CHAPTER / 13

Coordination Compounds

Topics *Covered*

Coordination Compounds: Their Nomenclature and Isomerism
- Terminology Related to Coordination Compounds
- Werner's Coordination Theory
- Isomerism in Coordination Compounds

Bonding in Coordination Compounds, Its Importance and Organometallic Compounds
- Bonding in Coordination Compounds
- Bonding in Metal Carbonyls
- Importance of Coordination Compounds
- Organometallic Compounds

TOPIC ~01 Coordination Compounds: Their Nomenclature and Isomerism

The addition compounds which do not dissociate and retain their identity in solution are known as coordination compounds. e.g. $K_2[PtCl_6]$, $K_4[Fe(CN)_6]$.

These are the complex compounds formed by the transition metals in which the metal atoms are bonded to the number of anions or neutral molecules through the coordinate bonds.

Difference between Double Salts and Coordination Compounds

Double salts	Coordination compounds
They lose their identity in solution.	They don't completely lose their identity in solution.
They exist only in solid state and dissociate into ions in aqueous solution or in other solvent.	They exist in solid state as well as ions when dissolved in water or any other solvent. They don't dissociate into simple ions completely.
Their properties are essentially the same as those of its constituent compounds.	Their properties are different from their constituents.
In a double salt, metal ions exhibit their normal valency.	In a complex compound or coordination compound, metal ion satisfies its two types of valencies called primary and secondary valencies.
e.g. Mohr's salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$, potash alum $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$, etc.	e.g. $[Ni(NH_3)_6]Cl_2$, $K_4[Fe(CN)_6]$, etc.

Terminology Related to Coordination Compounds

1. Coordination Complex and Complex Ions

Two stable chemical species (atoms, molecules, compounds, ions, etc.) combine to form a compound known as **coordination complex**.

The compounds retain its identity both in the solid as well as in dissolved state.

A complex ion is an electrically charged ion that contains a central metal atom or ions surrounded by a group of ions or neutral molecule.

e.g. $CuSO_4$ and NH_3 combine to form coordination complex $[Cu(NH_3)_4]SO_4$. For given coordination complex in water solution is called complex ion.

$[Cu(NH_3)_4]$ SO_4 contains $[Cu(NH_3)_4]^{2+}$ ion.

2. Coordination Entity

Coordination entity constitutes a central metal atom or ion attached to a fixed number of ions or molecules.
It may be positive, negative or neutral.

e.g. $[CoCl_3(NH_3)_3]$ is a coordination entity in which cobalt ion is surrounded by three NH_3 molecules and three Cl^- ions.

3. Central Metal Atom or Ion

In a coordination entity, the metal atom or ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it is called central metal atom or ions.

4. Ligands

The donor atoms, ions or molecules which donate a pair of electrons to the central metal atom or ion and form coordinate bonds are called ligands.

5. Coordination Number (CN)

The number of ligand donor atoms to which the metal is directly bonded is called coordination number.

In case of bidentate ligands, the number of donor atoms will be double e.g. in $[Cu(NH_3)_4]^{2+}$ and $[Fe(C_2O_4)_3]^{4-}$, coordination numbers of Cu and Fe are 4 and 6 respectively.

6. Coordination Sphere and Counter Ions

The central atom/ion and the ligands attached to it are enclosed in the square brackets are collectively known as **coordination sphere**.
The ionisable groups written outside the brackets are called **counter ions**. For example in $K_2[PtCl_6]$, $[PtCl_6]^{2-}$ is the coordination sphere and K^+ ions are the counter ions.

Werner's Coordination Theory

Alfred Werner, first to formulate his ideas about the structures of coordination compounds in 1898. He proposed the concept of a **primary valence** and a **secondary valence** for a metal ion.

The main postulates of Werner's theory are:

(i) Metal has two types of linkages (valencies) primary and secondary in a complex.

(ii) **Primary valency** is equal to the oxidation number of central ion. It is non-directional and ionisable. It is satisfied by negative ions, e.g. In $CrCl_3$, the primary valency is three.

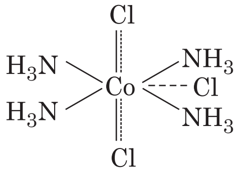
(iii) **Secondary valency** is equal to the coordination number of central atom/ion. It is directional and non-ionisable. It is satisfied either by neutral molecules or negative ions and is always fixed for a metal. Each metal ion has a fixed number of secondary valency.

e.g. In $[Co(NH_3)_6]Cl_3$, three Cl^- ions are held by primary valency and six NH_3 groups are held by secondary valency.

They are directed in space and account for shape or structure of a complex ion, e.g. $[Co(NH_3)_6]^{3+}$ has octahedral shape.

(iv) The ions or groups (ligands) are arranged around the central atom/ions in a spatial arrangement called as coordination pohyhedra.

e.g. Structure of $[CoCl_2(NH_3)_4]^+Cl^-$ is as follows:



Structure of $[CoCl_2(NH_3)_4]Cl$

.... Primary valency

_____ Secondary valency

Rules for Writing Formula of Mononuclear Coordination Compounds

(i) Formula of complex cation (simple or complex) is written first.

(ii) Coordination entity is enclosed in square brackets.

(iii) In coordination sphere, central atom is written first, followed by ligands in alphabetical order of their names.

(iv) In abbreviated ligands like en, ox, first letter of abbreviation is considered.

(v) When ligands are polyatomic, their formulas are enclosed in parenthesis.

(vi) There should be no space between the ligands and the metal within a coordination sphere.

(vii) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign.

(viii) The charge of the cation is balanced by the charge on the anion.

Rules of Naming of Mononuclear Coordination Compounds

(i) Complex cation is named first followed by anion. (if present)

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion.

(iii) Names of the anionic ligands end in $-o$. e.g. chloro, cyano etc. Neutral ligands have no special ending like NH_3(ammine), H_2O (aqua) and positive ligands end in - ium like NO^+ (nitrosonium).

(iv) Prefixes mono, di, tri etc. are used to indicate the number of individual ligands in coordination entity. When the names of the ligands includes a numerical prefix, then the terms, *bis*, *tris*, are used, the ligand to which they, refer being placed in parenthesis.

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. But if the complex ion is an anion, the name of the metal ends with the suffix '– *ate*'.

Isomerism in Coordination Compounds

This arises due to different structural arrangements (structural isomerism) or spatial arrangements (stereoisomerism) of compounds having same formula.

Structural Isomerism

1. Ionisation Isomerism

When the complexes with same composition give different ions in solution. e.g. $[Co(NH_3)_5 Br] SO_4$ and $[Co(NH_3)_5 SO_4] Br$.

2. Solvate/ Hydrate Isomerism

When complex differ in the number of water (Solvent) molecules present as ligand,

e.g. $[Cr (H_2O)_6] Cl_3$, $[Cr(H_2O)_5Cl] Cl_2 \cdot H_2O$ and $[Cr (H_2O)_4Cl_2]Cl \cdot 2H_2O$

3. Linkage Isomerism

When complexes differ only in the point of attachment of the ambidentate ligand with central metal atom. e.g. $[Co(NH_3)_5 (ONO)]^{2+}$ and $[Co (NH_3)_5 (NO_2)]^{2+}$

4. Coordination Isomerism

When the interchange of ligands take place between cationic and anionic entities of different metal ions present in a complex. e.g. $[Co (en)_3] [Cr (CN)_6]$ and $[Cr (en)_3] [Co(CN)_6]$.

Stereoisomerism

1. Geometrical Isomerism

When similar groups are present in adjacent position, it is *cis*. When they are present in opposite position it is *trans*. It occurs in square planar compound of type $[MA_2B_2]$, $[MA_2BC]$, $[M(AB)_2]$ [AB = unsymmetrical ligand] and octahedral complexes of type $[MA_4B_2]$, $[M(AA)_2B_2]$ or $[M(AA)_2 BC]$ [AA = symmetrical bidentate ligand] and $[MA_3B_3]$ shows *fac* and *mer* geometrical isomers.

2. Optical Isomerism

This is shown by complexes whose mirror images are non-superimposable. Such complexes are called optical isomers.

It is shown by octahedral complexes and exists in two forms *laevo* and *dextro*.

- The isomer which rotates the plane polarised light towards right is called *dextro* rotatory (d-)
- The other rotates towards left is called *laevo* - rotatory (l-).
- It is shown by the complexes of the type $[M(AA)_3]$, $[M(AA)_2B_2]$ [only *cis*- form shows optical isomerism but not *trans* form], $[M(AA)_2 AB]$ (only *cis* - form but not *trans* forms) and $M(AA)A_2B_2$. [AA = bidentate ligand like *en*, ox]

Tetrahedral complexes [MA_4 or MA_3B] do not show geometrical isomerism because the relative positions of unidentate ligands attached with central atom are the same with respect to each other.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 Write the IUPAC name of the following compounds.
(i) $[Co(NH_3)_6]Cl_3$ (ii) $Fe(CO)_5$ **[2018]**

Sol The IUPAC name of the following compounds is:
(i) $[Co(NH_3)_6]Cl_3$: Hexaaminecobalt(III)chloride
(ii) $Fe(CO)_5$: Pentacarbonyliron(0)

Q.2 Write the IUPAC name of $K_2[CrCO(CN)_5]$ **[2015]**

Sol The IUPAC name of $K_2[CrCO(CN)_4]$ is potassium carbonyl pentacyanidochromatate (III).

Q.3 The coordination number of cobalt in $[Co(NH_3)_3Cl_3]$ is **[2014]**
(a) 3 (b) 2 (c) 4 (d) 6

Sol (*d*) Coordination number is the total number of ligands that are directly attached to metal ion. The coordination number of Co in $[Co(NH_3)_3Cl_3]$ is 6

Q.4 Which of the following is the IUPAC name of $K_4[Fe(CN)_6]$? **[2014, 2012, 2009, 2008]**
(a) Potassium ferricyanide
(b) Potassium ferrocyanide
(c) Potassium hexacyanoferrate (III)
(d) Potassium hexacyanoferrate (II)

Sol (*d*) The IUPAC name of $K_4[Fe(CN)_6]$ is potassium hexacyanoferrate (II).

Q.5 Write the IUPAC name of $[Cr(NH_3)_6][Co(CN)_6]$. **[2012 Instant]**

Sol The IUPAC name of $[Cr(NH_3)_6][Co(CN)_6]$ is hexaaminechromium (III) hexacyanidocobalt (III).

Q.6 Write the IUPAC name of $Na[Al(OH)_4]$. **[2011]**

Sol The IUPAC name of $Na[Al(OH)_4]$ is sodium tetrahydroxyaluminate (III).

Q.7 To which isomers, the following compounds belong? **[2011]**
$[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$
(a) Geometrical isomerism (b) Linkage isomerism
(c) Ionisation isomerism (d) Ligand isomerism

Sol (*b*) $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$ compounds show linkage isomerism as it contain ambidentate ligand, NO_2.

Q.8 Write the IUPAC name of $K_3[Fe(CN)_5NO]$. **[2011 Instant]**

Sol The IUPAC name of $K_3[Fe(CN)_5NO]$ is potassium pentacyanido nitrosoferrate (III).

Q.9 Write the IUPAC name of $K_2[PtCl_6]$. **[2010]**

Sol The IUPAC name of $K_2[PtCl_6]$ is potassium hexachloridoplatinate (IV).

Q.10 Write IUPAC name of $[Pt(NH_3)_4][PtCl_4]$. **[2008]**

Sol IUPAC name of $[Pt(NH_3)_4][PtCl_4]$ is Tetrammineplatinum (II) tetrachloroplatinate (II).

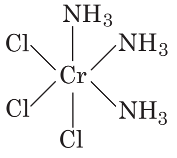
Q.11 Potash alum is an example of .... **[2006, 2003]**
(simple salt, double salt, complex salt)

Sol double salt

Important Questions

Q.12 Draw all possible isomers of $[Cr(NH_3)_3Cl_3]$.

Sol Octahedral complex of type (MA_3B_3) **[Textbook]**



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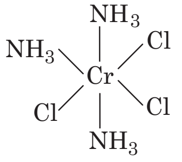

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Q.13 Give one example of both ionisation and hydrate isomerism in single compound. **[Textbook]**

Sol $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl \cdot H_2O$

Q.14 Draw the structure of triammine -1,2,3 trichloroplatinum (IV) chloride. **[Textbook]**

Sol $[Pt(NH_3)_3Cl_3]Cl$

Q.15 $[Rh(en)_3][IrCl_6]$ and $[Rh(en)_2Cl_2][Ir(en)Cl_4]$ are which type of isomers? **[Textbook]**

Sol Coordination isomers

Q.16 How many chloride ions can be precipitated from an aqueous solution of $[Cr(py)_2(H_2O)_2Cl_2]Cl$ with $AgNO_3$? **[Textbook]**

Sol As there is only one chloride ion present outside the coordination sphere. Thus, one chloride ion can be precipitated as AgCl from an aqueous solution of $[Cr(Py)_2(H_2O)_2Cl_2]$ Cl with $AgNO_3$.

Q.17 Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is

(a) 6 (b) 4 (c) 3 (d) 2

Sol (*a*) The coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is 6 due to three oxalate ions are bonded with each other having two donor sites.

Q.18 A group of atoms can function as a ligand only when

(a) it is a positively charged ion
(b) it is a negatively charged ion
(c) it has an unshared pair of electrons
(d) it is a small molecule

Sol (*c*) A ligand must carry an unshared pair of electrons in order to form a coordinate bond with the metal atom or ion.

Q.19 Werner's secondary valency are said to be ……… .

Sol Werner's secondary valency are said to be coordination number.

Q.20 Cyanide ion (CN^-) is ……… ligand.

Sol Cyanide ion (CN^-) is an ambidentate ligand.

Q.21 The number of secondary valencies in a complex is equal to the .... of the metal atom/ion. (Fill in the blank)

Sol coordination number

Q.22 The IUPAC name of the complex $[Co(en)_2Cl(ONO)]^+$ is………… ion.

Sol chlorido*bis*-(ethylenediamine) nitrito-O-cobalt(III).

Q.23 Fill in the blanks.

(i) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ show ………… isomerism. **[Textbook]**
(ii) $KCl \cdot MgCl_2 \cdot 6H_2O$ is a … , but $K_4[Fe(CN)_6]$ is a ….
(iii) $[Co(NH_3)_4Cl_2]Cl$ give ………… Cl^- ions in solution.
(iv) Complexes of type MA_4B_2 can exist as ……… isomers.

Sol (i) ionisation (ii) double salt, complex salt
(iii) one (iv) *cis-trans*(geometrical) **(½ × 4 = 2)**

Q.24 Fill in the blanks. **[Textbook]**

(i) Ethylene diamine is an example of …… ligand.
(ii) The IUPAC name of $Fe(CO)_5$ is ………
(iii) Dimethyl glyoxime is used for the gravimetric estimation of ……… ion.
(iv) EDTA is a ……… ligand.
(v) $K_4[Fe(CN)_6]$ is a complex compound, but potash alum is a ……… .
(vi) One molecule of $[Pt(NH_3)_6]Cl_4$ gives ……… ions in solution and requires ……… of $AgNO_3$ for complete precipitation of chloride ions.
(vii) Geometrical isomerism is not observed in complexes of coordination number 4 of ……… geometry.

Sol (i) bidentate (ii) pentacarbonyliron (0)
(iii) Ni^{2+} (iv) hexadentate
(v) double salt (vi) five, 4 molecules
(vii) tetrahedral **(7 × 1 = 7)**

Q.26 What is the coordination number of each ion in NaCl? **[Textbook]**

Sol 6 : 6

Q.27 (i) Write the name of the compound : $[Co(en)_2Cl_2]SO_4$ **[Textbook]**
(ii) Write the formula of the compound : Potassium pentachloroammineplatinate (IV).

Sol (i) dichloro *bis*-(ethane-1,2-diamine) cobalt (III) sulphate **(1/2)**
(ii) $K[Pt(Cl)_5(NH_3)]$ **(1/2)**

Q.28 (i) What is the IUPAC name of the following compound $K_3[Fe(CN)_6]$? **[Textbook]**
(ii) Write formula of the following : Ammonium diammine tetrathiocyanato chromate (III)

Sol (i) Potassiumhexacyanoferrate(III) **(1/2)**
(ii) $NH_4[Cr(NCS)_4(NH_3)_2]$ **(1/2)**

Q.29 Write the formula of the following complex: *tris* (ethylenediamine) cobalt (III) sulphate. **[Textbook]**

Sol $[Co(en)_3]_2(SO_4)_3$

Q.30 Write the name of the compound : $[(C_2H_5)_5N]_2[ZnCl_4]$ **[Textbook]**

Sol *bis*-(ethylenediamine)tetrachloridozinc(II) .

2 MARK *Questions*

Exams' Questions

Q.31 What are bidentate ligands? Give an example.

Sol **Bidentate ligands** When a ligand is bonded with two donor sites to the central metal atom/ion, it is called bidentate ligand,

e.g. 1, 2-ethanediamine (en).

$$NH_2 — CH_2 — CH_2 — NH_2. \quad \textbf{(2)}$$

Q.32 $FeSO_4$ 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? **(2018)**

Sol When $FeSO_4$ and $(NH_4)_2SO_4$ solution are mixed in 1 : 1 molar ratio, Mohr's salt is formed.

$$FeSO_4 + (NH_4)_2SO_4 \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$$

Mohr's salt is a double salt, which dissociates into its ions and shows their properties, its aqueous solution gives the test of Fe^{2+} ions. **(1)**

But when $CuSO_4$ is mixed with ammonia coordination complex is formed and following reaction occurs:

$$CuSO_4\,(aq) + 4NH_3\,(aq) \longrightarrow [Cu(NH_3)_4]SO_4$$

This complex does not produce Cu^{2+} ion and doesn't show the contituent properties. So, the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion. **(1)**

Q.33 What is the difference between double salts and complex compounds? **[2014,2010]**

Or What is the difference between molecular compound and complex compound? **[Textbook]**

Sol

Double salt	Coordination compound
They lose their identity in solution.	They do not completely lose their identity in solution.
They exist only in solid state and dissociate into ions in aqueous solution or in other solvent.	They exist in solid state as well as dissolved in water or any other solvent. They do not dissociate into simple ions completely.
In a double salt, metal ions exhibit their normal valency.	In a complex compound or coordination compound, metal ion is surrounded by a number of oppositely charged ions or neutral molecules more than its normal valency.
e.g. Mohr's salt ($FeSO_4 \cdot (NH_4)_2\,SO_4 \cdot 6\,H_2O$), potash alum	e.g. $[Ni(NH_3)_6]Cl_2$, $K_4[Fe(CN)_6]$, etc.

(2)

3 MARK *Questions*

Important Questions

Q.34 Give IUPAC names of the following compounds. $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^+$, $[Cr(H_2O)_4Cl_2]$, $K_2[PtCl_6]$, $[Fe(CN)_6]^{4-}$, $[Co(en)_2Cl_2]_2SO_4$, **[Textbook]**

Sol $[Ag(NH_3)_2]^+$ = Diamminesilver(I) ion

$[Cu(NH_3)_4]^+$ = Tetrammine copper (I) ion

$[Cr(H_2O)_4Cl_2]$ = Tetraquadichlorido chromium (II)

$K_2[PtCl_6]$ = Potassiumhexachloroplatinum (IV)

$[Fe(CN)_6]^{-4}$ = Hexacyanoferrate(II) ion

$[CO(en)_2Cl_2]_2SO_4$ = Dichlorido-*bis* (ethane-1, 2-diamine cobalt (II) sulphate). **[1/2× 6 = 3]**

Q.35 Write the formula of the following complexes:

(i) Hexaaminenickel (II) chloride **[Textbook]**
(ii) Hexaamminechromium (III) nitrate
(iii) Potassium hexachloroplatinate (IV)
(iv) Trinitritoamminecobalt (III)
(v) Potassium hexacyanoferrate (II)
(vi) Potassium hexacyanoferrate (III),

Sol

(i) $[Ni(NH_3)_6]Cl_2$	(ii) $[Cr(NH_3)_6](NO_3)_3$
(iii) $K_2[Pt(Cl)_6]$	(iv) $[Co(NH_3)(NO_2)_3]$
(v) $K_4[Fe(CN)_6]$	(vi) $K_3\,[Fe(CN)_6]$

(1/2× 6 = 3)

7 MARK *Questions*

Exams' Question

Q.36 Write a note on Werner's theory of coordination compounds. **[2013, 2006,2005, 2003,2001]**

Sol Refer to the text on page 191. **(7)**

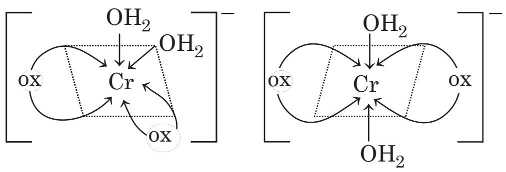
Important Questions

Q.37 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) $[Pt(NH_3)(H_2O)Cl_2]$

Sol (i) $K[Cr(H_2O)_2(C_2O_4)_2]$ or $K[Cr(H_2O)_2(ox)_2]$ (where, ox = oxalate ion)

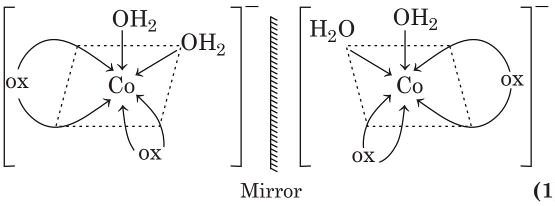
(a) It exists as geometrical isomers, *cis* and *trans* forms.



cis *trans*

(In *cis*-form, the same groups occupy adjacent positions, while in *trans*-form, they are present at alternate positions.) **(1)**

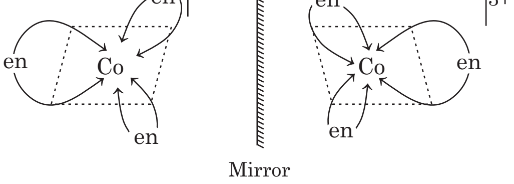
(b) The *cis*-isomer can also exist as a pair of optical isomers (i.e. *d*-and *l*-forms) (due to the absence of plane of symmetry).



(1)

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

It has two optical isomers (i.e. *d*-and *l*-forms).



(1)

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

It can exist as a pair of ionisation isomers as well as linkage isomers.

Ionisation isomers $[Co(NH_3)_5(NO_2)](NO_3)_2$ and $[Co(NH_3)_5(NO_3)](NO_2)(NO_3)$.

as they give different ions on ionisation.

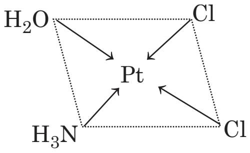
$$[Co(NH_3)_5(NO_2)](NO_3)_2 \xrightarrow{\text{Ionisation}} [Co(NH_3)_5(NO_2)]^{2+} + 2NO_3^-$$

$$[Co(NH_3)_5(NO_3)](NO_2)(NO_3) \xrightarrow{\text{Ionisation}} [Co(NH_3)_5NO_3]^{2+} + NO_2^- + NO_3^- \quad \textbf{(2)}$$

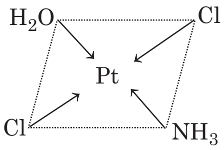
Linkage isomers $[Co(NH_3)_5(NO_2)](NO_3)_2$ and $[Co(NH_3)_5(ONO)](NO_3)_2$ as it contains ambidentate ligand, NO_2. **(1)**

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

It can exist as two geometrical isomers, is and *trans* form.



cis



trans

(1)

TOPIC TEST 1

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

(a) +1 (b) +3

(c) –1 (d) –3

2. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_2)]Cl_2$ is

(a) diamminetetraaquacobalt (III) chloride

(b) diamminetetraaquacobalt (II) chloride

(c) tetraaquadiamminecobalt (III) chloride

(d) tetraaquadiamminecobalt (IV) chloride

3. The ligand $N(CH_2CH_2NH_2)_3$ is

(a) tridentate

(b) hexadentate

(c) tetradentate

(d) bidentate [***Ans.*** **1.** (c), **2.** (b), **3.** (c)]

4. The addition compounds which retain their identity in solution are said to be .... [***Ans.*** complexes]

5. Oxalate ion is an example of .... ligand. [***Ans.*** bidentate]

6. What is the difference between primary valency and secondary valency?

7. Square planar do not show optical isomerism. Why?

8. In which type of coordination complex, optical isomerism is common?

9. A complex having molecular formula $Cr(NH_3)_4Cl_2Br$ has two isomers '*A*' and '*B*'. The isomer '*A*' gives white precipitate with $AgNO_3$ solution, while '*B*' gives a yellow precipitate. Identify '*A*' and '*B*'.

10. (i) Draw the structures of geometrical isomers of $Fe(NH_3)_2(CN)_4]$.

(ii) Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*- $[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

TOPIC ~02 Bonding in Coordination Compounds, Its Importance and Organometallic Compounds

Bonding in Coordination Compounds

Werner was the first to describe the bonding in coordination compounds. But this theory fail to explain important points.

These are as follows :

(i) Only certain element can form coordination compounds.
(ii) Define geometry of coordination compounds.
(iii) Presence of magnetic and optical properties of coordination compounds.

Many approaches have been put to explain the nature of bonding in coordination compounds, Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT).

Valence Bond Theory (VBT)

Its postulates are :

(i) Metal-ligand bond is formed by the donation of electrons by ligand to metal.
(ii) Metal atom/ion must have vacant orbitals of equal energies, equal to the number of ligands to be attached.
(iii) Sometimes unpaired $(n-1)d$ electrons pair up to create empty orbitals.
(iv) Depending upon the type of hybridisation d^2sp^3 (or sp^3d^2), dsp^2 and sp^3, the shapes of the complex are octahedral, square planar and tetrahedral respectively.
(v) If no unpaired electron is present, then complex is **diamagnetic.** If unpaired electrons are present, complex is **paramagnetic.**
(vi) If coordination number is 6, complex is octahedral with sp^3d^2 or d^2sp^3-hybridisation.
(vii) In strong field ligand, the d-electrons of central metal are pair up against Hund's rule. e.g; CO, NO, CN^-, NO_2^-, NH_3, en (ethylene diamine). Some weak field ligands are H_2O, X^-, NO_3^-, ROH, etc.
(viii) If complex formed involves inner $(n-1)d$ orbitals for hybridisation, it is called **inner orbital** or **low spin** or **spin paired complex**, e.g. $[Ni(CN)_4]^{2-}$. Whereas, if complex formed involves **outer** $(n)d$ **orbitals** for hybridisation, it is called **outer orbital**, **high spin** or **spin free complex**, e.g. $[Ni(H_2O)_6]^{2+}$.

Limitations of VBT

(i) It does not distinguish between weak and strong ligands.
(ii) It could not give any satisfactory explanation for the colour of the complexes.
(iii) It does not give an exact explanation of thermodynamic or kinetic stabilities of coordination compounds.
(iv) It does not give quantitative interpretations of magnetic moment data.
(v) It fails to explain relative energies of different shapes.
(vi) It fails to predict tetrahedral and square planar structures of some 4-coordinate complexes.
(vii) It is based on the number or assumptions.

Crystal Field Theory (CFT)

It is more appropriate theory than VBT. According to CFT, under the influence of ligand field, degeneracy of the d-orbital is destroyed and it splits into two or more energy levels.

The extent of splitting depends upon the strength of ligand.

A strong ligand causes greater splitting while a weak ligand causes smaller splitting.

The difference of energy between the two sets of d-orbital (in octahedral complexes) is called **Crystal Field Splitting Energy** (CFSE) **or** Δ_o. In case of octahedral complexes, e_g set $[d_{x^2-y^2}, d_{z^2}]$ is of higher energy while in case of tetrahedral complexes t_{2g} set (d_{xy}, d_{yz}, d_{zx}) has higher energy.

Factors Affecting the Magnitude of CFSE

Spectrochemical Series

The ligands with smaller size, large negative charge, with good σ donor and π acceptor properties will give large field splitting.

The increasing order of the values Δ_o is given below

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$$

This series is called **spectrochemical series.** In case of d^4 ions, two possible pattern of electron distribution arise.

These are explained below.

(i) If $\Delta_o < p$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\, e_g^1$. Ligands for which $\Delta_o < p$, are weak field ligands and they form high spin complexes.

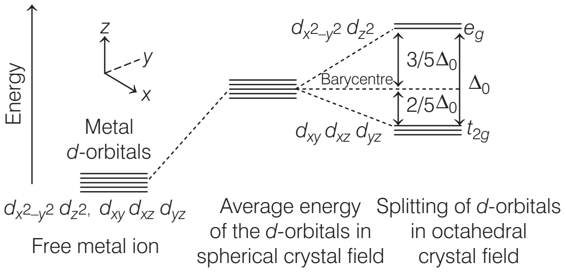
(ii) If $\Delta_o > p$, the fourth electron enters t_{2g} orbital giving the configuration $t_{2g}^4\, e_g^0$. Ligands for which $\Delta_o > p$, are strong field ligands and they form low spin complexes.

Oxidation State of *M*-Ion

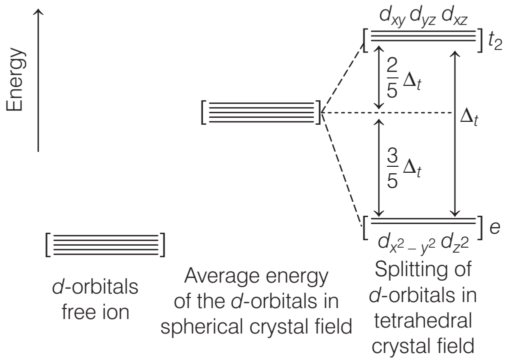
Higher is the oxidation state of *M*-ion higher is the CFSE.

Geometry of the Complex

Splitting is different for tetrahedral and octahedral complexes.



d-orbital splitting in an octahedral crystal field



d-orbital splitting in a tetrahedral crystal field

Colour in Coordination Compounds

When light of certain frequency falls on the complex, it absorbs light from visible range for transition of electrons from lower *d*-energy level to higher *d*-energy level.

Colour of the compound is the complementary colour of the absorbed light. This is called ***d-d* transition of electron.**

Limitations of CFT

CFT is successful in explaining the colour, magnetic properties, the effects of weak and strong field ligands in coordination compounds.

However, it has the following limitations:

(i) As the ligands are point charges, the anionic ligands should exert the greatest splitting effect.

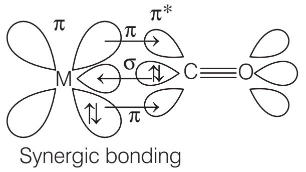
(ii) CFT treats the metal-ligand bond as purely ionic and it does not take into account the covalent character of bonding between the ligand and the central atom.

Bonding in Metal Carbonyls

Compounds which have at least one metal-carbon bond are called **organometallic compounds**.The metal-carbon bond in metal carbonyls possesses 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 electron from a filled *d*-orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a **synergic effect** which strengthens the bond between CO and the metal. In these the oxidation state of metal is zero.



Example of synergic bonding interactions in a carbonyl compounds

Importance of Coordination Compounds

In Biological Systems

(i) Haemoglobin, the oxygen carrier in blood is a coordination complex of Fe^{2+} with porphyrin.

(ii) The pigment chlorophyll in plants, responsible for photosynthesis is a coordination complex of Mg^{2+} with porphyrin.

(iii) Vitamin B_{12} is a coordination complex of cobalt.

In Medicinal Chemistry

(i) The platinum complex *cis*-$[Pt(NH_3)_2Cl_2]$ (*cis*-platin) is used in the treatment of cancer.

(ii) EDTA complex of calcium is used in the treatment of lead poisoning.

(iii) The excess of copper and iron present in animal system are removed by the chelating ligands, D-penicillamine and desferrioxime B- *via* the formation of complexes.

In Analytical Chemistry (Qualitative Analysis)

(i) Detection of Cu^{2+}.

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

(iii) The separation of Ag^{+} and Hg^{2+} in group 1 is based on the fact that AgCl dissolves in NH_3, while Hg_2Cl_2 makes an insoluble black substance with it.

In Extraction/Metallurgy of Metals

Extraction of various metals from their ore involves complex formation, e.g. silver and gold are extracted from their ore by forming cyanide complex.

Organometallic Compounds

Compounds containing atleast one carbon metal bond are known as organometallic compounds. The first organometallic compound was made by Zessie in 1830 by the action of ethylene on a solution of potassium chloroplatinate (II).

Grignard reagent, $RMgX$ is a familiar example of organometallic compounds, where R is an alkyl group. Other organometallic compounds include diethyl zinc $[Zn(C_2H_6)_2]$, tetraethyl lead $[Pb(C_2H_5)_4]$, dibenzene chromium $[Cr(C_6H_6)_2]$, ferrocene $[Fe(C_5H_5)_2]$ and metal carbonyls.

Classification of Organometallic Compounds

Organometallic compounds are classified into three types:

1. Sigma (σ) Bonded Organometallics

In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond.

e.g.

- Dialkyl zinc, R_2Zn i.e. $(C_2H_5)Zn$.
- Grignard reagent, $RMgX$, where R is an alkyl or aryl group and X is a halogen.

2. Pi (π) Bonded Organometallics

Metals form compounds with alkenes, alkynes, benzene and other ring compound present in this type. In these complexes, the metal and ligand form a bond involving π-electrons of the ligand. e.g. Zeise's salt, ferrocene. They have the formula $K[PtCl_3(\eta^2 - C_2H_4)]$, $Fe(\eta^2 - C_5H_5)_2$, respectively, where prefixes η^2 (etc), represent that 2, carbon atoms are bound to the metal in the compound.

3. Sigma (σ) Pi (π) Bonded Organometallics

Metal carbonyls which are formed between metal and carbon monoxide belong to this class. They have both σ and π bonding. The oxidation state of the metal atoms in these compounds is zero. Common examples are tetracarbonyl nickel (0), $Ni(CO)_4$, pentacarbonyl iron (0), $Fe(CO)_5$, hexacarbonyl chromium (0), $Cr(CO)_6$, and $Fe_2(CO)_9$, etc.

Applications of Organometallic Compounds

(i) Organometallic compounds are often used as homogeneous and heterogeneous catalysts. *Zeigler-Natta* catalyst [$TiCl_4$ and triethyl aluminium] acts as a catalyst in the polymerisation of ethylene to polythene.

(ii) Grignard reagents and organoalkali are used in many organic synthesis.

(iii) Tetraethyl lead (TEL) is used as an antiknock compound in gasoline.

(iv) Silicones are used as polymers with unique properties.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Question

Q.1 $Ni(CO)_4$ is an example of .... and .... bonded organometallics. **[2016]**

Sol sigma (σ) and pi (π).

Important Questions

Q.2 The reaction, $[Fe(CNS)_6]^{3-} \longrightarrow [FeF_6]^{3-}$ takes place with

(a) increase in coordination number
(b) increase in magnetic moment
(c) decrease in coordination number
(d) decrease in magnetic moment

Sol (*b*) In $[Fe(CNS)_6]^{3-}$, $Fe^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

CNS^- is a strong ligand, pairing of electrons within $3d$ level results in one unpaired electron and the magnetic moment,

$$\begin{aligned}\mu &= \sqrt{n(n+2)}\\ &= \sqrt{1(1+2)} = \sqrt{3}\\ &= 1.732 \text{ BM}\end{aligned}$$

In $[FeF_6]^{3-}$, $Fe^{3+} = 3d^5$, F^- is a weak ligand and no pairing of electrons occur.

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ BM}$$

Q.3 ……… and ……… properties of coordination compound can be explained by VBT. (Fill in the blanks)

Sol Shapes and magnetic.

Q.4 $[Zn(NH_3)_4]^{2+}$ show ……… behaviour.

Sol diamagnetic behaviour.

Q.5 If the strong ligand is present, then unpaired electrons get ………..

Sol paired

Q.6 When the complex formed involves the inner $(n-1)d$-orbitals for hybridisation, the complex is called ………. .

Sol inner orbital complex

Q.7 The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is ……… . **[Textbook]**

Sol paramagnetism

Q.8 Name the complex which is responsible for photosynthesis.

Sol Chlorophyll is the complex which is responsible for photosynthesis.

Q.9 What is the role of the following complex in analytical chemistry?

(i) EDTA (ii) DMG

Sol (i) Hardness of water (ii) Detection of nickel

Q.10 In which case will splitting be larger, $3d$ orbital or $4d$ orbital?

Sol In $4d$-orbital splitting is larger.

2 MARK *Questions*

Exams' Question

Q.11 What are organometallic compounds? Give two examples. **[2012, 2009]**

Sol Compounds containing atleast one carbon metal bond are known as organometallic compounds. The first organometallic compound was made by Zessie in 1830 by the action of ethylene on a solution of potassium chloroplatinate (II).

e.g. Grignard reagent, $RMgX$ is a familiar example of organometallic compounds, where R is an alkyl group. Other organometallic compounds include diethyl zinc $[Zn(C_2H_6)_2]$, tetraethyl lead $[Pb(C_2H_5)_4]$, dibenzene chromium $[Cr(C_6H_6)_2]$, ferrocene $[Fe(C_5H_5)_2]$ and metal carbonyls. **(2)**

Important Questions

Q.12 Why is splitting pattern of d-orbital in octahedral and tetrahedral geometry reversed?

Sol **Crystal Field Splitting in Octahedral and Tetrahedral Complexes** In octahedral complexes, the six ligands approaches the central metal ion along the coordinate axes, thus $d_{x^2-y^2}$ and d_{z^2} orbitals point towards the axes along the direction of ligand will experience more repulsions, than t_{2g} of orbitals which are directed between the axes.

In tetrahedral complex, four ligands may be imagined to occupy the alternate corners of the cube and the centre ion at the centre of the cube and thus orbitals (d_{xy}, d_{yz}, d_{xz}) which are directed between the axes experience more repulsions and, therefore t_{2g} set of d-orbitals have higher energy than e_g set of orbitals. **(2)**

Q.13 What will be the correct order for the wavelength of absorption in the visible region for the following? $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

Sol In all the given complexes, the metal ion is Ni^{2+}. The increasing field strengths of the ligands present as per electrochemical series are in order.

$H_2O < NH_3 < NO_2$

As $E = hc/\lambda$, which implies that, the wavelength is inversely proportional to energies.

So, order for the wavelength of absorption is

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

Q.14 Use EAN rule and predict the molecular formula of nickel carbonyl? **[2017]**

Sol EAN rule states that in a number of metal complexes, the metal atom tends to surround itself with sufficient ligands that the resulting effective atomic number is numerically equal to the atomic number of the noble gas element formed in the same period in which the metal is situated.

The molecular formula of nickel carbonyl that follows EAN rule is $Ni(CO)_4$.

For $Ni(CO)_4$, EAN $= [28 - 0 + 2(4)] = 36$ **(2)**

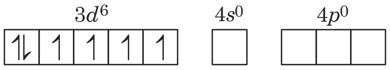
3 MARK *Questions*

Exams' Questions

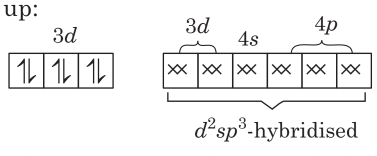
Q.15 Discuss the structure of $[Co(NH_3)_6]^{3+}$ ion on the basis of valence bond theory. Whether, it is an inner-orbital or outer orbital complex ion. **[2019]**

Sol **Structure of $[Co(NH_3)_6]^{3+}$** Here, Co is our central metal element. Configuration of Co (atom) is $[Ar]\,3d^7\,4s^2$.

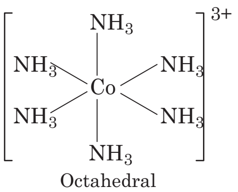
Configuration of Co^{3+} ion $= [Ar]\,3d^6$, i.e.



∵ Co^{3+} ion has 4 unpaired electrons in $3d$-subshell and NH_3 is a strong ligand. Therefore, electrons get paired up:



Thus, Co^{3+} in $[Co(NH_3)_6]^{3+}$ is in d^2sp^3 (inner orbital octahedral complex) and is diamagnetic in nature due to absence of unpaired electrons.



Octahedral **(3)**

Important Questions

Q.16 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.

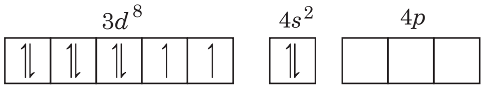
Or

Account for the following on the basis of valence bond theory. **[Textbook]**

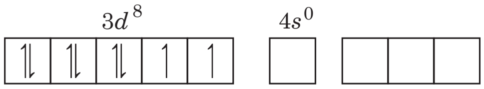
(i) $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar.

(ii) $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral.

Sol Outer electronic configuration of $_{28}Ni$ atom $= [Ar]\,3d^8\,4s^2$

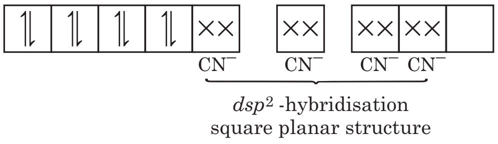


Ni^{2+} ion $= [Ar]\,3d^8\,4s^0$



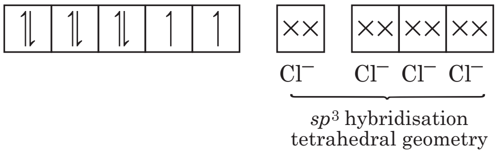
(CN^- being strong field ligand pair up the d-electrons of metal atom). **(1)**

$[Ni(CN)_4]^{2-}$ ion =



- It involves dsp^2 hybridisation and has square planar geometry. In this complex, each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The complex is diamagnetic in nature as it has no unpaired electrons. **(1)**
- In the complex ion $[NiCl_4]^{2-}$, nickel is in +2 oxidation state and has the electronic configuration $3d^8$ also. But Cl^- being weak field ligand cannot cause pairing.

  $[NiCl_4]^{2-}$ =

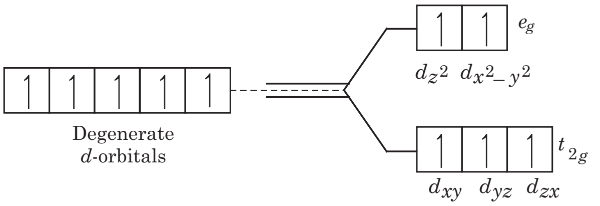


Four pair of electrons one from each Cl^- ion occupy the four hybrid orbitals. Thus, the complex has tetrahedral geometry (sp^3). Paramagnetic in nature as it has two unpaired electrons. **(1)**

Q.17 The hexaaquamanganese (II) ion contains five unpaired electrons, while the hexacyano ion contains only one paired electron. Explain using crystal field theory.

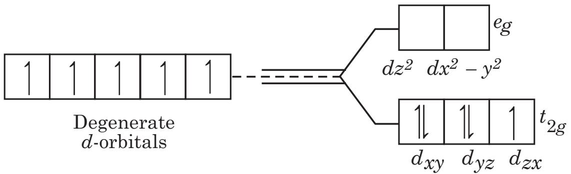
Sol The presence of six ligands indicates that the complex is octahedral and, thus d-orbital split up into lower energy t_{2g} orbitals and higher energy e_g orbitals.

CN^- is a strong field ligand (thus, causes pairing) and H_2O is a weak field ligand. Mn (II) ion has $3d^5$ configuration. In the presence of H_2O molecules (acting as weak field ligands), the distribution of these five electrons is t_{2g}^3, e_g^2 i.e. all the electrons remain unpaired to form a high spin complex. **(1)**



Splitting in the presence of octahedral weak field **(1)**

However, in the presence of CN^- (acting as strong field ligands), the distribution of these electrons is t_{2g}^5, e_g^0 i.e. two t_{2g} orbitals contain paired electrons, while the third t_{2g} orbital contains one unpaired electron.The complex formed is a low spin complex.



Splitting in presence of strong field ligand **(1)**

Q.18 (i) What are the postulates of valence bond theory?

(ii) Distinguish between inner and outer orbital complex with suitable examples. **[Textbook]**

Sol (i) Postulates of valence bond theory. Refer text on page 197. **(1½)**

(ii) Inner and outer orbital complex. Refer text on page 197. **(1½)**

7 MARK *Questions*

Exams' Questions

Q.19 Write the assumptions of crystal field theory. Discuss the pattern of splitting of d-orbitals under the effect of an octahedral crystal field. **[2018]**

Sol The main assumptions of crystal field theory are as follows:

(i) The transition metal ion is surrounded by the ligands with lone pairs of electrons and the complex is a combination of central ion surrounded by other ions or molecules or dipoles, e.g. ligands. **(1)**

(ii) All types of ligands are regarded as point charges in case of anions and as dipoles in case of neutral molecules. **(1)**

(iii) The interactions between the metal ion and the negative ends of anion (or ion dipoles) is purely electrostatic, i.e. the bond between the metal and ligand is considered to be 100% ionic. **(1)**

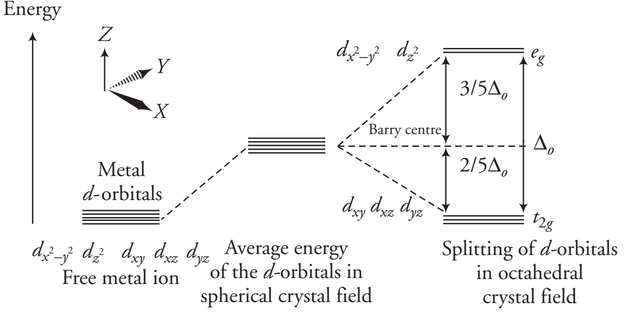
(iv) The ligands surrounding the metal ion produces electrical field and this electrical field influences the energies of the orbitals of central metal ion particularly d-orbitals. **(1)**

(v) In the case of free metal ion, all five d-orbitals have the same energy. Orbitals having the same energies are called degenerate orbitals.

The five degenerate d-orbitals of the metal ion split into different sets of orbital having different energies in the presence of electrical field of ligands. This is called **crystal field splitting**. **(1)**

(vii) The number of ligands and their arrangement (geometry) around the central metal ion will have different effect on the relative energies of the five d-orbitals. **(1)**

Splitting of d-orbitals under the effect of an octahedral crystal field



The degeneracy of the d-orbitals has been removed due to ligand-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of electric field of ligands in a definite geometry is termed as **crystal field splitting**. **(1)**

Q.20 (i) Write notes on Werner's theory of coordination compounds. **[Textbook, 2015]**

(ii) The coordination complex $[Cu(OH_2)_6]^{2+}$ has one unpaired electron. According to VBT, which of the following statements are true?

(a) The complex is octahedral
(b) The complex is an outer orbital complex
(c) The complex is d^2sp^3-hybridised
(d) The complex is diamagnetic

(e) The coordination number is 6

(iii) Which type of ligand is EDTA?

Sol (i) **Werner's Coordination Theory** To explain the formation and structure of complex compounds Werner in 1898 put forward the theory of coordination for which he was awarded Nobel prize in Chemistry. He is known as the father of coordination Chemistry.

Postulates

(a) Metal atoms in coordination compounds exhibit two types of valencies:

I. Primary valency II. Secondary valency

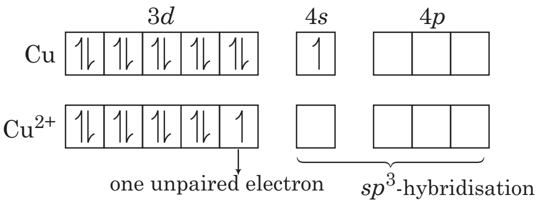
The primary valency is non-directional and ionisable. It corresponds to oxidation state of central atom. The secondary valency is directional and non-ionisable. It corresponds to coordination number.

(b) Each metal atom exhibits a fixed number of secondary valencies i.e. it has a fixed coordination number.

(c) The primary valencies are satisfied by negative ions, whereas the secondary valencies are satisfied either by negative ions or by neutral molecules.

(d) The secondary valencies are responsible for imparting a particular geometry to the coordination compound. e.g. if the central metal ion has four secondary valencies, then they form either a tetrahedral or square planar arrangement around the central metal ion. If the central metal ion has six secondary valencies, then these are arranged octahedrally around the metal ion. In otherwords, the **stereochemistry** of the complex is determined by the secondary valencies. **(3)**

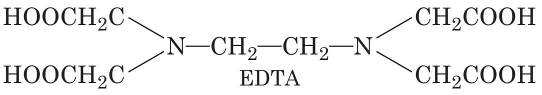
(ii) **$[Cu(OH_2)_6]^{2+}$** The coordination number of metal ion Cu^{2+} is 6. Cu (Atomic no. 29) $3d^{10}4s^1$



So, complex is paramagnetic hybridisation is sp^3 and the complex is tetrahedral. It is an outer-orbital complex so,

(a) False (b) True (c) False (d) False (e) True **(3)**

(iii) Ethylene diamine tetracetic acid (EDTA) is an important hexadentate ligand. It binds through two Nitrogen and four oxygen atoms of four —COOH groups to the central metal ion.



(1)

Important Questions

Q.21 (i) Compare the following complexes with respect to structural shapes, magnetic behaviour and hybrid orbitals involved.

$[Ni(CN)_4]^{2-}$ (b) $[NiCl_4]^{2-}$ (c) $[CoF_6]^{3-}$

{Atomic number of Co = 27, Cr = 24, Ni = 28}

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

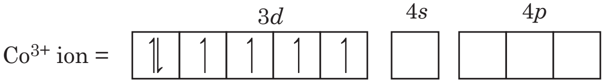
Sol (i)

	Complexes	Magnetic behaviour	Hydridisa-tion	Shape
(a)	$[Ni(CN)_4]^{2-}$	Diamagnetic	dsp^2	Square planar
(b)	$[NiCl_4]^{2-}$	Paramagnetic	sp^3	Tetrahedral
(c)	$[CoF_6]^{3-}$	Paramagnetic	sp^3d^2	Octahedral

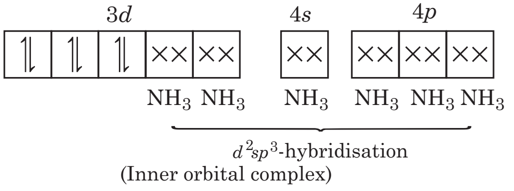
(3)

(ii) In inner orbital complexes, $(n-1)$ d-orbitals are used and in outer orbital complexes, nd-orbitals are used for hybridisation.

In $[Co(NH_3)_6]^{3+}$, Co is present as Co^{3+} and has $3d^6$ configuration. In the presence of strong field ligand NH_3, the 3d-electrons pair up leaving two d-orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex in the case of $[Co(NH_3)_6]^{3+}$.

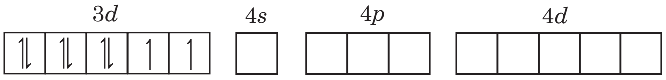


$[Co(NH_3)_6]^{3+}$ =



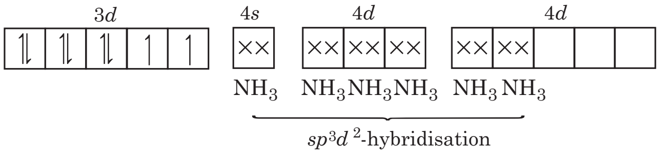
(2)

In $[Ni(NH_3)_6]^{2+}$, Ni is in + 2 oxidation state and has d^8-configuration. **(1)**



As NH_3 is a strong field ligand, pairing of electrons can occur but pairing will not result into two empty d-orbitals.

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



Thus, $(n-1)$ d-orbitals are not available but the nd-orbitals are used in bond formation, i.e. in hybridisation, the complex is called **outer orbital complex.** **(1)**

Q.22 (i) Discuss briefly, how crystal field theory explains the magnetic properties of complexes of transition metals? **[Textbook]**

(ii) Discuss the structure of following complexes on the basis of CFT.

(a) $[Cu(NH_3)_6]^{3+}$ (b) $[Fe(CN)_6]^{4-}$

Sol (i) Transition metal complexes exhibit magnetic properties. The magnetic nature depends on the number of unpaired electrons present.

On this basis, the complexes can be paramagnetic (having unpaired electrons) or diamagnetic (having paired electrons) in nature.

Magnetic nature or magnetic moment can be determined by the relation,

$$\mu = \sqrt{N\,(N+2)}\ \text{BM},$$

where, N is the number of unpaired electrons.

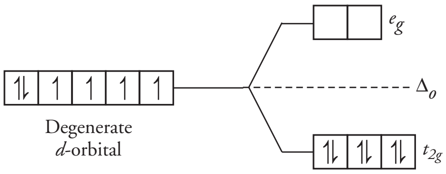
The magnetic properties of transition metals can be explained with the help of crystal field theory.

For instance, $[Fe(H_2O)_6]^{2+}$ is paramagnetic but $[Fe(CN)_6]^{4+}$ is diamagnetic in nature.

This can be explained as, since, H_2O is a weak field ligand, it does not pair up the electrons and forms high spin complex. While, CN^- is a strong field ligand, pairs the electrons and forms low spin complex. **(3)**

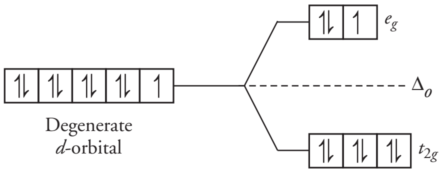
(ii) As both the complexes have six ligands. So, they will have octahedral geometry. According to spectrochemical series, both CN^- and NH_3 being strong field ligand pair up the t_{2g} electrons before filling e_g set.

In $[Fe(CN)_6]^{4-}$, $Fe^{2+} = d^6 \Rightarrow t_{2g}^6 e_g^0$



Thus, it is a low spin complex. **(2)**

In $[Cu\,(NH_3)_6]^{2+}$, $Cu^{2+} = d^9 \Rightarrow t_{2g}^6 e_g^3$



Thus, it is a high spin complex. **(2)**

TOPIC TEST 1

1. Give the electronic configuration of the following complexes on the basis of crystal field splitting theory.

(a) $[CoF_6]^{3-}$ (b) $[Fe(CN)_6]^{4-}$

2. Accout for different magnetic behaviour of hexacyanoferrate (III) and hexafluoroferrate (III).

3. What is crystal field splitting? Draw a sketch to show the splitting of d-orbitals in an octahedral crystal field.

4. Amongst the following ions, which one has the highest magnetic moment value?

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$

(c) $[Zn(H_2O)_6]^{2+}$

5. Write the three role of coordination compounds in biological systems.

6. What are sigma bonded complexes?

7. Out of the following complexes, which one carries more number of unpaired electrons?

Chapter Test

8. $CuSO_4 \cdot 5H_2O$ is blue in colour, while $CuSO_4$ is colourless. Why?

9. Calculate the magnetic moment of the complex $[MnF_6]^{3-}$.

10. What are the limitations of valence bond theory?

1 MARK *Questions*

1 The number of ions produced from the complex $[Cu(H_2O)_4]SO_4$ in solution is ....

2 The species having tetrahedral shape is
- (a) $[PdCl_4]^{2-}$
- (b) $[NiCl_4]^{2-}$
- (c) $[Pd(CN)_4]^{2-}$
- (d) $[Ni(CN)_4]^{2-}$

[***Ans***. **1.** (c), **2.** (c)]

3 What is the coordination number of Fe in $[Fe(CN)_6]^{4-}$?

4 Give an example of coordination isomerism.

5 Whether $[Cr(en)_3Cl_3]$ exhibits optical isomerism or not? **[Textbook]**

6 What are inner and outer orbital complexes?

7 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

8 What are primary and secondary valencics? **[Textbook]**

2 MARK *Questions*

9 Specify the oxidation number of the metals in the following coordination entities.
- (i) $[CoBr_2(en)_2]^+$
- (ii) $[PtCl_4]^{2-}$
- (iii) $[Cr(NH_3)_3]_3Cl_3$
- (iv) $K_3[Fe(CN)_6]$

10 Using IUPAC norms, write the systematic names of the following.
- (i) $[Co(en)_3]^{3+}$
- (ii) $[NiCl_4]^{2-}$
- (iii) $[Mn(H_2O)_6]^{2+}$
- (iv) $[Co(NH_3)_6]Cl_3$

11 Name the following coordination compounds according to the IUPAC system of nomenclature.
- (i) $[CoCl(NO_2)(NH_3)_4]Cl$
- (ii) $[Co(NH_3)_6][Cr(CN)_6]$

12 What is a ligand? Give an example of bidentate ligand.

13 Define the following terms by giving an example.
- (i) Chelating ligands
- (ii) Coordination compounds

14 Write the formulae for the following coordination compounds.
- (i) Potassium tetrahydroxozincate (II)
- (ii) Tetracarbonyl nickel (0)
- (iii) Diamminesilver (I) dicyanoargentate (I)
- (iv) *Tris*-(ethane-1,2-diamine) cobalt (III) sulphate

3 MARK *Questions*

15 Draw all the isomers (geometrical and optical) of
- (i) $[CoCl_2(en)_2]^+$
- (ii) $[Co(NH_3)Cl(en)_2]^{2+}$
- (iii) $[Co(NH_3)_2Cl_2(en)]^+$

16 Using valence bond theory, explain the following in relation to the complexes, given below.
$[Mn(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$.
- (i) Type of hybridisation
- (ii) Magnetic behaviour
- (iii) Inner or outer orbital complex

17 Give some examples of optical isomerism exhibited by complexes of coordination number 6. **[Textbook]**

7 MARK *Questions*

18
- (i) Define double salts and coordinate compounds. Distinguish between them with suitable examples.
- (ii) How does coordination number differ from oxidation number?

19 Give detail description of CFT for different types of ligand and explain how CFT explain colour of coordination compound? Use suitable examples to explain.

20 Explain the hybridisation, geometry, magnetic properties, IUPAC nomenclature of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$.