)_6]^{4-}$ has no unpaired electrons because CN^- is a strong field ligand.

(*c*) Ionisation isomerism. On addition of dilute HCl followed by aqueous $BaCl_2$, $[Co(NH_3)_5Br]SO_4$ will give a white precipitate while the other coordination compound will not give any white precipitate.

Q3. Give the electronic configuration of

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

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

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

Ans. (*a*) In $[Ti(H_2O)_6]^{3+}$ ion

Oxidation state of Ti = + 3

There is only one electron in the *d*-orbital and its configuration is $t_{2g}{}^1\ e_g{}^0$

(*b*) Due to *d*–*d* transition, the configuration becomes $t_{2g}{}^0 e_g{}^1$.

(*c*) On heating $[Ti(H_2O)_6]^{3+}$ ion becomes colourless as there is no ligand (H_2O) left after heating. In the absence of ligand, crystal field splitting does not occur.

Q4. Give a suitable example for each, explain the following:

(*i*) Crystal field splitting.

(*ii*) Linkage isomerism.

(*iii*) Ambidentate ligand. [*AI* 2009]

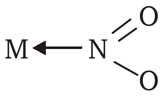
Ans. (*i*) In most of the transition metal complexes, either six or four ligands surround the metal/ion. It gives rise to octahedral and tetrahedral structures. In both the cases, the field produced by the ligands is not spherically symmetrical. As a result, *d*-orbitals are not equally affected by the field. It results in splitting of the *d*-orbital energies.

(*ii*) *Linkage isomerism*: It occurs in complexes when an ambidentate ligand occurs in the coordination sphere,

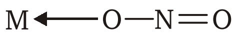
e.g., $[Co(NH_3)_5NO_2]^{2+}$ and
$[Co(NH_3)_5(–ONO)]^{2+}$

Another example is
$[Cr(H_2O)_5(SCN)]^{2+}$ and
$[Cr(H_2O)_5(NCS)]^{2+}$

(*iii*) *Ambidentate ligand*: Ligands which can ligate through two different atoms present in it are called ambidentate ligands, *e.g.* NO_2^-, SCN^-



Nitrito – N



Nitrito – O

Q5. Compare the following complexes with respect to structural shapes of complexes, magnetic behaviour and hybrid orbitals involved in the complexes.
$[Co(NH_3)_6]^{3+}$,$Cr[(NH_3)_6]^{3+}$,$[Ni(CO)_4]$
[At No: Co = 27, Cr = 24, Ni = 28].

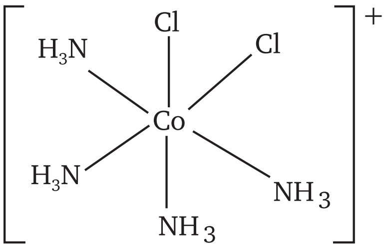
Ans.

Complexes	Magnetic behaviour	Hybridi-sation	Shape
(*i*) $[Co(NH_3)_6]^{3+}$	diamagnetic	d^2sp^3	Octahedral
(*ii*) $[Cr(NH_3)_6]^{3+}$	paramagnetic	d^2sp^3	Octahedral
(*iii*) $[Ni(CO)_4]$	diamagnetic	sp^3	Tetrahedral

Q6. (*a*) Draw the structure and write the hybridisation state of Co in *cis* – $[Co(NH_3)_4Cl_2]^+$

(*b*) Using the IUPAC norms name the following complex:
$[Co(NH_3)_4Cl(ONO)]Cl$
[*CBSE* 2008 *C*]

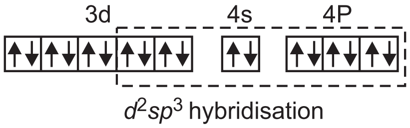
Ans. (*a*) Structure of *cis* $[Co(NH_3)_4Cl_2]^+$:



(*b*) *cis*-tetramminedichloro cobalt(III) ion.

Q7. Using the valence bond approach, deduce the shape and magnetic character of $[Co(NH_3)_6]^{3+}$ ion.
[Given Atomic No. of Co = 27]
[*CBSE* 2008]

Ans. Co (27) : $4s^2\ 3d^7$
Co^{3+} : $4s^03d^6$
$[Co(NH_3)_6]^{3+}$:



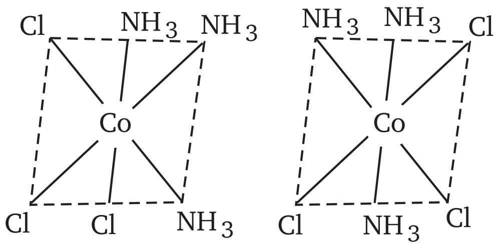
It has d^2sp^3 hybridisation, therefore, forms an inner orbital complex.
$[Co(NH_3)_6]^{3+}$ complex has octahedral geometry and it is diamagnetic because of the absence of unpaired electrons.

Q8. (*a*) What is the basis of formation of spectro-chemical series?

(*b*) Draw the structures of geometrical isomers of the following coordination complexes:
$[Co(NH_3)_3Cl_3]$ and $[CoCl_2(en)_2]^+$
[*AI* 2008]

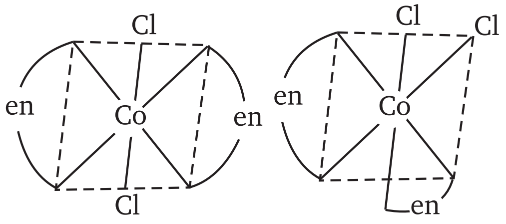
Ans. (*a*) *Spectrochemical series*: The arrangements of ligands in the order of their increasing field strength, *i.e.* increasing crystal field splitting energy (CFSE) value is called spectrochemical series.
Crystal field splitting energy is the basis of formation of the spectrochemical series.

(*b*)



cis-isomer trans-isomer

(*ii*) $[CoCl_2(en)_2]^+$ ions exists in two geometrical isomers as shown below:



trans-form *cis*-form

Q9. (*a*) What is a ligand? Give an example of a bidentate ligand.

(*b*) Explain how the two complexes of nickel: $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures but do not have their different magnetic behaviour. (Ni = 28).

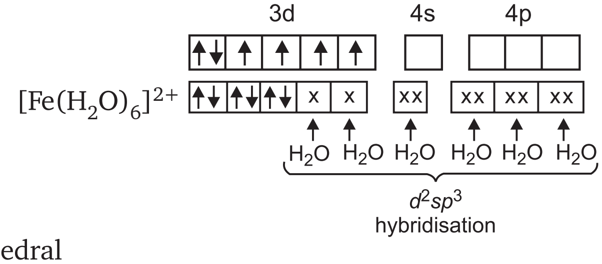
Ans. (*a*) *Ligands:* The ions or molecules bound to the central atom ion in the coordination entity are called ligands. Example of bidentate ligand:

$H_2NCH_2CH_2NH_2$
(ethylene diammine)

(*b*) $[Ni(CN)_4]^{2-}$ is a square planar complex, which is diamagnetic as no unpaired electron is present.
$[Ni(CO)_4]$ is a tetrahedral complex, which is diamagnetic due to the absence of unpaired electrons.

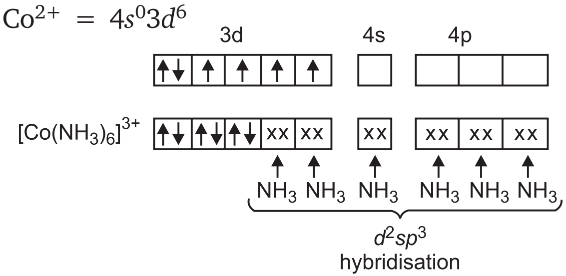
Q10. Describe the type of hybridisation shape and magnetic property of any two of the following complex ions:
(*i*) $[Fe(H_2O)_6]^{2+}$ (*ii*) $[Co(NH_3)_6]^{3+}$
(*iii*) $[NiCl_4]^{2-}$
[At. No., Fe = 26, Co = 27, Ni = 28] [*CBSE* 2007]

Ans. (*i*) Fe(26) E.C.: [Ar] $4s^2\ 3d^6$
E.C. of $Fe^{2+} = 4s^0 3d^6$



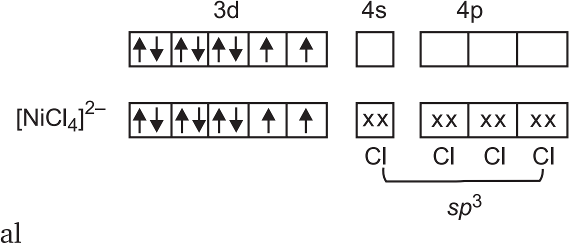
Shape = octahedral
Magnetic property = diamagnetic

(*ii*) $[Co(NH_3)_6]^{3+}$
Co(27): E.C. = $4s^2 3d^7$
Configuration of $Co^{2+} = 4s^0 3d^6$



Shape – octahedral
Magnetic property – diamagnetic

(*iii*) $[NiCl_4]^{2-}$
Ni(28): E.C. = $[Ar]4s^2 3d^8$
Configuration of $Ni^{2+} = 4s^0\ 3d^8$



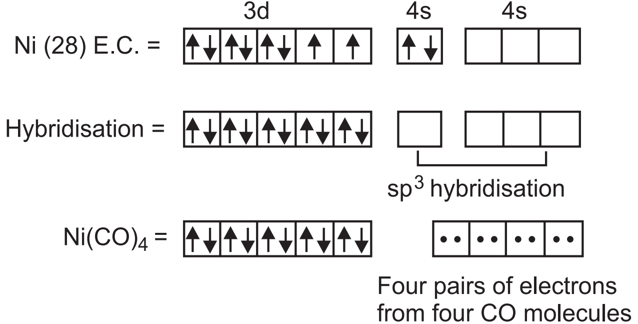
Shape – tetrahedral
Magnetic property = paramagnetic

Q11. (*a*) Using valence bond theory, predict the shape and magnetic character of $[Ni(CO)_4]$·[Ni = 28].

(*b*) Give one example of applications of coordination compounds in medicines.

[*AI CBSE* 2006]

Ans. (*a*) Oxidation state of Ni in $Ni(CO)_4$ is zero.



Shape – Tetrahedral
hydridisation – sp^3
Magnetic character – diamagnetic

(*b*) The platinum complex cis–platin $[Pt(NH_3)Cl_2]$ is used in the treatment of cancer.

Q12. (*a*) What are ambidentate ligands? Give an example.

(*b*) Write the IUPAC names of the following:

(*i*) $K_3[Fe(C_2O_4)_3]$ (*ii*) $Pt[(NH_3)_6]Cl_4$

(*c*) Draw the structure of cis isomer of $[Co(NH_3)_4Cl_2]^+$. [*AI CBSE* 2005]

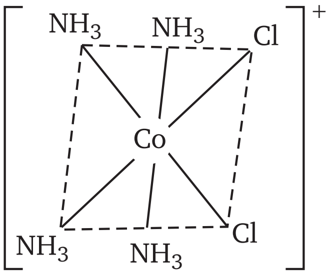
Ans. (*a*) **Ambidentate ligands:** Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligands, e.g.,

NO_2^-, $SCN^-M \leftarrow SCN$ $M \leftarrow NCS$
Thiocyanato Isothiocyanato

(*b*) (*i*) Potassium Trioxalatoferrate(III)

(*ii*) Hexaamine platinum(IV) chloride.

(*c*) *cis*-$[Co(NH_3)_4Cl_2]^+$



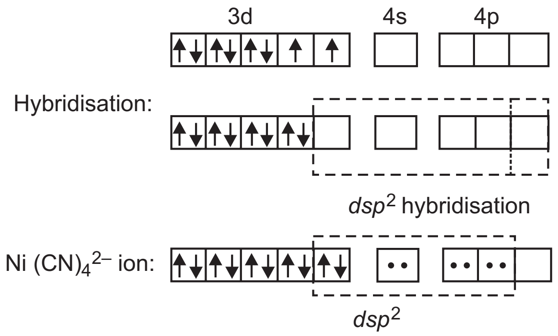
Q13. (*a*) Give the names of two complexes which are used in medicines.

(*b*) Using valence bond theory of complexes explain the geometry and magnetic nature of $[Ni(CN)_4]^{2-}$, (At. No. of Ni = 28) [*CBSE* 2005]

Ans. (*a*) (*i*) EDTA is used in the treatment of lead poisoning.

(*ii*) $[Pt(NH_3)_2Cl_2]$ known as cis platin is used as an anti tumour agent in the treatment of cancer.

(*b*) Ni atom (Z = 28)
E.C. of Ni = [Ar] $4s^2 3d^8$
E.C. of Ni^{2+} = [Ar] $4s^0 3d^8$



It is diamagnetic, due to the absence of unpaired electrons.
Shape – Square planar.

Q14. (*a*) Give the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$

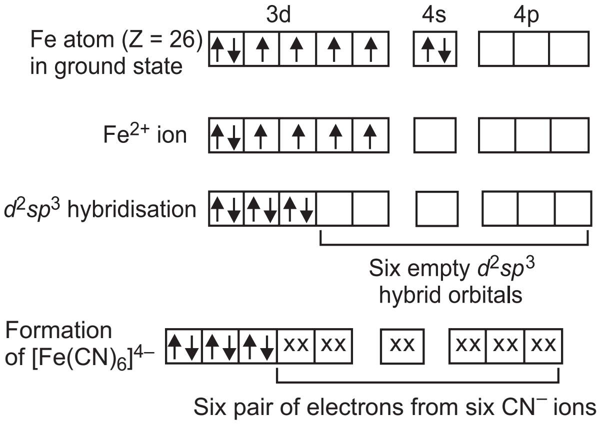
(*b*) Compare the magnetic behaviour of the complex entities $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ (Fe = 26) [*CBSE* 2002]

Ans. (*a*) Diamminechloro (methylamine) platinum (II) chloride.

(*b*) Oxidation state of Fe in $[Fe(CN)_6]^{4-}$

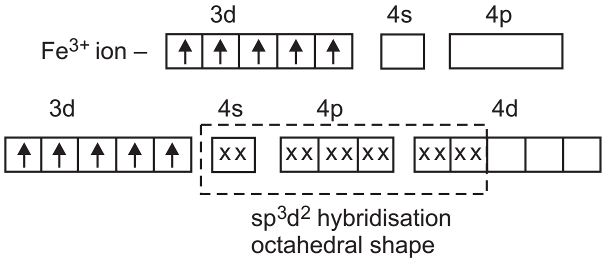
O.S. of Fe = +2

We have



Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

$[FeF_6]^{3-}$ ion



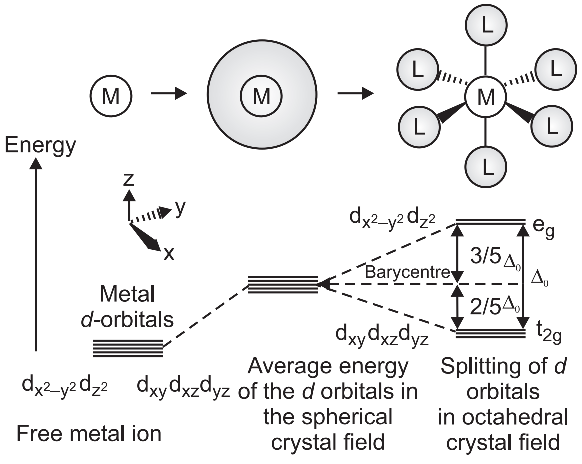
F^- is a weak field ligand, so it does not cause pairing of electrons.

Complex ion contains five unpaired electrons and is highly paramagnetic in nature.

Q15. Draw a figure to show splitting of degenerate *d* orbitals in an octahedral crystal field. How does the magnitude of Δ_0, decides the actual configuration of *d* orbitals in a complex entity?

Ans. (*i*) If $\Delta_0 < P$ the fourth electron enters one of the e_g orbital, giving the configuration $t_{2g}^3 e_g^1$.

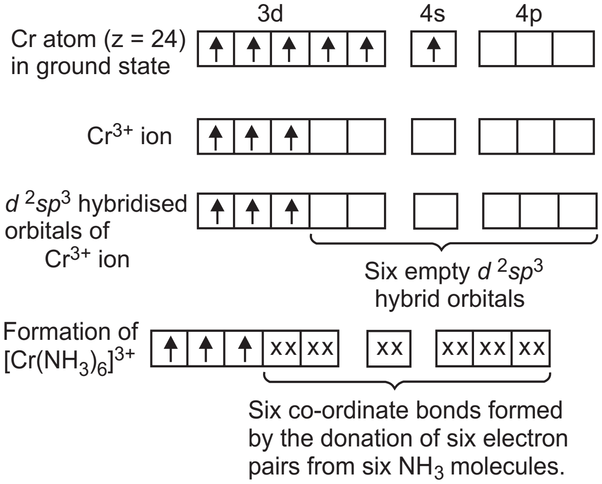
(*ii*) If $\Delta_0 > P$. It becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with the configuration $t_{2g}^4 e_g^0$.



Q16. Using the valence bond approach, deduce the shape and magnetic behaviour of $[Cr(NH_3)_6]^{3+}$ ion. [At no. of Cr = 24]. [*Foreign* 2003]

Ans. Cr(24): [Ar] $4s^1 3d^5$

Cr^{3+}(24): [Ar] $4s^0 3d^3$



The resulting complex $[Cr(NH_3)_6]^{3+}$ involving d^2sp^3 hybridisation and is thus octahedral.

The presence of an unpaired electron shows that it is paramagnetic in nature.

Q17. How is magnitude of Δ_0 affected by (*i*) nature of ligand, (*ii*) oxidation state of metal ion. [*CBSE* 2004]

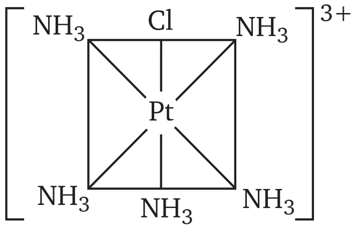
Ans. (*i*) Greater the strength of the ligand, greater is the value of Δ_0.

(*ii*) Higher the ionic charge on the central metal ion, greater will be the value of Δ_0.

Q18. Write the IUPAC name and draw the structure of coordination entities of $[PtCl(NH_3)_5]Cl_3$. [*CBSE* 2004]

Ans. **IUPAC name.** Pentaamminechlorido platinum (IV) chloride.

It has octahedral structure.



Q19. Using the valence bond approach, deduce the shape and magnetic character of $[Cr(CO)_6]$ [At. No. of Cr = 24] [*CBSE* 2003]

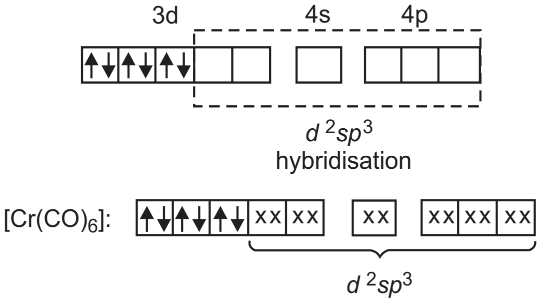
Ans. Cr(24)

Electronic configuration – [Ar] $4s^1 3d^5$

Oxidation state of Cr = 0

In $[Cr(CO)_6]$, Cr has the electronic configuration: [Ar] $4s^0 3d^5$

CO will cause pairing of electrons as it is a strong field ligand.



Shape – Octahedral

Magnetic character – Diamagnetic

Q20. Mention the applications of coordination compounds in the following areas giving an example of each:

(*a*) *Analytical chemistry*

(*b*) *Extraction of metals*

Ans. (*a*) **Analytical chemistry:** (*i*) EDTA is used for the estimation of Ca^{2+} and Mg^{2+} ions in hard water.

(*b*) **Extraction of metals:** (*i*) Silver and gold are extracted by treating zinc metal with their cyanide complexes.

Q21. Briefly describe the nature of bonding in metal carbonyls.

Ans. The metal-carbon bond in metal carbonyls possesses both *s*&*p* character. The M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant d-orbital of the metal. M–C π bond is formed by the donation of a pair of electrons from a filled *d*-orbital of the metal into the vacant antibonding, π^* orbital of carbon monoxide.

Q22. What is meant by hexadentate ligand? Give one example. How is such ligand useful for measuring hardness of water.

Ans. Hexadentate ligand is a ligand which has 6 donor atoms. *e.g.*, EDTA.
EDTA forms complex with Ca^{2+} and Mg^{2+} ions, therefore it is used for estimating the hardness of water.

Q23. Explain why a chelating complex is more stable than a non-chelated complex.

Ans. Chelating complex is more stable than a non-chelated complex because there is strong forces of attraction between the metal cation and polydentate ligand in case of a chelating ligand as compared to monodentate ligand in case of non-chelated ligand.

Q24. Write the formulae of the following complexes:

(*i*) Pentaamminechloro cobalt(III) ion
(*ii*) Lithium tetrahydroaluminate(III)

Ans. (*i*) $[Co(NH_3)_5Cl]^{2+}$ (*ii*) $Li\ [AlH_4]$

Q25. Define coordination number. What is the coordination number of central atom in

(*i*) $[Co(NH_3)_5Cl]Cl_2$ (*ii*) $K_2[FeCl_4]$

Ans. It is the total number of co-ordinate bonds with which the central metal atom is linked to the ligands in the complex.

(*i*) Coordination number of Co = 6
(*ii*) Coordination number of Fe = 4

Q26. Square planar complexes with a coordination number 4 exhibits geometrical isomerism whereas tetrahedral complexes do not, why?

Ans. The tetrahedral complexes do not show geometrical isomerism because the relative positions of the atoms with respect to each other will be the same. The square planar complexes on the other hand show geometrical isomerism because if same kind of ligands occupy positions adjacent to each other it is called *cis*-form and if these are opposite to each other it is called the *trans*-form.

Q27. Write the chemical formulae of the following complexes:

(*i*) Hexaammine platinum(IV) chloride.
(*ii*) Tetraamminedichloro cobalt(III) ion.

Ans. (*i*) $Pt[(NH_3)_6]Cl_4$
(*ii*) $[CoCl_2(NH_3)_4]^+$

Q28. (*a*) Name two main factors that favours a metal ions forming complex.

(*b*) Give an example of an industrial application of coordination complexes.

(*c*) Write the IUPAC name of $[Co(en)_2Cl(ONO)]^+$

Ans. (*a*)(*i*) Smaller size of cation and higher charge.

(*ii*) Presence of vacant *d*-orbitals.

(*b*) Silver and gold are extracted by treating zinc with their cyanide complexes. For e.g., $K[Ag(CN)_2]$ is used for electroplating of silver, $K[Au(CN)_2]$ is used for gold plating.

(*c*) Chloridobis(ethane-1, 2-diamine) nitro cobalt(III) ion.

Q29. (*a*) A coordination compound has the formula $CoCl_34NH_3$. It does not liberate ammonia but forms a precipitate with $AgNO_3$. Write the structure and IUPAC name of the complex compound.

(*b*) Name a ligand which is bidentate and give an example of the complex formed by this ligand. [*CBSE* 2003 *C*]

Ans. (*a*) $[Co(NH_3)_4Cl_2]Cl$

Its IUPAC name — tetraamminechloro cobalt(III) chloride.

(*b*) Ethylene diamine(*en*) is a bidentate ligand, for example $[Co(en)_3]^{3+}$. Its IUPAC name is tris(ethylene diamine) cobalt(III) ion.

Q30. How the given factors affect the stability of complex?

(*i*) Size of cation

(*ii*) Charge on cation

(*iii*) Nature of ligand?

Explain with the help of one example in each case.

Ans. (*i*) Smaller the size of cation, greater will be the stability of complex. For example, Fe^{3+} forms more stable complexes than Fe^{2+} ion.

(*ii*) Greater the charge on the central metal ion, more stable will be the complex. For example Pt^{4+} forms more stable complex than Pt^{2+} ion.

(*iii*) Stronger the ligand, more stable will be the complex formed. For example CN^- forms more stable complex than NH_3.

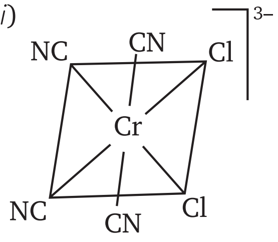
Q31. Draw the structures of the following:

(*i*) *cis*-dichlorotetracyano chromate(III)

(*ii*) pentaamminethiocyanato cobalt (III)

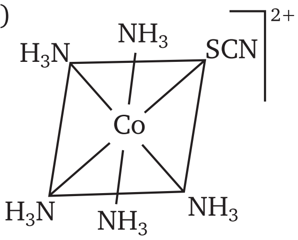
(*iii*) Hexamethyldialuminium. [*AI* 2006 *C*]

Ans. (*i*)

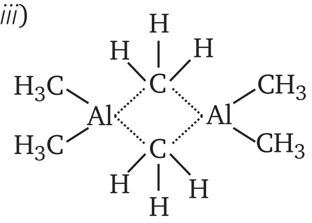


cis-isomer

(*ii*)

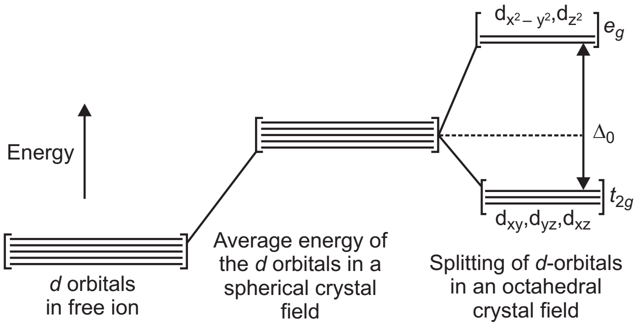


(*iii*)



Q32. Draw a sketch to show the splitting of *d*-orbitals in an octahedral crystal field. State for a d^6 ion, how the actual configuration of the splitted d-orbitals in an octahedral crystal field is decided by the relative values of Δ_0 and P. [*CBSE* 2005]

Ans.



d-orbital splitting in an octahedral crystal field

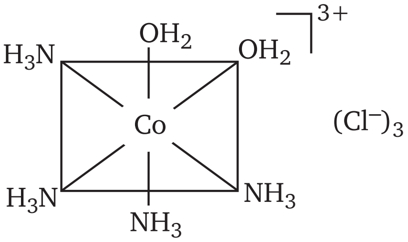
For a d^6 ion, the actual configuration of the splitting of d-orbitals in an octahedral field takes place as follows:

(*i*) If $\Delta_0 < P$, it is a weak field and high spin complexes are formed. The fourth electrons enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g^1$.

(*ii*) If $\Delta_0 > P$, then it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4\ e_g^0$ and low spin complexes are formed.

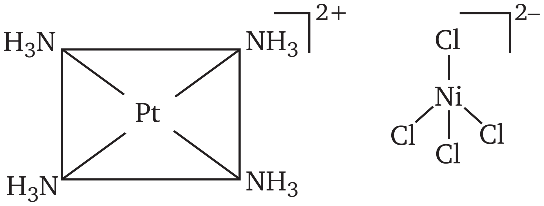
Q33. Write the name and draw the structure of each of the following complex compounds:
(*i*) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (*ii*) $[Pt(NH_3)_4][NiCl_4]$ [*CBSE* 2007]

Ans. (*i*)



Tetraamminediaqua cobalt(III) chloride

(*ii*)



Tetraammineplatinum(II) tetrachloronickelate(II)

Q34. (*a*) Write the IUPAC name of the ionisation isomer of $[Ni(NH_3)_5Cl]NO_3$.

(*b*) How are coordination compounds useful in biological processes? Give two uses. [*AI CBSE* 2004 *C*]

Ans. (*a*) Pentaamminechlorido nickel(II) nitrate.

(*b*) (*i*) Haemoglobin is a complex compound of iron, which acts as oxygen carrier in human body. Chlorophyll is a complex of Mg and it helps in photosynthesis.

Q35. (*a*) Write the formulae of the following complexes:

(*i*) Hexaammine platinum(IV) chloride.

(*ii*) Dichlorotetrammine cobalt(III) ion

(*b*) The values of dissociation constant of $[Cu(NH_3)_4]^{2+}$ and $[Co(NH_3)_6]^{3+}$ are 1.0×10^{-12} and 6.2×10^{-36} respectively. Which complex would be more stable and why? [*CBSE* 2004 *C*]

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

(*ii*) $[CoCl_2(NH_3)_4]^+$

(*b*) $[Co(NH_3)_6]^{3+}$ is more stable because it has low value of dissociation constant, therefore, will have high stability constant.

Q36. How would you account for the following?

(*a*) $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

(*b*) $[Fe(CN)_6]^3$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

(*c*) $Ni(CO)_4$ possess tetrahedral geometry while $[Pt(NH_3)_2Cl_2]$ is square planar and diamagnetic.

Ans. (*a*) $[Ti(H_2O)_6]^{3+}$ is coloured because it has unpaired electrons and it can undergo *d–d* transition.

$[Sc(H_2O)_6]^{3+}$ is colourless because it does not have any unpaired electron, that is does not undergo *d–d* transition.

(*b*) $[Fe(CN)_6]^{3-}$ is weakly paramagnetic because of the presence of one unpaired electron.

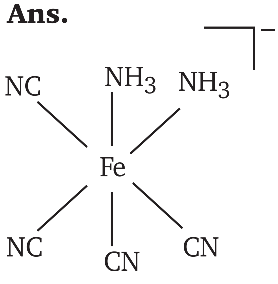
$[Fe(CN)_6]^{4-}$ is diamagnetic due to the absence of unpaired electrons.

(*c*) $Ni(CO)_4$ has sp^3 hybridisation, therefore, the shape is tetrahedral.

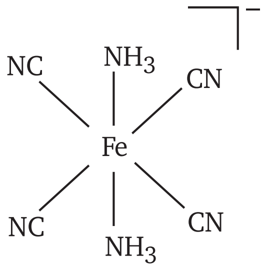
$[Pt(NH_3)_2Cl_2]$ has dsp^2 hybridisation, therefore it is square planar and due to absence of unpaired electron it is diamagnetic.

Q37. Draw the structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$.

Ans.



(*cis*)



(*trans*)

Q38. Write the formulae for the following coordination compounds:

(*i*) Potassium tetrahydroxozincate(II)

(*ii*) Potassium trioxalatoaluminate(III)

(*iii*) Dichloridobis cobalt(III) (ethane–1, 2 diamine)

Ans. (*i*) $K_2[Zn(OH)_4]$ (*ii*) $K_3[Al(C_2O_4)_3]$

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

Q39. Write the IUPAC names of the following coordination compounds:

(*a*) $K_3[Cr(C_2O_4)_3]$ (*b*) $Hg[Co(SCN)_4]$

(*c*) $[Co(NH_3)_5(CO_3)]Cl$

Ans. (*a*) Potassium trioxalato chromate(III)

(*b*) Mercuric tetrathiocyanato cobaltate(III)

(*c*) Pentaamminecarbonato cobalt(III) chloride.

Q40. How is stability of coordination compounds determined in an aqueous solution?

Ans. The stability of a coordination compound is measured in terms of stability constant.

Thus if we have a reaction of the type

$$M + 4L \rightleftharpoons ML_4, \text{ then}$$

$$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

Stability constant, will give the measurement of the stability of the complex.

Q41. (*i*) Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$.

(*ii*) What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (en=ethane–1, 2–diamine)

(*iii*) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. nos.: Cr = 24, Co = 27, Ni = 28) [*CBSE* 2016]

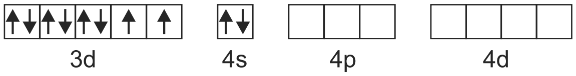
Ans. (*i*) IUPAC name of the complex: $[Cr(NH_3)_4Cl_2]Cl$ is Tetraamminedichlorochromium (III) ions.

(*ii*) Optical isomerism is exhibited by the complex: $[Co(en)_3]^{3+}$.

(*iii*) $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ both are tetrahedral. But their magnetic characters are different. This is due to difference in the nature of ligands attached to Ni^{2+}–metal ion. Ni^{2+} = [Ar] $4s^o3dB$

Ni^{2+} has 2 unpaired electrons, hence this complex is paramagnetic.

In $Ni(CO)_4$, Ni is in zero oxidation state, *i.e.* it has a configuration of $3d^8\ 4s^2$.
Ni = [Ar] $4s^2\ 3d^8$



Q42. (*i*) Write down the IUPAC name of the following complex:

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

(*ii*) Write the formula for the following complex: Potassium tetracyanidonickelate(II).

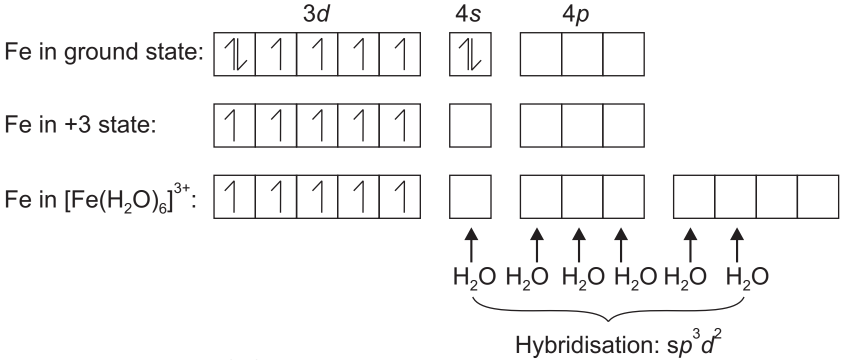
Ans. (*i*) $[Co(NH_3)_5(NO_2)(NO_3)]_2$
IUPAC name: Pentaamminenitrocobalt(III) nitrate.

(*ii*) Potassium tetracyanidonickelate(II).
Formula of the complex: $K_2[Ni(CN)_4]$

Q43. (*a*) For the complex $[Fe(H_2O)_6]^{3+}$, write the type of hydridisation, magnetic character and spin of the complex. (At, number : Fe = 26)

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

Ans.



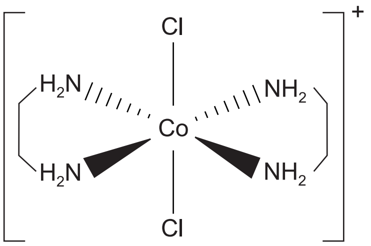
Hybridisation : sp^3d^2
Magnetic character : Paramagnetic
Spin of the complex : High spin

Q44. (*i*) Draw the geometrical isomers of the complex: $[Co(en)_2Cl_2]^+$.

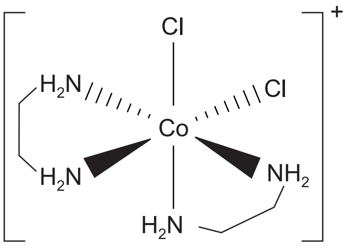
(*ii*) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_0 > P$.

(*iii*) $[NiCl_4]^{2-}$ is paramagnetic, while $[Ni(CO)_4]$ is diamagnetic, though both are tetrahedral. Why? (Atomic number of Ni = 28)

Ans. (*i*) Geometrical isomers of $[Co(en)_2Cl_2]^+$:



trans–$[CoCl_2(en)_2]^+$



cis–$[CoCl_2(en)_2]^+$

(*ii*) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4\ e_g^0$.

(*iii*) In $[NiCl_4]^{2-}$, Ni is in the +2 oxidation state. Cl^- is a ligand which is a weak field ligand which does not cause pairing of unpaired 3*d* electrons. Hence, it is paramagnetic.

In $[Ni(CO)_4]$, Ni has zero oxidation state. CO is a strong field ligand, which causes pairing of unpaired 3*d* electrons. No unpaired electrons are present in this case. So, it is diamagnetic.

III. Long Answer Type Questions

(5 *Marks*)

Q1. What are the shortcomings of valence bond theory for bonding in complexes? Briefly describe the crystal field theory.

Ans. (*i*) A number of assumptions are made.

(*ii*) The theory does not explain the colour and spectra of the complexes.

(*iii*) It does not make exact predictions regarding the tetrahedral and square planar structures of four coordinate complexes.

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

Crystal field theory: CFT of coordination compounds is based on the effect of different crystal field (provided by the ligands taken as point charges) on the degeneracy of *d*-orbitals energies of the central metal atom/ion. The splitting of *d*-orbitals provide different electronic arrangements in the strong and weak crystal field.

Q2. Briefly describe the importance of coordination compounds in:

(*i*) Qualitative analysis

(*ii*) Extraction of metals

(*iii*) Biological systems

Ans. (*i*) **Qualitative analysis**

- EDTA is used for the estimation of Ca^{2+} and Mg^{2+} ions in hard water.
- Ni^{2+} ion is tested and estimated by DMG (dimethyl glyoxime).

(*ii*) **Extraction of metals**

- Silver and gold are extracted by treating zinc with their cyanide complexes.
- Bauxite is purified by forming complexes with NaOH.
- Impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

(*iii*) **Biological systems**

- The pigment responsible for photosynthesis, i.e. chlorophyll is a coordination compound of Mg.
- Haemoglobin is a coordination compound of iron.
- Vitamin B_{12}, cyanocobalamine, the antipernicious anaemia factor is a coordination compound of cobalt.

Q3. (*a*) Draw all the possible isomers having the formula — $Cr[(NH_3)_4Cl_2]^+$

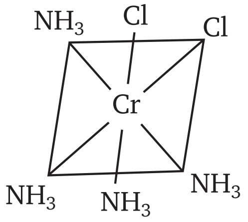
(*b*) Illustrate the following with an example:

(*i*) Linkage isomerism

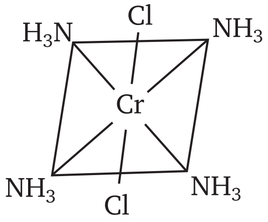
(*ii*) Coordination isomerism.

(*c*) Why is $[NiCl_4]^{2-}$ is paramagnetic (Ni = 28)?

Ans. (*a*)



cis-(violet)



trans-(green)

(*b*) (*i*) *Linkage isomerism*: The isomerism in which a ligand can form linkage with metal through different atoms, e.g., nitro group ($-NO_2$) can link to metal either through nitrogen atom or through oxygen atom, e.g.

$[Co(NH_3)_5ONO]Cl_2$

IUPAC name: Pentaamminenitrito–o–cobalt(III) chloride.

$[Co(NH_3)_5NO_2]Cl_2$

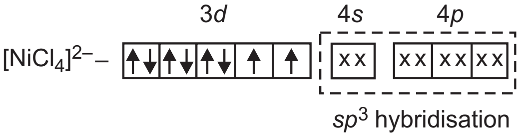
IUPAC name: Pentaamminenitrito-N-cobalt(III) chloride.

(*ii*) *Coordination isomerism*: This type of isomerism occurs when both the cations and anions are complexes and they differ in the coordination of ligands.

e.g. $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$ are coordination isomers.

(*c*) Ni^{2+} (28) = $4s^0\ 3d^8$,

Cl^- is a weak ligand and it does not cause pairing of electrons.



Due to the presence of 2 unpaired electrons, it is paramagnetic in nature.

Q4. What are the two types of organometallic compounds? How are these classified? Give examples.

Ans. An organometallic compound is a compound which contains at least one of the following bonds.

Metal – Carbon bond

Metalloid (B, Si, As, Te) – Carbon bond.

Classification of Organometallic Compounds:

Based on the nature of metal-carbon bond they are broadly classified into two types as follows:

(*i*) *σ-bonded organometallic compounds.* In these compounds, the bonding consists of localised carbon-metal σ bonds formed by sharing of an electron pair.

Example: Grignard reagents

R – Mg – X

(Where R = alkyl group, aryl group)

(X = halogen)

(*ii*) *π bonded organometallic compounds:* Transition metals form organometallic compounds of this type. For example: $K[PtCl_3(\eta^2 - C_2H_4)]$, Zeise salt.

IV. Value-Based Questions

Q1. $CoCl_3.4NH_3$ precipitates silver chloride with $AgNO_3(aq)$ reacting in equimolar amounts, though it has three moles of chloride ions per mole. Further the compound was exhibiting different colours when prepared at different times—sometimes green and some–times violet.

(*a*) Give IUPAC name of the compound.

(*b*) Why does it exhibit different colours?

(*c*) What are the values that can be attached with the observation?

Ans. (*a*) Tetraaminedichlorido cobalt(III) chloride.

(*b*) The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to the different coordination numbers.

(*c*) Scientific attitude and Critical thinking.

Q2. Lots of children working in a lead industry were rescued by NGO's activists. The children sent to the hospital and found to be suffering from a disease caused due to excess exposure to lead called lead poisoning.

(*i*) Name the ligand (compound) used for treatment of lead poisoning.

(*ii*) During this rescue operation which values are shown by NGO's activists.

Ans. (*i*) EDTA (ethylenediamine tetraacetic acid) is used for the treatment of lead poisoning.

(*ii*) Social responsibility and Self awareness.

Q3. Cancer is not a communicable disease. It occurs due to unlimited growth of body cells leading to tumours. We should shake hand, eat together with people suffering from cancer. These activities boost up the confidence in them for living.

(*i*) Write the name of coordination compound used as a chemotherapeutic agent to curb the growth of tumours.

(*ii*) By showing such attitude to cancer patients, mention the values reflected by us.

Ans. (*i*) *cis*-platin $[Pt(NH_3]_2Cl_2]$

(*ii*) Critical thinking and Self awareness.

V. HOTS Questions

Q1. $CuSO_4$ on mixing with NH_3(1:4 ratio) does not give test for Cu^{2+} ions but gives test for SO_4^{2-} ions. Why?

Ans. It is because when NH_3 coordinates to Cu^{2+} ions and it forms the complex $[Cu(NH_3)_4]SO_4$. Copper ions are present in coordination sphere, therefore, they are non-ionisable whereas SO_4^{2-} ions are counter ions which are ionisable.

Q2. Give a chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. What kind of isomerism do they exhibit?

Ans.

(*i*) $[Co(NH_3)_5Br]SO_4 + Ba^{2+} \longrightarrow \underset{\text{White ppt}}{BaSO_4}$

$[Co(NH_3)_5Br]SO_4 + Ag^{+} \longrightarrow \text{No ppt}$

(*ii*) $[Co(NH_3)_5SO_4]Br + Ba_{2+} \longrightarrow \text{No ppt}$

$[Co(NH_3)_5SO_4]Br + Ag^{+} \longrightarrow AgBr$

Yellow ppt White ppt.

They exhibit ionisation isomerism.

Q3. Name the metal present in

(*i*) Chlorophyll

(*ii*) Haemoglobin

(*iii*) Vitamin B_{12}

(*iv*) Cis-platin

Ans. (*i*) Mg (*ii*) Fe

(*iii*) Co (*iv*) Pt

Q4. (*i*) Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$.

(*ii*) What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (en = ethane-1,2-diamine)

(*iii*) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic?
(At. no.: Ni = 28)

Ans. (*i*) The IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$ is Tetraamminedichlorochromium(III) chloride.

(*ii*) The complex $[Co(en)_3]^{3+}$ exhibits optical isomerism.

(*iii*) In $[NiCl_4]^{2-}$, the oxidation state of Ni is +2. Chloride is a weak field ligand and it does not cause pairing of electrons, against the Hund's rule of maximum multiplicity. As a result, two unpaired electrons are present in the valence *d*-orbitals of Ni which impart paramagnetic character to the complex. On the other hand, carbonyl is a strong field ligand and it causes pairing up of electrons against the Hund's rule of maximum multiplicity. As a result, no unpaired electrons are present and hence the complex is diamagnetic in nature.

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