# 09

# Coordination Compound

**Syllabus**

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## 9.1 Introduction

**Q.1 Explain the given terms and give examples.**
**i. Coordination compound**
**ii. Ligand**
**iii. Central metal atom or ion**

**Ans :**

i. **Coordination compound** -A coordination compound consist of central metal atom or ion surrounded by atoms or molecules.

For examples : Chemotherapy drug, cisplatin $Pt(NH_3)_2Cl_2$.

In $Pt(NH_3)_2Cl_2$, is a coordinate compound in which the central platinum metal ion is surrounded by two ammonia molecules and two chloride ions.

ii. **Ligands** - The species surrounding the central metal atom or ion are called ligands.

Example - In $Pt(NH_3)_2Cl_2$ two ammonia ($NH_3$) molecules and two chlorine molecules ($Cl_2$) are ligands.

iii. **Central metal atom or ion** - In co-ordination compound the central metal atom or ion is usually an electron deficient species accepts an electron deficient species accepts an electrons while the ligands serve as electron donors.

Example - In $Pt(NH_3)_2Cl_2$, Pt(II) is central metal ion.

**Q.2 What are coordinate bonds ?**

**Ans :** The ligands are directly linked directly to central metal ion through coordinate bonds. A formation of coordinate bond occurs when the shared electron pair is contributed by ligands. The coordinate bond is conveniently represented by an arrow $\longrightarrow$ where the arrow head points to electron acceptor.

**Q.3 What is the difference between the central metal atom or ion and the ligand in coordinate compounds ?**

**Ans :** The central metal atom or ion usually an electron pair while the ligand serve as electron donors.

**+Q.4 Can you recall ?**

**What are lewis acids and bases ?**

**Ans :** A Lewis acid is a substance that donates a pair of electrons to form a covalent bond.

A Lewis base is a substance that donates a pair of electrons to donate a pair of electron.

**Q.5 Explain - Formation of coordination compound can be looked upon as the lewis acid-base interaction.**

**Ans :**

i. In coordination compound, the ligands being electron pair donors are lewis bases. The central metal ion being electron pair donors are Lewis bases. The central metal ion being electron pair acceptor serves as lewis acids.

ii. In cisplatin $Pt(NH_3)_2Cl_3$ two ammonia molecule and two chloride ligands utilize their lone pairs of electrons to form bonds with the Pt(II).

iii. The donor nitrogen and chlorine atoms of the ligands are directly attached to and form bonds with platinum.

**Q.6 Name the Lewis acids and bases in the complex $\left[PtCl_2(NH_3)_2\right]$.**

**Ans:** Lewis acid : Platinum (II) ion, ($Pt^{2+}$)
Lewis bases : Chloride ion ($Cl^-$),
ammonia ($NH_3$).

## 9.2 Types of Ligands

**Q.7 What are ligands ? What are their types? Give example of each type.**

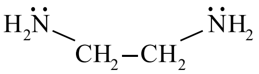
**Ans:** The species surrounding the central metal atom or ion are called ligands.

i. The ligands can be classified as monodentate and polydentate ligands depending on the number of electron donor atoms they have.

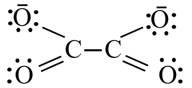
a. **Monodentate ligands :**
A monodentate ligand is the one where a single donor atom shares an electron pair to form a coordinate bond with the central metal ion. For example: the ligands $Cl^-$, $OH^-$ or CN attached to metal have electron pair on Cl, O and N, respectively which are donor atoms :

b. **Polydentate ligands :**
A polydentate ligand has two or more donor atoms linked to the central metal ion. For example, ethylenediamine and oxalate ion. Each of these ligands possesses two donor atoms. These are bidentate ligands.

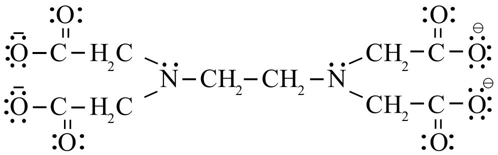
ii. Ethylenediamine binds to metal using electron pair on each of its two nitrogens.



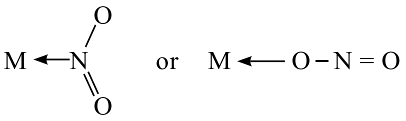
Similarly oxalate ion $(C_2O_4)^{2-}$ utilizes electron pair on each of its negatively charged oxygen atoms upon linking with the metal.



b. Ethylenediamine tetraacetate ion $(EDTA)^{4-}$ binds to metal ion by electron pairs of four oxygen and two nitrogen atoms. It is a hexadentate ligand.



iii. The ligands which have two donor atoms and use the electron pair of either donor atoms to form a coordinate bond with the metal ion, are ambidentate ligands. For example, the ligand $NO_2^-$ links to metal ion through nitrogen or oxygen.



Similarly, $SCN^-$ has two donor atoms nitrogen and sulfur either of which links to metal depicted as M ← $SCN^-$ or M ← $NCS^-$.

***Q.8 What are bidentate ligands ? Give one example.**

**Ans :** Refer Q7 (ii) (a)

**Q.9 Classify the below given ligands into monodentate, polydentate and ambidentate ligands.**

**i. $CN^-$ ii. $Cl^-$**
**iii.$(C_2O_4)_2^-$ iv. $NO_2^-$**
**v. $SCN^-$ vi.$(EDTA)_4^-$**

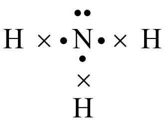
**Ans :**

| Types of ligand | Monodenate | Polydentate | Ambidentate |
|---|---|---|---|
| Ligand | $CN^-$, $Cl^-$ | $(C_2O_4)^{2-}$ ,<br>$(EDTA)^{4-}$ | $NO_2^-$, SCN |

**+Q. 10 Use your brain power**
**Draw Lewis structure of the following ligands identify the donor atom in them : $NH_3$, $H_2O$**

**Ans :**

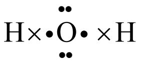
i. Lewis structure of $NH_3$:



$$H \times \bullet \ddot{N} \bullet \times H \atop {\bullet \atop {\times \atop H}}$$

In $NH_3$, Nitrogen (N) is donor atom.

ii. Lewis structure of $H_2O$ :



$$H \times \bullet \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \bullet \times H$$

In $H_2O$, Oxygen (O) is the donor atom.

## 9.3 Terms used in coordination chemistry

**Q.11 Define the given terms and give examples.**

**i. Coordination sphere**

**ii. Complex ion.**

**iii. Counter ion.**

**Ans:**

i. **Coordination sphere.**

A discrete structural unit in which the cental metal ion and ligands linked to it are enclosed in a square bracket is called coordenation sphere. For example - In compound $K_4[Fe(CN)_6$. $[Fe(CN)_6]^{4-}$ is coordination sphere.

ii. **Complex ion-**

The coordination sphere comprising central metal ion and the surrounding ligand together carrying a net charge, it is called the complex ion.

For example- In $K_4[Fe(CN)_6]$ $[Fe(CN)_6]^{4-}$ is a complex ion.

iii. **Counter ion-**

The ionisable groups shown outside the bracket in a coordination compound are the counter ions.

For example

Compound $K_4[Fe(CN)_6]$ will ionize as

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

Here $K^+$ is the counter ion.

**Q.12 Try This**

**Can you write ionisation of $[Ni(NH_3)_6]Cl_2$? Identify coordination sphere and counter ions.**

**Ans:** The compound $[Ni(NH_3)_6]Cl_2$ ionzes as :

$$[Ni(NH_3)_6]Cl_2 \rightarrow [Ni(NH_3)_6]^{2+} + 2Cl^-$$

The compound $[Ni(NH_3)_6]Cl_2$ has $[Ni(NH_3)_6]^{2+}$ as coordination sphere $Cl^-$ as counter ion and $[Ni(NH_3)_6]^{2-}$ as complex ion.

**Q.13 What is charge number of complex ion in coordination compound?**

**Ans:** The net charge residing on the complex ion is its charge number. It is algebraic sum of the charges carried by the metal ion and the ligands.

For example - $[Fe(CN)_6]^{4-}$ has charge number of -4.

**Q.14 Calculate the oxidation state of Fe in $[Fe(CN)_6]^{4-}$**

**Ans:** The complex $Fe[CN_6]^{4-}$ has charge number of – 4.

It can be utilised to calculate O.S. of Fe. Thus,

Charge number of complex = -4

= (O.S. of Fe + 6 × Charge of $CN^-$ ion)

= (O.S. of Fe + 6 × (1)

Therefore, O.S. of Fe = –4 + 6 = + 2.

**Q.15 Can you tell ?**

**A complex is made of Co(III) and consists of four $NH_3$ molecules and two $Cl^-$ ions as ligands. What is the charge number and formula of complex ion ?**

**Ans:** The formula of the complex ion is $[Co(NH_3)_4Cl_2]$ and the charge on the complex ion is +1.

**Q.16 What is coordination number (C.N.)?**

**Ans:** C.N. of metal ion in a complex is the number of ligand donor atoms directly attached to it or the number of electron pairs involved in the coordinate bond.

**Q.17 Find out the coordination number of the following coordination compounds.**

**i. $[Co(NH_3)_4Cl_2]^+$**

**ii. $[Fe(C_2O_4)_3]^{3-}$**

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

**Ethylenediammine (en)**

**Ans:**

i. **$[Co(NH_3)_4Cl_2]^+$**

The central metal atom is co lignad are $NH_3$ and Cl

Total number of ligand = $(NH_3)_4 + Cl_2 = 6$

Type of ligand is monodentate.

(Only one donor atom)

Therefore total 6 donor atoms are attached to co ion.

Therefore, the coordination number of $Co^{3+}$ ion in the complex is six.

ii. **$[Fe(C_2O_4)_3]^{3-}$**

The central metal atom is Fe

Ligand is $(C_2O_4)$

Total number of ligands = $(C_2O_4)_3 = 3$

Type of ligand = Bidentate (two donor atom).

Total 6 donor atoms are there in the complex.

Therefore the coordination of $Fe^{3+}$ ion in the complex is six.

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

The central metal atom is Co.

The ligand is Ethylenediammine (en)

Total number of ligand = $(en)_3 = 3$

The type of ligand is bidentate (two donor atom)

Total 6 donor atoms are there in the complex.

Therefore the coordination of $Co^{3+}$ ion in the complex is 6.

**Q.18 Use your brain power.**

**Coordination number used in coordination of compound is somewhat different than that used in solid state. Explain.**

**Ans:** In coordination compound, coordination number is the number of ligands (or groups) that surrounds the central metal atom or ion. In solid state.coordination number is the number of spheres (or Particles) that is directly connected with any given sphere.

**Q.19 What is the coordination number and oxidation state of metal ion in the complex $[Pt(NH_3)Cl_5]^-$ ?**

**Ans:** In the coordination compound $[Pt(NH_3)Cl_5]^-$ the oxidation state of metal ion is +4 and the coordination number of metal ion is +4.

**Q.20 Can you tell ?**

**What is the coordination number of**

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

**ii. Ir in $[Ir(C_2O_2)_2Cl_2]^{3+}$ and**

**iii. Pt in $[Pt(NO_2)_2(NH_3)_2]$ ?**

**Ans:**

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

The central metal atom is cobalt (Co) there are two ligands Cl and (en) ethylenediammine. There are two types of ligands, i.e. Cl which is monodentate and (en) bidentate.

Therefore total 6 donor atoms are there in the complex.

Therefore the coordination number of Co in $[CoCl_2(en)_2]^+$ is six.

**ii. Ir in $[Ir(C_2O_2)_2Cl_2]^{3+}$**

**Ans:** The central metal atom is Ir.

There are two ligands i.e. $(C_2O_2)$ and Cl.

There are two types of ligands, $(C_2O_2)$ which is bidentate and Cl is monodentate Total 6 donor atoms are there in the complex.

Therefore, The coordination number of Ir in $[Ir(Pt(C_2O_2)_2Cl_2]^{3+}$ is six.

**iii. Pt in $[Pt(NO_2)_2(NH_3)_2]$**

**Ans:** The central metal atom is Pt there are two ligands i.e. $(NO_2)$ and $(NH_3)$

Both the ligands are monodentate total 4 donor atoms are there in the complex.

Therefore, the coordination number of Pt in $[Pt(NO_2)_2(NH_3)_2]$ is four.

**Q.21 What is the coordination number and oxidation state of metal ion in the complex $[Pt(NH_3)Cl_5]$ ?**

**Ans:** In $[Pt(NH_3)Cl_5]^-$ complex, The coordination number of metal ion is 6 and oxidation state of metal ion is +4.

In $[Pt(NH_3)Cl_5]^-$ the central metal atom is Pt. There are two ligand i.e.$NH_3$ and Cl Both the ligands are monodentate therefore total number of donor atoms are 6.

The total charge on complex is –1.

Chrge on ligands

Charge on $NH_3$ = 0.

Charge on $Cl^-$ ion = –1.

| Total Charge = on complex | Oxidation + State of Pt | Charge on ligands. |
|---|---|---|

$$-1 = \underset{\text{state to Pt}}{\text{Oxidation} +} \; \underset{\text{of } NH_3)}{(1 + \text{Charge} +} \; \underset{\text{of } Cl^{-} \text{ ion)}}{(5 \times \text{charge}}$$

–1 = Oxidation state of Pt + 1(0) + 5 × (–1)

–1 = Oxidation state of Pt + 0 –5

–1 + 5 = Oxidation state of Pt

Oxidation state of Pt = +4

**Q.22 Combination of the two or more stable compounds in stoichiometric ratio can give two types of substance. Name the types.**

**Ans:**

i. Double salt

ii. Coordination complex.

**Q.23 How double salt and coordination complex dissociates in water?**

**Ans:** A double salt dissociates in water completely into simple ions. For example (i) Mohr's salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ dissociates as :

$$FeSO_4(NH_4)_2SO_4.6H_2O \xrightarrow{\text{water}} Fe^{2+}(aq) + 2NH_4^{+}(aq) + 2SO_4^{2-}(aq)$$

ii. Carnalite $KCl.MgCl_2.6H_2O$ dissociates as

$$KCl.MgCl_2.6H_2O \xrightarrow{\text{water}} K^{+}(aq) + Mg^{2+}(aq) + 3Cl^{-}(aq)$$

complex : A coordination complex dissociates in water with at least one complex ion. For example, $K_4[Fe(CN)6]$ dissociates as the complex ion and counter ion.

$$K_4[Fe(CN)_6 \rightarrow \underset{\text{(counter ion)}}{4K^{+}(aq)} + \underset{\text{(complex ion)}}{[Fe(CN)_6]^{4-}}$$

**Q.24 What is difference between a double salt and a complex? give an example.**

**Ans:**

**i.** A double salt dissociates in water completely into simple ions.
Example – Mohr's salt dissociates as

$$\underset{\text{Mohr's salt}}{FeSO_4(NH_4)_2SO_4.6H_2O} \xrightarrow{\text{water}} Fe^{2+}(aq) + 2NH_4^{+}(aq) + 2SO_4^{2-}(aq)$$

ii. A coordination complex dissociates in water with at least one complex ion.
For Example–

$$K_4[Fe(CN)_6] \rightarrow \underset{\text{(counter ion)}}{4K^{+}(aq)} + \underset{\text{(complex ion)}}{[Fe(CN)_6]^{4-}}$$

**Q.25 Give the postulates of Werner theory of coordination complexes.**

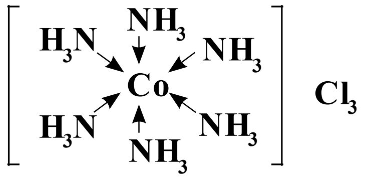
**Ans:** The first attempt to explain nature of bonding in coordination compounds was put forth by Werner. The postulates of Werner theory are as follows.

i. Unlike metal salts, the metal in a complex possesses two types of valencies : primary (ionizable) valency and secondary (nonionizable) valency.

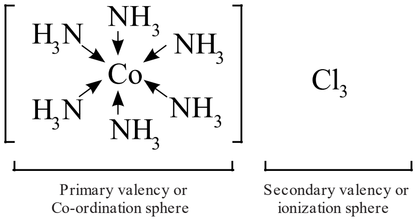
ii. The ionizable sphere consists of entities which satisfy the primary valency of the metal. Primary valencies are generally satisfied by anions.

iii. The secondary coordination sphere consists of entities which satisfy the secondary valencies and are non ionizable.

**Q.26 Identify the primary valency or Co-ordination sphere and secondary valency or ionization sphere.**



**Ans :**



**Q.27 Why $[Co(NH_3)_6]Cl_3$ does not give the test for $Co^{3+}$ or $NH_3$ when dissolved in water?**

**Ans:** When a complex is brought into solution it does not dissociate into simple metal ions. When $[Co(NH_3)_6]$ $Cl_3$ is dissolved in water it does not give the test for $Co^{3+}$ or $NH_3$.

**Q.28 What happen when aqueous solution of $[Co(NH_3)_6]Cl_3$ is treated with $AgNO_3$**

**Ans:** However, on reacting with $AgNO_3$ a curdy white precipitate of AgCl corresponding to 3 moles is observed.

**+Q.29 One mole of a purple coloured complex $CoCl_3$ and $NH_3$ on treatment with excess $AgNO_3$ produces two moles AgCl. Write the formula of the complex if the coordination number of Co is 6.**

**Ans :** One mole of the complex gives 2 moles of AgCl. It indicates that two Cl ions react with Ag. ions. The complex has two ionisable Cl ions. The formula of the complex is then $[Co(NH_3)_5Cl]Cl_2$.

**+Q.30 Can you tell ?**

**One mole of a green coloured complex of $CoCl_3$ and $NH_3$ on treatment with excess of $AgNO_3$ produces 1 mole of AgCl. What is the formula of the complex ? (Given : C.N. of Co is 6)**

**Ans:** One mole of complex on reaction with excess $AgNO_3$ produces 1 mole of AgCl. The excess of $AgNO_3$ reacts with $Cl^-$ giving AgCl. One mole of AgCl is obtained means only one Cl is free thus.The formula of the complex is $[Co(NH_3)_5Cl]Cl_2$.

**Q.31 What will be the shape of a complex in which the coordination number of central metal ion is 6**

**Ans:** A complex with coordinaiton number six will have octahedral structure.

**Q.32 What will be the shape of a complex in which the coordination number of central metal ion is 4 ?**

**Ans:** A complex with coordination number four will have square planar or octanedral structure.

## 9.4 Classificaiton of Complexes

**Q.33 How are complexes classified on the basis of types of ligands**

**Ans:** Classification on the basis of types of ligands

i. Homoleptic complexes : Consider $[Co(NH_3)_6]^{3+}$. Here only one type of ligands surrounds the $Co^{3+}$ ion. The complexes in which metal ion is bound to only one type of ligands are homoleptic.

ii. Heteroleptic complexes : Look at the complex $[Co(NH_3)_4Cl_2]^+$. There are two types of ligands, $NH_3$ and Cl attached to $Co^{3+}$. ion. Such complexes in which metal ion is surrounded by more than one type of ligands are heteroleptic.

**+Q.34 Use your brain power**

**Classify the complexes as homoleptic and heteroleptic**

**$[Co(NH_3)_5Cl]SO_4$, $[Co(ONO)(NH_3)_5]Cl_2$ $[CoCl(NH_3)(en)_2]^{2+}$ and $[Cu(C_2O_4)_3]^{3-}$**

**Ans :**

| **Homoleptic Complexes** | **Heteroleptic Complexes** |
|---|---|
| $[Cu(C_2O_4)_3]^{3-}$ | $[Co(NH_3)_5]Cl_4$ |
| | $[Co(ONO)(NH_3)_5]Cl_2$ |
| | $[CoCl(NH_3)(en)_2]^{2+}$ |

**★Q.35 What are cationic, anionic and neutral complexes? Give one example of each.**

**Ans:** **Cationic complexes :** A positively charged coordination sphere or a coordination compound having a positively charged coordination sphere is called cationic sphere complex.

Example - $[Zn(NH_3)_4]^{2+}$

**Anionic sphere complexes :** A negatively charged coordination sphere or a coordination compound having negatively charged coordination sphere is called

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

**Neutral sphere complexes :** A neutral coordination complex does not possess cationic or anionic sphere.

Example - $[Pt(NH_3)_2Cl_2]$

**Q.36 Use your brain power.**

**Classify the complexes as cationic, anionic or neutral. $Na_4[Fe(CN)_6]$, $Co(NH_3)_6Cl_2$, $Cr(H_2O)_2(C_2O_4)_2$ $^{3-}$, $PtCl_2(en)_2$ and $Cr(CO)_6$.**

**Ans:**

| **Cationic Complexes** | **Anionic Complexes** | **Neutral Complexes** |
|---|---|---|
| $Co(NH_3)Cl_2$ | $Na_4[Fe(CN)_6]$ | $PtCl_2(en)_2$ |
| | $Cr(H_2O)_2(C_2O_4)_2^{3-}$ | $Cr(Co)_6$ |

**Q.37 Classify follwing complexes as homolptic and heteroleptic**

**$[Cu(NH_3)_4]SO_4$, $[Cu(en)_2(H_2O)Cl]^{2+}$ $[Fe(H_2O)_5(NCS)]^{2+}$, tetraamminezinc (III) nitrate.**

**Ans:**

| Homoleptic Complexes | Heteroleptic Complexes |
|---|---|
| $[Cu(NH_3)_4]SO_4$ | $[Cu(en)_2(H_2O)Cl]^{2+}$ |
| tetraammine zinc(III)nitrate. | $[Fe(H_2O)_5(NCS)]^{2+}$ |

## 9.5 IUPAC nomenclature of coordination compounds

**Q.38 Give the rules for naming coordination compounds recommended by IUPAC.**

**Ans:**

Rules for naming coordination compounds recommended by IUPAC are as follows:

i. In naming the complex ion or neutral molecule, name the ligand first and then the metal.

ii. The names of anionic ligands are obtained by changing the ending -ide to -o and -ate to-ato.

iii. The name of a complex is one single word. There must not be any space between different ligand names as well as between ligand name and the name of the metal.

iv. After the name of the metal, write its oxidation state in Roman number which appears in parentheses without any space between metal name & parentheses. If complex has more than one ligand of the same type, the number is indicated with prefixes, di-, tri-, tetra-, penta-, hexa- and so on.

vi. For the complex having more than one type of ligands, they are written in an alphabetical order. Suppose two ligands with prefixes are tetraaqua and dichloro. While naming in alphabetical order, tetraaqua is first and then dichloro.

vii. If the name of ligand itself contains numerical prefix then display number by prefixes with bis for 2, tris for 3, tetrakis for 4 and so forth. Put the ligand name in parenthese. For example, $(ethylenediamine)_3$ or $(en)_3$ would appear as tris(ethylenediamine) or tris(ethane-1, 2-diamine).

viii. The metal in cationic or neutral complex is specified by its usual name while in the anionic complex the name of metal ends with 'ate'.

| Anionic ligand | IUPAC name | Anionic ligand | IUPAC name |
|---|---|---|---|
| $Br^{\ominus}$, Bromide | Bromo | $CO_3^{2\ominus}$, Carbonate | Carbonato |
| $Cl^{\ominus}$, Chloride | Chloro | $OH^{\ominus}$, Hydroxide | Hydroxo |
| $F^{\ominus}$, Fluoride | Fluoro | $C_2O_4^{2\ominus}$, Oxalate | Oxalato |
| $I^{\ominus}$ Iodide | Iodo | $NO_2^{\ominus}$, Nitrite | Nitro(For N - bonded ligand) |
| $CN^{\ominus}$, Cyanide | Cyano | $ONO^{\ominus}$, Nitrite | Nitrito(For O-bonded ligand) |
| $SO_4^{2\ominus}$, Sulphate | Sulphato | $SCN^{\ominus}$, Thiocyanate | Thiocyanato (For ligand donor atom S) |
| $NO_3^{\ominus}$, Nitro | Nitrato | $NCS^{\ominus}$, Thiocyanate | Isothiocyanato (For ligand donor atom N) |
| Neutral ligand | IUPAC name | Neutral ligand | IUPAC names |
| $NH_3$, Ammonia | Ammine (Note the spelling) | $H_2O$, water | Aqua |
| CO, Carbon monoxide | Cabonyl | en, Ethylene diamine | Ethylenediamine |

**IUPAC name of anionic and neutral ligands**

| Metal | IUPAC name | Metal | IUPAC name |
|---|---|---|---|
| Aluminium, Al | Aluminate | Chromium, Cr | Chromate |
| Cobalt, Co | Cobaltate | Copper, Cu | Cuprate |
| Gold,Au | Aurate | Iron, Fe | Ferrate |
| Manganese, Mn | Maganate | Nickel, Ni | Nickelate |
| Platinum, Pt | Platinate | Zinc, Zn | Zincate |

**IUPAC name of metals and anionic complexes**

| Complex | IUPAC name |
|---|---|
| i.Anionic complexes :<br>a.$[Ni(CN)_4]^{2\ominus}$<br>b. $[Co(C_2O_4)_3]^{3\ominus}$<br>c. $[Fe(CN)_6]^{4\ominus}$ | Tetracyanonickelate(II) ion<br>Trioxalatocobaltate(III) ion<br>Hexacyanoferrate(II) ion |
| ii. Compounds containing complex anions and metal cations : | |
| a. $Na_3[Co(NO_2)_6]$<br>b. $K_3[Al(C_2O_4)_3]$<br>c. $Na_3[AlF_6]$ | Sodium hexanitrocobaltate(III)<br>Potasium trioxalatoaluminate(III)<br>Sodium hexafluoroaluminate(III) |
| iii. Cationic complexes :<br>a. $[Cu(NH_3)_4]^{2+}$<br>b.$[Fe(H_2O)_5(NCS)]^{2+}$<br>c.$[Pt(en)_2(SCN)_2]^{2+}$ | Tetraamminecopper(II) ion<br>Pentaaquaisothiocyanatoiron(III) ion,<br>Bis(ethylenediamine)dithiocyanatoplatinum(IV). |
| iv. Compounds containing complex cations and anion : | |
| a. $[PtBr_2(NH_3)_4]Br_2$<br>b. $[Co(NH_3)_5CO_3]Cl$<br>c. $[Co(H_2O)(NH_3)_5]I_3$ | Tetraamminedibromoplatinum(IV)bromide,<br>Pentaamminecarbonatocobalt(III)chloride,<br>Pentaammineaquacobalt(III)iodide. |
| v. Neutral complexes:<br>a. $[Co(NO_2)_3(NH_3)_3]$<br>b. $Fe(CO)_5$<br>c. $[Rh(NH_3)_3(SCN)_3]$ | Triamminetrinitrocobalt(III)<br>Pentacarbonyliron(0)<br>Triamminetrithiocyanatorhodium(III) |

**IUPAC name of some complexes**

**+Q.39 Try this**

**Write the representation of**

**i. Tricarbonatocobaltate (III) ion.**

**ii. Sodium hexacyanoterrate (III).**

**iii. Potassium hexacynoferrate (II).**

**iv. Aquachiorobis (ethylenediamine) cobalt (III).**

**v. Tetraauadichlorochromium (III) chloride.**

**vi. Diamminedichloroplatinum (II)**

**Ans:**

i. **Tricarbonatocobaltate (III) ion** :
$[Co(CO_3)_3]^{3-}$

ii. **Sodium hexacynoferrate (III) :**
$[Na_3[Fe(CN)_6]$

iii. **Potassium hexacyanoterrate (II) :**
$K_4[Fe(CN)_6]$

iv. **Aquachlorobis (ethyenediamine) cobalt (III) :**
$[Co(H_2O)Cl(en)_2]^{2+}$

v. **Tetraaqudichlorochromium (III) chloride :**
$[Cr(H_2O)_4Cl_2]Cl$

vi. **Diamminedichioroplatinum (II):**
$[Pt(NH_3)_2Cl_2]$

**★ Q.40 Write formula of the following complexes.**

**i. Potassium amminetrichloro platinate (II)**

**ii. Dicyanoaurate (I) ion.**

**Ans:**

i. $[Pt(NH_3)_4Cl_3]$

ii. $[Au(CN)_2]^-$

**Q.41 Write the formula for tetraammineplatinum (II) chloride.**

**Ans:** tetraammineplatinum (II) chloride :
$[Pt(NH_3)_4Cl_2]$

**Q.42 Write IUPAC name of the following complexes.**

**i. $[Pt(NH_3)_2Cl(NO_2)]$**
**ii. $K_3[Fe(CN)_6]$**
**iii. $[Ni(NH_3)_6]Cl_2$**
**iv. $[Co(Co_3)(NH_3)_4]Cl$**
**v. $[Ag(NH_3)_2Cl]$**
**vi. $[Co(en)_2Cl_2]Cl$**
**vii. $Na_3[AlF_6]$**
**viii. $K_2[PdCl_4]$**

**Ans:**

i. Diamminechloridonitrito - N - Platinum (II).
ii. Potassium hexacyanoterrate (III)
iii. Hexaamminenickel (III) chloride.
iv. Tetraamminecarbonatocobalt (III) chloride.
v. Diamminsilver (I) chloride.
vi. Dichloridobis (ethane –1, 2– diamine) cobalt (III) chloride.
vii. Sodiumhexafluraaluminate (III)
viii. Potassiumtetrachloridepalladate (II)

## 9.6 Effective Atomic Number (EAN rule)

**+Q.43 State and explain : Effective atomic number (EAN) rule.**

**Ans:**

i. Sidgwick who proposed an empirical rule known as effective atomic number (EAN) rule.
ii. EAN equals total number of electrons around the central metal ion in the complex.
iii. Rule states that a metal ion continues to accept electrons pairs till it attains the electronic configuration of the next noble gas.
iv. Thus if the EAN is equal to 18 (Ar), 36 (Kr), 54 (Xe), or 86 (Rn) then the EAN rule is obeyed. EAN can be calculated with the following formula
EAN = number of electrons of metal ion + total number of electrons donated by ligands = atomic number of metal (Z) – number of electrons lost by metal to form the ion (X) + number of electrons donated by ligands (Y) = Z – X + Y.

**+Q.44 Try This**

**Find out the EAN of :**
**i. Zn in $[Zn(NH_3)_4]^{2+}$**
**ii. Fe in $[Fe(CN)_6]^{4-}$**

**Ans:**

i. Zn in $[Zn(NH_3)_4]^{2+}$
Oxidation state of Zn(x) = +2
Atomic number of Zn(Z) = 30
Number of electrons donated by ligands (v) = 8
EAN of $Zn^{2+}$ = Z – X + Y
= 30 – 2 + 8 = 36

ii. Fe in $[Fe(CN)_6]^{4-}$
Oxidation number of Fe(X) = +2
Atomic number of Fe (Z) = 26
Number of electrons donated by ligands (v) = 12
EAN of $Fe^{2+}$ = Z – X + Y
= 26 – 2 + 12 = 36.

**Q.45 Do the following complexes following complexes follow the EAN rule.**

**i. $Cr(CO)_6$** **ii. $[Fe(CN)_6]^{4-}$**
**iii. $[Fe(CN)_6]^{3-}$** **iv. $Cu[NH_3]_4^{2+}$**

**Ans:**

i. **$Cr(Co)_6$**
Oxidation number of Cr(X) = 0
Atomic number of Cr(Z) = 24
Number of electrons donated by ligands (Y) = 12
EAN of Cr = Z – X + Y
= 24 – 0 + 12 = 36
$Cr\ (Co)_6$ obeys effective nuclear charge (EAN) rule.

ii. **$[Fe(CN)_6]^{4-}$**
Oxidation number of Fe (X) = 2
Atomic number of Fe (Z) = 26
Number of electrons donated by ligands (Y) = 12
EAN of $Fe^{2+}$ = Z – X + Y
= 26 – 2 + 12 = 36
$[Fe(CN)_6]^{3-}$ obey effective nuclear charge

iii. **$[Fe(CN)_6]^{3-}$**

Oxidation number of Fe (X) = +3

Atomic number of Fe(Z) = 26

Number of electrons donated by lignads (Y) = 12

EAN of $Fe^{3+}$ = Z – X + Y

= 26 –3 + 12 = 35

$[Fe\ (CN)_6]^{3-}$ do not obey effective nuclear charge.

**+Q.46 Use your brain power**

**Do the following complexes follow EAN rule?**

**i. $Cr(CO)_4$** **ii. $Ni(CO)_4$**
**iii. $Mn(CO)_5$** **iv. $Fe(CO)_5$**

**Ans:**

i. **$Cr(CO)_4$**

Oxidation number of Cr(X) = 0

Atomic number of Cr (Z) = 24

Number of electrons donated by ligands = (Y) = 8

EAN of Cr = Z – X + Y = 24 – 0 + 8 = 34

$Cr(CO)_4$ do not obey effective nuclear charge rule.

ii. **$Ni(CO)_4$**

Oxidation number of Ni(X) = 0

Atomic number of Ni(Z) = 28

Number of electrons donated by ligands (Y) = 8

EAN rule for Ni = Z – X + Y = 28 – 0 + 8 = 36

$Ni(CO)_4$ obeys effective nuclear charge (EAN) rule.

iii. **$Mn(CO)_5$**

Oxidation number of Mn(X) = 0

Atomic number of Mn (Z) = 25

Number of electrons donated by ligands = 10

EAN rule for $Mn(CO)_5$ = Z – X + Y

= 25 – 0 + 10 = 35

$Mn(CO)_5$ does not obey effective nuclear charge EAN rule.

iv. **$Fe(CO)_5$**

Oxidation state of Fe (X) = 0

Atomic number of Fe (Z) = 26

Number of electrons donated by ligands (Y) = 10

EAN rule for $Fe(CO)_5$ = Z – X + Y

= 26 – 0 + 10 = 36

$Fe(CO)_5$ obeys effective nuclear charge EAN rule.

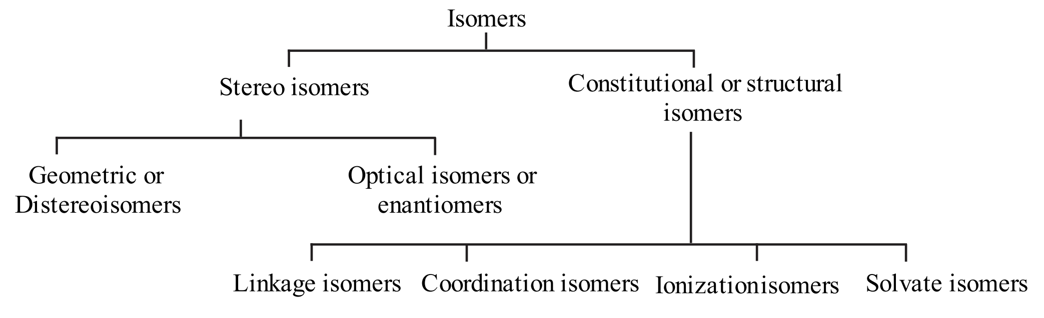
## 9.7 Isomerism in coordination compound

**Q.47 What are isomers ?**

**Ans:** Isomers are different compounds that have the same molecular formula. Their chemical reactivities and physical properties such as colour, solubility and melting point are different.

**Q.48 Draw the flow chart representing classification of isomers in coordination compounds.**

**Ans:**



**Classification of isomers in coordination compounds**

**Q.49 What are stereoisomers? And name the two kinds of isomers.**

**Ans:** Stereoisomers have the same links among constituent atoms however the arrangements of atoms in space are different. There are two kinds of stereoisomers in coordination compounds: (a) geometric isomers or distereoisomers and (b) enantiomers or optical isomers.

**Q.50 Explain the term distereoisomers or geometric isomers.**

**Ans:** **Geometric isomers or distereoisomers :** These are non superimposable mirror image isomers. These are possible in heteroleptic complexes. In these isomers, there are cis and trans types of arrangements of ligands.

**cis-isomers :** Identical ligands occupy adjacent positions.

**Trans-isomer :** Identical ligands occupy the opposite positions. Cis and trans isomers have different properties. Cis trans isomerism is observed in square planar and octahedral complexes.

**Q.51 Explain cis and trans isomers in square planar complexes.**

**Ans :**

i. Cis and trans isomers in square planar complexes : The square planar complexes of $MA_2B_2$ and $MA_2BC$ type exist as cis and trans isomers, where A, B and C are monodentate ligands, M is metal.

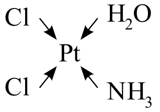
ii. For example : $Pt(NH_3)_2Cl_2$, ($MA_2B_2$ type). Here the cis isomer is more soluble in water than the trans isomer.

iii. The cis isomer named cisplatin is an anticancer drug while the trans isomer is physiologically inactive.

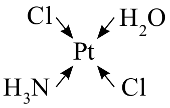
iv. The cis isomer is polar with non-zero dipole moment.

v. The trans isomer has zero dipole moment as a result of the two opposite Pt - Cl and two Pt-$NH_3$ bond moments, which cancel each other.

$[Pt(NH_3)(H_2O)Cl_2]$ ($MA_2BC$ type)



cis isomer

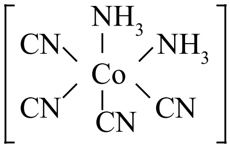


trans isomer

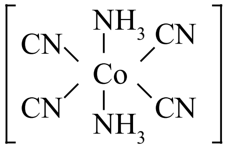
**+Q.52 Try this**

**Draw structures of the cis and trans isomers of $[Fe(NH_3)_2(CN)_4]^-$**

**Ans:** Cis and trans isomers of $[Fe(NH_3)_2(CN)_4]^-$



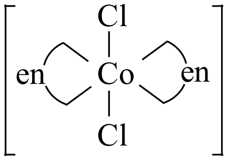
cis isomer



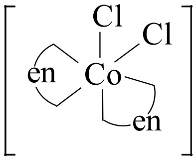
trans isomer

**Q.53 Draw structures of the cis and trans isomers of $[CoCl_2(en)_2]^+$**

**Ans:**



trans$[CoCl_2(en)_2]^+$



cis isomer $[CoCl_2(en)_2]^+$

**Q.54 Write a short note on : optical isomerism.**

**Ans:** **Optical isomers (Enantiomers) :**

i. The complex molecules or ions that are non superimposable mirror images of each other are enantiomers.

ii. The non superimposable mirror images are chiral. (A more elaborate discussion on chirality and optical isomerism is included)

iii. Enantiomers have identical properties however differ in their response to the plane polarized light.

iv. The enantiomer that rotates the plane of plane-polarized light to right (clockwise) is called the dextro *(d)* isomer, while the other that rotates the plane to left (anticlockwise) is called laevo *(l)* isomer.

v. Square planar complexes do not show enantiomers since they have mirror plane and axis of symmetry

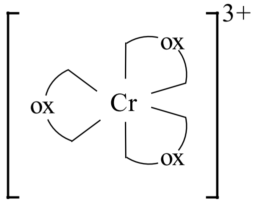
**Remember**

Our hands are non superimposable mirror images. When you hold your left hand upto a mirror the image looks like right hand.

**Q.55 Try this**

**i. Draw enantiomers of $[Cr(ox)_3]^{3-}$**

**Ans :**



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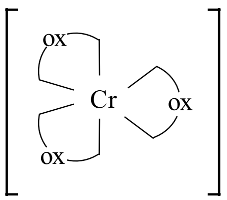

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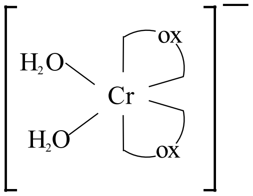
**ii. Draw enantiomers and cis and trans isomers of $[Cr(H_2O)_2(ox)_2]^-$ (where ox = $C_2O_4^{2-}$)**

**Ans :**

a. Eantiomers of $[Cr(H_2O)_2(ox)_2]$



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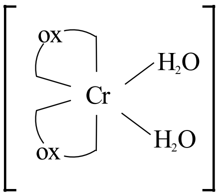

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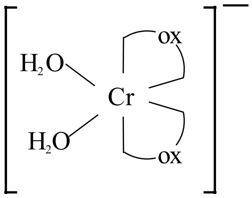
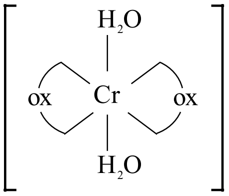
b. Cis and trans isomers of $[Cr(H_2O)_2(ox)_2]^-$



cis-$[Cr(H_2O)_2(ox)_2]^-$



trans-$[Cr(H_2O)_2(ox)_2]^-$

**★ Q.56 Draw isomers in each of the following**

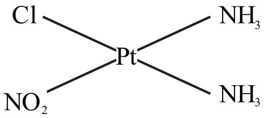
**i. $Pt(NH_3)_2ClNO_2$**

**ii. $Ru(NH_3)_4Cl_2$**

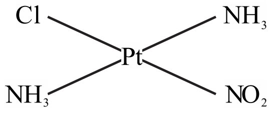
**iii. $[Cr(en)_2Br_2]^+$**

**Ans :**

i. $Pt(NH_3)_2ClNO_2$

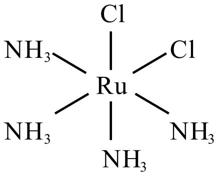


cis-$[Pt(NH_3)_2ClNO_2]$

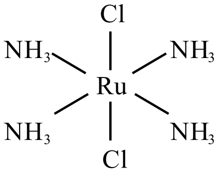


trans-$[Pt(NH_3)_2ClNO_2]$

ii. $Ru(NH_3)_4Cl_2$



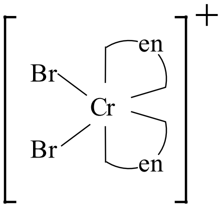
cis - $[Ru(NH_3)_4Cl_2]$



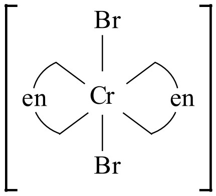
trans - $[Ru(NH_3)_4Cl_2]$

iii. $[Cr(en)_2Br_2]^+$

a. cis and trans isomers of $[Cr(en)_2Br_2]^+$

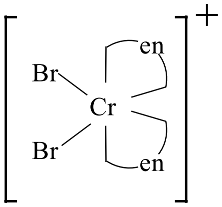


cis-$[Cr(en)_2Br_2]^+$



trans-$[Cr(en)_2(Br)_2]^+$

b. Optical isomers of $[Cr(en)_2Br_2]^+$



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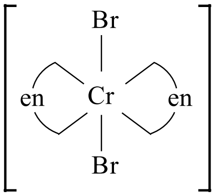

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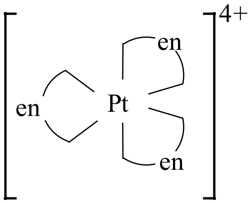
**★ Q.57 Draw geometric isomers and enantiomers of the following complexes.**

**i. $[Pt(en)_3]^{4+}$**

**ii. $[Pt(en)_3]^{4+}$**

**Ans :**

i. enantiomers of $[Pt(en)_3]^{4+}$



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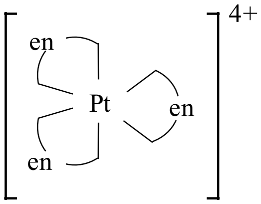

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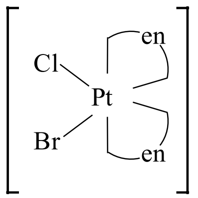
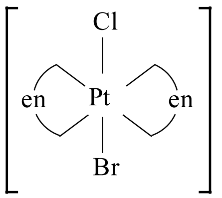
ii. a. Geometric isomers of $[Pt(en)_2ClBr]^{2+}$

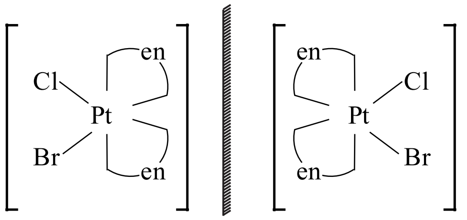


cis-$[Pt(en)_2ClBr]^{2+}$



trans-$[Pt(en)_2ClBr]^{2+}$

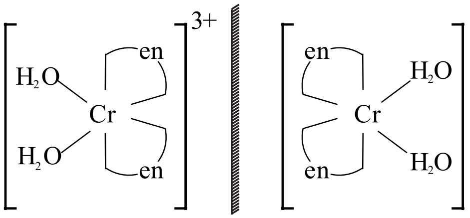
b. Optical isomers or enantiomers of $[Pt(en)_2ClBr]^{2+}$



★ **Q.58 Predict whether the $[Cr(en)_2(H_2O)_2]^{3+}$ complex is chiral. Write the structure of its enantiomers.**

**Ans :** i. $[Cr(en)_2(H_2O)_2]^{3+}$ is chiral complex.

ii. Optical isomers of $[Cr(en)_2(H_2O)_2]^{3+}$



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**Q.59 What are structural isomers or constitutional isomers ? How they are classified ?**

**Ans :**

i. Structural isomers possess different linkages among their constituent atoms and have, their chemical formulae to be the same.

ii. They can be classified as linkage isomers, ionization isomers, coordination isomers and solvate isomers.

**Q.60 Write a short note on linkage isomers.**

**Ans :**

i. These isomers are formed when the ligand has two different donor atoms.

ii. It coordinates to the metal via different donor atoms.

iii. Thus the nitrite ion $NO_2^-$ having two donor atoms show isomers as: $[Co(NH_3)_5(NO_2)]^{2-}$ and $[Co(NH_3)_5(ONO)]^{2+}$

iii. The nitro complex has Co-N bond and the nitrito complex is linked through Co–O bond. These are linkage isomers.

**+Q.61 Can you tell?**

**Write linkage isomers of $[Fe(H_2O)SCN]^+$. wirte their IUPAC names.**

**Ans :**

i. The linkage isomer of $[Fe(H_2O)SCN]^+$. is$[Fe(H_2O)_5(NCS)]^+$

ii. IUPAC Names:

a. $[Fe(H_2O)_5SCN]^+$ : Pentaaquathiocyanatoiron(III)ion.

b. $[Fe(H_2O)(NSC)]^+$ : pentaaquaisothiocyanatoiron(III)ion.

**Q.62 Write a short note on ionization isomers.**

**Ans:**

i. Ionization isomers involve exchange of ligands between coordination and ionization spheres. for example:

$\underset{(I)}{[Co(NH_3)_5SO_4]Br}$ and

$\underset{(II)}{[Co(NH_3)_5Br]SO_4}$

ii. In compound I, anion $SO_4^{2-}$, bonded to Co is in the coordination sphere while $Br^-$ is in the ionization sphere.

iii. In compound II, anion $Br^-$ is in the coordination sphere linked to Co while $SO_4^{2-}$ is in the ionisation sphere.

iii. These complexes in solution ionize to give different ions.

$$[Co(NH_3)_5SO_4]Br \rightarrow [Co(NH_3)_5SO_4]^+ Br^-$$

$$[Co(NH_3)_5Br]SO_4 \rightarrow [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$$

I and II are examples of ionization isomers.

**+Q.63 Can you tell?**

**Can you write IUPAC name of isomers $[Co(NH_3)_5SO_4]$ Br and $[Co(NH_3)_5Br]SO_4$**

**Ans:**

i. $[Co(NH_3)_5SO_4]Br$

IUPAC names: Pentamminesulphatocobalt (III)bromide.

ii. $[Co(NH_3)_5Br]SO_4$

IUPAC Names: Pentamminebromocobalt (III)sulphate.

**Q.64 What are ionization isomers? Give an example.**

**Ans:** Isomers which involve exchange of ligands are called ionization isomers.

For example:

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

**Q.65 Explain : Coordination isomers.**

**Ans:**

i. Coordination isomers show interchange of ligands between cationic and anionic spheres of differnt metal ions. For example:

$$\underset{(I)}{\underset{\text{(cationic)}}{[Co(NH_3)_6]}\underset{\text{(anionic)}}{[Cr(CN)_6]}}$$

$$\underset{(II)}{\underset{\text{(cationic)}}{[Cr(NH_3)_6]}\underset{\text{(anionic)}}{[Co(CN)_6]}}$$

ii. In isomer I, cobalt is linked to ammine ligand and chromium t cyanide ligand.

iii. Inisomer II the lingand coordinating to metals are interchanged.

iv. Cobalt coordinates with cyanide ligand and chromium to $NH_3$ ligand.

v. I and II are examples of coordination isomers.

**Q.66 What are solvate isomers?**

**Ans:**

i. These are similar to ionization isomers. Look at the complexes.

$$\underset{(I)}{[Cr(H_2O)_6Cl_3}\text{ and}\underset{(II)}{[Cr(H_2O)_5Cl]Cl_2.H_2O}$$

ii. In compound I the solvent water is directly bonded to Cr. In compound II, $H_2O$ appears as the free solvent molecule. I an II represent solvate (hydrate) isomers.

## 9.8 Stability of the coordination compounds

**Q.67 Explain the stability of the coordination compound.**

**Ans:**

i. The stability of coordination compounds can be explained by knowing their stability constants.

ii. The stability is governed by metal, ligand interactions.

iii. In this the metal serves as electron-pair acceptor while the ligand as Lewis base (since it is electron donor).

iv. The metal-ligand interaction can be realized as the Lewis acid-Lewis base interaction.

v. Stronger the interaction greater is stability of the complex.

vi. Consider the equilibrium for the metal ligand interaction:

$$M^{a+}nL^{x-} \rightleftharpoons [ML_n]^{a++nx-}$$

vii. where a, x, [a+ + nx-] denote the charge on the metal, ligand and the complex, respectively.

viii. Now, the equilibrium constant Kis given by

$$K = \frac{[ML_n]^{a++nx-}}{[M^{a+}][L^{x-}]^n}$$

Stability of the complex can be explained in terms of K.

ix. Higher the value of K larger is the thermodynamic stability of the complex.

**Q.68 How stability of the coordination compound can be explained in terms of equilibriam constant?**

**Ans:**

i. The equibibria for the complex formation with the corresponding K values are given below.

$$Ag^+ + 2Cn^- \rightleftharpoons [Ag(CN)_2]^-\ K = 5.5\times10^{18}$$

$$Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}\ K = 2.0\times10^{27}$$

$$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}\ K = 5.0\times10^{33}$$

ii. From the above data, $[Co(NH_3)_6]^{3+}$ is more stable than $[Ag(CN)_2]^-$ and $[Cu(CN)_4]^{2-}$.

**Q.69 Name the factors governing the equilibrium constants of the coordination compounds.**

**Ans:** Stability of a complex is governed by

a. charge to size ratio of the metal ion and

b. nature of the ligand.

**Q.70 Explain the factors governing the stability of the complex.**

**Ans:** The factors that governs the stability of the complexes are :

i. **Charge to size ratio of the metal ion :**

a. Higher the ratio greater is the stability.for the divalent metal ion complexes their stability shows the trend:

$Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Cd^{2+}$

b. The above stability order is called Irving-William order. In the above list both Cu and Cd have the charge +2, however, the ionic radius of $Cu^{2+}$ is 69 pm and that of $Cd^{2+}$is 97 pm.

c. The charge to size ratio of $Cu^{2+}$is greater than that of $Cd^{2+}$

d. Therefore the $Cu^{2+}$ forms stable complexes than $Cd^{2+}$

ii. **Nature of the ligand**

a. A second factor that governs stability of the complexes is related to how easily the ligand can donate its lone pair of electrons to the central metal ion that is, the basicity of the ligand.

b. The ligands those are stronger bases tend to form more stable complexes.

**+Q.71 Use your brain.**

**The stability constant K or the $[Ag(CN)_2]^-$ is $5.5\times10^{18}$ while that for the corresponding $[Ag(NH_3)_2]^+$ is $1.6\times10^7$. Explain why $[Ag(CN)_2]^2$ is more stable.**

**Ans:**

i. The stability of the complex is determined by the value of the stability complex (K).

ii. The stability constant (K) of $[Ag(CN)_2]^-$ is higher than the stability constant of $[Ag(NH_3)_2]^+$

## 9.9 Theories of bonding in complexes

**Q.72 Name the theories that describes metal-ligand bonding in coordination compounds.**

**Ans:** The metal-ligand bonding in coordination compounds has been describes by valence bond theory (VBT) and crystal field theory (CFT).

**+Q.73 Can you recall ?**
**What is valence bond theory and concept of Hybridization ?**

**Ans:**

i. The valence bond theory uses a process called hybridization in which atomic orbitals that are similar in energy but not equivalent are combined mathematically that are properly oriented to form bonds.

ii. These new combinations are called hybrid atomic orbitals because they are produced by hybridizing two or more atomic orbitals from the same atom.

iii. The hybridized state is a theoretical step that describes how complexes are formed. VBT is based on the concept of hybridization. The hybrid orbitals neither exist nor can be detected help us to describe structure of coordination compounds.

**Q.74 What are the steps that are involved in describing bonding in coordination compounds ?**

**Ans:** The steps involved in describing bonding in coordination compounds using the VBT are given below :

i. Metal ion provides vacant d orbitals for formation of coordinate bonds with ligands.

ii. The vacant d orbitals along with s and p orbitals of the metal ion take part in hybridisation.

iii. The number of vacant hybrid orbitals formed is equal to the number of ligand donor atoms surrounding the metal ion which equals the coordination number of metal.

iv. Overlap between the vacant hybrid orbitals of the metal and filled orbitals of the ligand leads to formation of the metal-ligand coordinate bonds.

v. The hybrid orbitals used by the metal ion point in the direction of the ligand.

vi. The (n-1)d or nd orbitals used in hybridisation allow the complexes the be classified as (a) outer orbital and (b) inner orbital complexes.

vii. For hybridisaiton in the outer orbital complex nd orbitals are used, whereas in the inner orbital complexes (n-1)d orbitals are used.

viii. Type of hybridisation decides the structure of the complex. For example when the hybridisation is $d^2sp^3$ th structure is octahedral.

**Q.75 Complete the missing entries.**

| Coordination number | Geometry of complex | Hybridization |
|---|---|---|
| 2 | | sp |
| 4 | Tetrahedral | |
| 4 | Square planar | |
| 6 | | $d^2sp^3$ / $sp^3d^2$ |

**Ans:**

| Coordination number | Geometry of complex | Hybridization |
|---|---|---|
| 2 | Linear | sp |
| 4 | Tetrahedral | $sp^3$ |
| 4 | Square plannar | $dsp^3$ |
| 6 | Octahedral | $d^2sp^3$ / $sp^3d^2$ |

**Q.76 Write the steps involved to understand the metal-ligand bonding in coordination complex using valence bond theory.**

**Ans:** Steps to understand the metal-ligand bonding include:

i. Find oxidation state of central metal ion

ii. Write valence shell electronic configuration of metal ion.

iii. See whether the complex is low spin or high spin. (applicable only for octahedral complexes with d4 to d8 electronic configurations).

iv. From the number of ligands find the number of metal ion orbitals required for bonding.

v. Identify the orbitals of metal ion available for hybridisation and the type or hybridisation involved.

vi. Write the electronic configuration after hybridisation.

vii. Show filling of orbitals after complex formation.

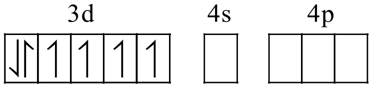
viii. Determine the number of unpaired electrons and predict magnetic behaviour of the complex.

**Q.77 Explain the structure of octahedral high spin complex.[CoF]$^{3-}$**

**Ans:** $[Co(NH_3)_6]^{3+}$ low spin

i. Oxidation state of Cobalt : +3

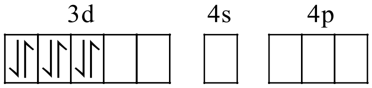
ii. Valence shell electronic configuration of $Co^{3+}$ is represented in box diagram as shown below:



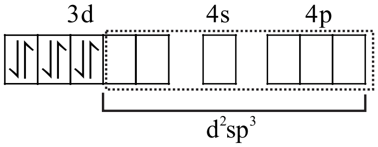
iii. Number of ammine ligands is 6, number of vacant metal ion orbitals required for bonding with ligands must be six.

vi. Complex is low spin, so pairing of electrons will take place prior to hybridisation.

v. Electronic configuration after pairing would be



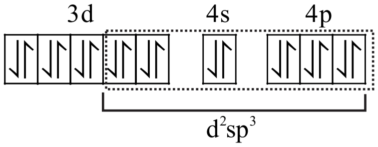
vi. Six orbitals available for hybridisation are two 3d, one 4s, three 4p orbitals.

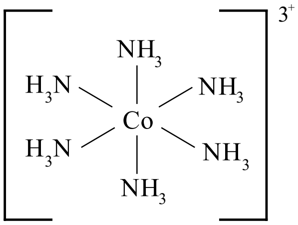


vii. The orbitals for hybridization are decided from the number of ammine ligands which is six.

viii. Here (n-1)d orbitals participate in hybridization since it is the low spin complex.

ix. Electronic configuration after complex formation.





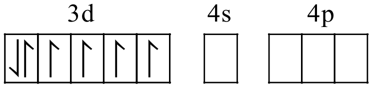
x. As all electrons are paired the complex is diamagnetic.

**Q.78 Explain the structure of octahedral high spin complex$[CoF_6]^{3-}$**

**Ans:** $[CoF_6]^{3-}$ high spin

i. Oxidation state of central metal Co is 3+

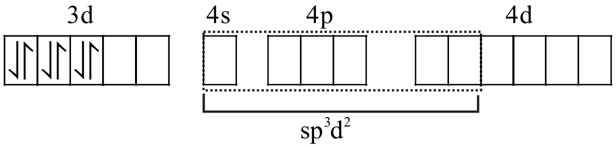
ii. Valence shell electronic configuration of $Co^{3+}$ is



iii. Six fluoride $F^-$ ligands, thus the number of vacant metal ion orbitals required for bonding with ligands would be six.

iv. Complex is high spin, that means pairing of electrons will not take place prior to hybridisation. Electronic configuration would remain the same as in the free state shown above.

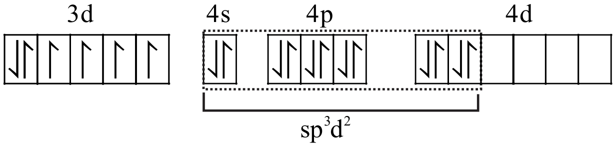
v. Six orbitals available for the hybridisasation. Those are one 4s, three 4p, two of 4d orbitals



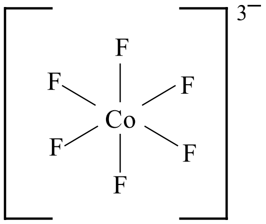
six metal orbitals after bonding with six $F^-$ ligands led to the $sp^3d^2$ hybridization. the d orbitals participating in hyridisation for this complex are nd.

vi. Six vacant $sp^3d^2$ hybrid orbital of $Co^{3+}$ overlap with six orbitals of fluoride forming Co-F coordinate bonds.

vii. Configuration after complex formation.



viii. The complex is octahedral and has four unpaired electrons and hence, is paramagnetic.

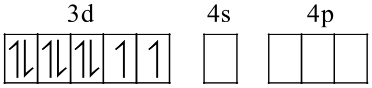


**Q.79 Explain the structure of tetrahedral $[Ni(Cl)_4]^{2-}$ complex.**

**Ans:** Tetrahedral complex $[Ni(Cl)_4]^{2-}$

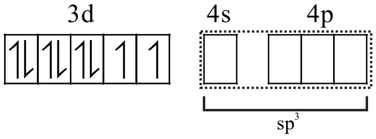
i. Oxidation state of nickel is +2

ii. Valence shell electronic configuration of $Ni^{2+}$



iii. Number of $Cl^-$ ligands is 4. Therefore number of vacant metal ion orbitals required for bonding with ligands must be four.

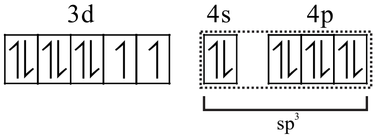
iv. Four orbitals on metal available for hybridisation are one 4s, three 4p, the complex is tetrahedral.



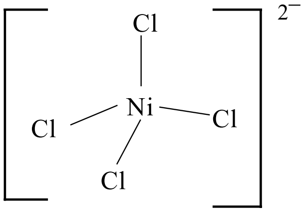
v. The four metal ion orbitals for bonding with $Cl^-$ ligands are derived from the $sp^3$ hybridization.

vi. Four vacant $sp^3$ hybrid orbital of $Ni^{2+}$ overlap with four orbitals of $Cl^-$ ions.

vii. Configuration after complex formation would be.



viii. The complex has four unpaired electrons and hence, paramagnetic.

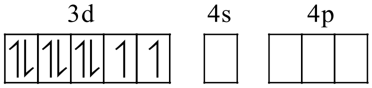


**Q.80 Explain the structure of square planar $[Ni(CN)_4]^{2-}$ complex.**

**Ans:** Square planar complex $[Ni(CN)_4]^{2-}$

i. Oxidation state of nickel is +2

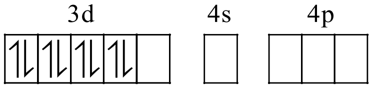
ii. Valence shell electronic configuration of $Ni^{2+}$



iii. Number of $CN^-$ ligands is 4, so number os vacant metal ion orbitals required for bonding with ligands would be four.

iv. Complex is square planar so $Ni^{2+}$ ion uses $dsp^2$ hybrid orbitals.

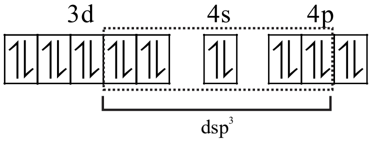
v. 3d electrons are paired prior to the hybridisation and electronic configuration of $Ni^{2+}$ becomes :



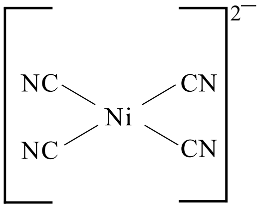
vi. Orbitals available for hybridisation are one 3d, one 4s two 4p which give dsp$^2$ hybridization.

vii. Four vacant dsp$^2$ hybrid orbitals or $Ni^{2+}$ overlap with four orbitals of $Ni^-$ ions to form Ni – CN coordinate bonds.

vii. Configuration after the complex formation becomes.



viii. The complex has no unpaired electrons and hence, diamagnetic.



**Q.81 Try this**

**Give VBT description of bonding in each of the following complexes. Predict their magnetic behaviour.**

**i.** $[ZnCl_4]^{2-}$

**ii.** $[Co(H_2O)_6]^{2+}$ **(high spin)**

**iii.** $[Pt(CN)_4]^{2-}$ **(square planar)**

**iv.** $[CoCl_4]^{2-}$ **(tetrahedral)**

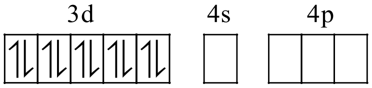
**v.** $[Cr(NH_3)_6]^{3+}$

**Ans :**

i. $[ZnCl_4]^{2-}$

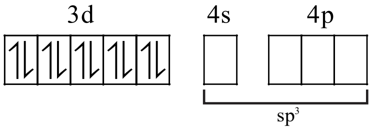
a. The oxidation state of central metal Zn is +2

b. Valence shell electronic configuration of $Zn^{2+}$ is



c. Number of $Cl^-$ ligand is 4. Therefore number of vacant metal ion orbitals required for bonding with ligand must be 4.

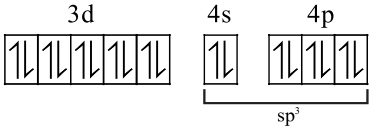
d. Four orbitals of metal available for hybridisation are one 4s and Three 4p The complex is tetrahedral.



e. The four metal ion orbitals for bonding with $Cl^-$ ligands are derived from the sp$^3$ hybridization.

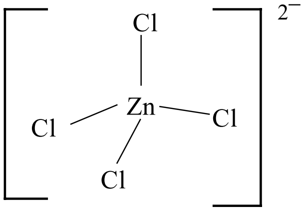
f. Four vacant sp$^3$ hybrid orbital of $Zn^{2+}$ overlap with four orbitals of $Cl^-$ ions.

g. Electronic configuration after complex formation would be



h. The complex has no unpaired electrons and hence, diamagnetic

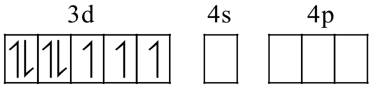
The structure of $ZnCl_2$ is



ii. $[Co(H_2O)_6]^{2+}$

a. The oxidation state of central metal is +2

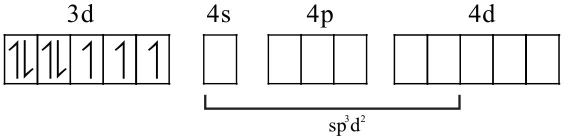
b. Valence shell electronic configuration of $Co^{2+}$ is



c. The Number of $H_2O$ ligand is 6. Therefore number of vacant metal ion orbitals required for bonding with ligand must be six.

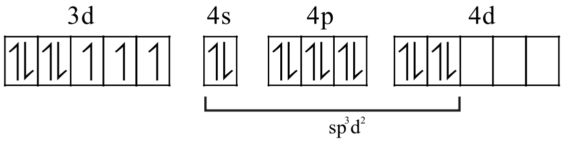
d. Complex is high spin, that means pairing of electrons will not take place prior to hybridisation. Electronic configuration would remain the same asin the free state.

e. Six orbitals of metal available for hybridization are one 4s, Three 4p and two 4d. The complex is octahedral.

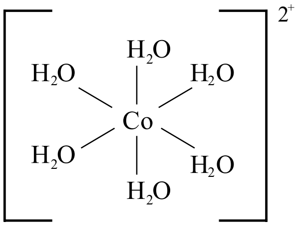


f. The six metal ion orbitals for bonding with $H_2O$ ligands are derived from the sp$^3$d$^2$ hybridization. Six vacant sp$^3$d$^2$ hyprid orbitals of $Co^{2+}$ overlap with six orbitals of $H_2O$.

g. Configuration after complex formation would be



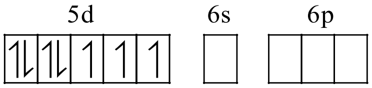
h. The complex has three unpaired electrons and hence, paramagnetic.
The structure of $[Co(H_2O)_6]^{2+}$is



**iii. $[Pt(CN)_4]^{2-}$ (square planar)**

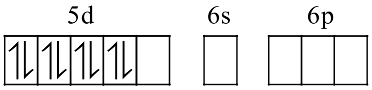
a. The oxidation number of central metal atom is +2.

b. The Valence shell electronic configuration of $Pt^{2+}$ is

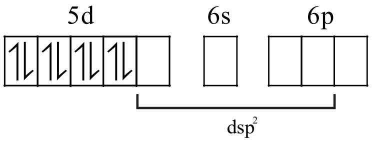


c. The Number of $CN^-$ ligand is 6. Therefore the number of vacant metal ion orbitals required for bonding with liagnd must be four.

d. 5d electrons are paired prior to the hybridization and electronic configuration of $Pt^{2+}$ becomes :



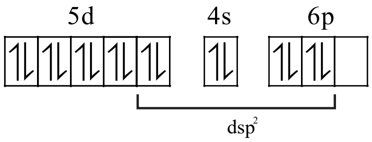
e. Four orbitals of metal available for hybridisation are one 5d one 6s and three 6p and the complex is square planar.



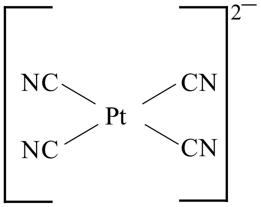
f. The four metal ion orbitals for bonding with $CN^-$ ligands are derived from the $dsp^2$ hybridization.

g. Four vacant $dsp^2$ hybrid orbital of $Pt^{2+}$ overlap with four orbitals of $CN^-$ ions.

h. Configuration after complex formation would be



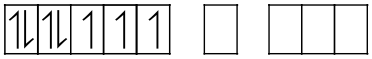
i. The complex has no unpaired electrons and hence, diamagnetic.
The structure of $[Pt(CN)_4]^{2-}$ is



**iv. $[CoCl_4]^{2-}$ (tetrahedral)**

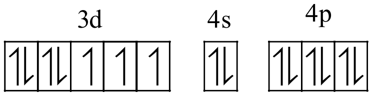
a. The oxidation number of central metal atom cobalt is +2.

b. The Valence shell electronic configuration of $Co^{2+}$ is



c. The Number of $Cl^-$ ligand is 4. Therefore the number of vacant metal ion orbitals required for bonding with ligand must be four.

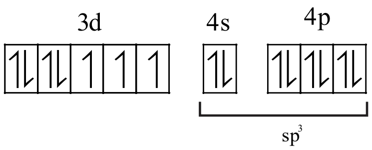
d. Four orbitals of metal available for hybridization are one 4s one 4s and three 4p The complex is tetrahedral



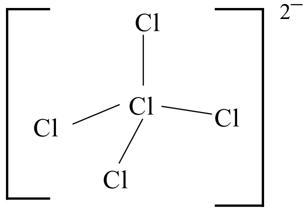
e. The four metal ion orbitals for bonding with $Cl^-$ ligand are derived from the $sp^3$ hybridization.

f. Four vacant $sp^3$ hybrid orbital of $Co^{2+}$ overlap with four orbitals of $Cl^-$ ions.

g. The Electronic configuration after complex formation would be



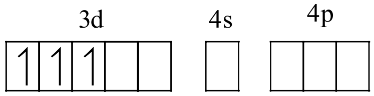
h. The complex has three unpaired electrons and hence, paramagnetic.
The structure of $[CoCl_4]^{2-}$ is



v. **$[Cr(NH_3)_6]^{3+}$**

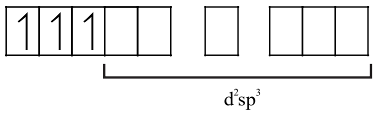
a. The oxidation state of chromium is +3.

b. The Valence shell electronic configuration of $Cr^{3+}$ is



c. The Number of $NH_3$ ligand is 6. Therefore the number of vacant metal ion orbitals required for bonding with ligand must be six.

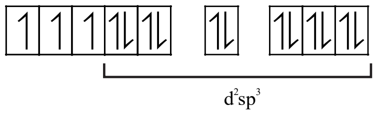
d. Six orbitals on metal available for hybridisation are two 3d, one 4s and Three 4p and The complex is octahedral.



e. The four metal ion orbitals for bonding with $NH_3$ ligands are derived from the $d^2sp^3$ hybridization.

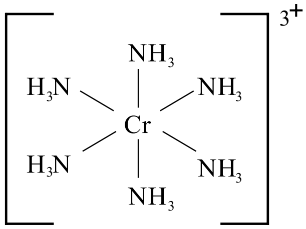
f. Six vacant $d^2sp^3$ hyprid orbital of $Cr^{3+}$ overlap with six orbitals of $NH_3$ molecule.

g. The electronic configuration after complex formation would be



h. The complex has three unpaired electrons and hence, paramagnetic.

The structure of $[Cr(NH_3)_6]^{3+}$ is



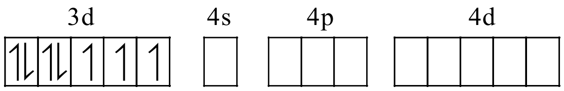
**Q.82 Try this**

**Based on the VBT predict structure and magnetic behaviour of the $[Ni(NH_3)_6]^{3+}$complex.**

**Ans :**

i. The oxidation state of nickel is = 3

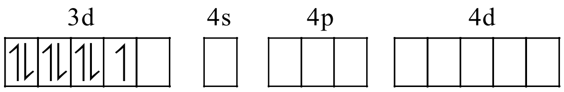
ii. The valence shell electronic configuration of $Ni^{3+}$.



iii. The number of $NH_3$ ligand is 6. Therefore the number of vacant metal ion orbitals required for bondings with ligands would be six.

iv. Since, $NH_3$ is a low spin complex, so pairing of electrons will take place prior to hybridization.

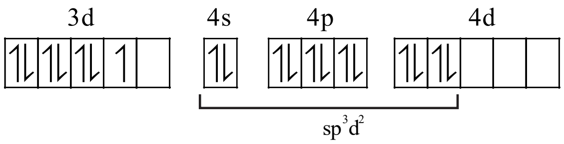
Therefore the electronic configuration of $Ni^{3+}$ becomes.



v. Orbitals available for hybridization are one 4s three 4p and two 4d which gives $sp^3d^2$ hybridization and the complex is octahedral.

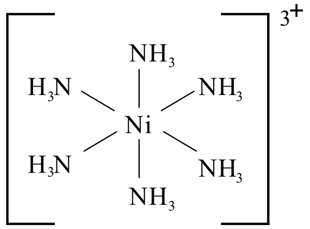
vi. Six vacant $sp^3d^2$ hybrid orbitals of $Ni^{3+}$ overlap with six orbitals of $NH_3$ molecules to form Ni-$NH_3$ coordinate bonds.

vii. Therefore, the electronic configuration after the complex formation becomes.



viii. The complex has one unpaired electrons and hence paramagnetic.

The structure of complex is

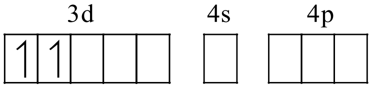


**Q.83 Give valence bond description for the bonding in the complex $[VCl_4]^{-1}$. Draw digrams for free metal ion. which hybrid orbitals are used by the metal? State the number of unpaired electrons.**

**Ans:**

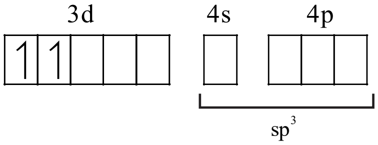
i. The oxidation state of central metal atom vanadium is +3.

ii. Valence shell electronic configuration of metal ion $V^{3+}$ is



iii. The number of $Cl^-$ ligand is 4. Therefore, the number of vacant metal ion orbitals required for bonding with ligands must be four.

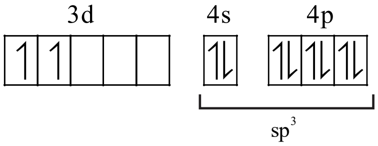
iv. Four orbitals on metal available for hybridisation are one 4s and three 4p and the complex is tetrahedral



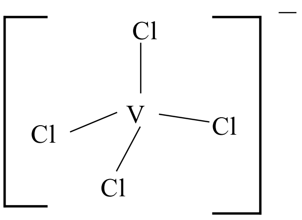
v. The four metal ion orbitals for bonding with $Cl^-$ ligands are derived from the $sp^3$ hybridization.

vi. Four vacant $sp^3$ hybrid orbitals of $V^{3+}$ overlap with four orbitals of $Cl^-$ ions.

vi. Electronic configuration after complex formation would be

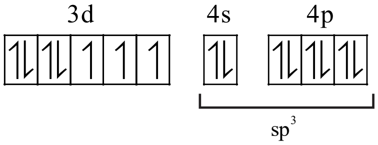


viii. The complex has two unpaired electrons the structure of $[VCl_4]$ is



**Q.84 $[CoCl_4]^{2-}$ is a tetrahedral complex. Draw its box orbital diagram. State which orbitals participate in hybridization.**

**Ans :** Box orbital diagram configuration of $[CoCl_4]^{2-}$



**Q.85 Give the limitations of valence bond theory.**

**Ans:**

i. It does not explain the high spin or low spin nature of the complex. In other words, strong and weak field nature of ligands can not be distinguished.

ii. It does not provide any explanation for the colour of coordination compounds.

iii. The structure of the complexes predicted from the VBT would not always match necessarily with those determined from the experiments.

**Q.86 What are the assumptions of crystal field theory (CFT).**

**Ans:** C.F.T. is based on following assumptions

i. The ligands are treated as point charges. The interaction between metal ion and ligand is purely electrostatic or there are no orbital interactions between metal and ligand.

ii. In an isolated gaseous metal ion the five d orbitals, $d_{x^2-y^2}$, $d_{z^2}$, $d_{xy}$, $d_{yz}$, $d_{zx}$ have the same energy i.e. they are degenerate.

iii. When ligands approach the metal ion they crate crystal-field around the metal ion. If it were symmetrical the degeneracy of the d orbitals remains intact.

iv. Usually the field created is not symmetrical and the degeneracy is destroyed. The d orbitals thus split into two sets namely, **(**$d_{xy}$, $d_{yz}$, $d_{xz}$**)** usually referred by $t_{2g}$ and ($d_{x^2-y^2}$, $d_{z^2}$) called as $e_g$.

v. These two sets of orbitals now have different energies. A separation of energies of these two sets of d orbitals is the crystal field splitting parameter. This is denoted by $\Delta_0$ (O for octahedral).

vi. The $\Delta_0$ depends on strength of the ligands. the ligands are then classified as (a) strong field and (b) weak field ligands. Strong field ligands are those in which donor atoms are C, N or P. Thus $CN^-$, $NC^-$, CO, $NH_3$, EDTA, en (ethylendediammine) are considered to be strong ligands.

vii. They cause larger splitting of d orbitals and pairing of electrons is favoured. These ligands tend to form low spin complexes.

viii. Weak field ligands are those in which donor atoms are halogens, oxygen or sulphur. For example, $F^-$, $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $C_2O_4^{2-}$

ix. In case of these ligands the $\Delta_0$ parameter is smaller compared to the energy required for the pairing of electrons, which is called as electron pairing energy.

x. The ligands then can be arranged in order of their increasing field strength as

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

**Q.87 What is electron pairing energy ?**

**Ans:** The energy required for pairing of electrons in Cl - orbital is called electron pairing energy. It depends on the crystal field splitting larger the splitting Cl-orbital and pairing of electron is favoured.

**Q.88 What are strong field and weak field ligands. Give one example of each.**

**Ans:**

i. **Strong field ligands**

Strong field ligands are the ligands that cause larger splitting of Cl-orbital and favours pairing of electrons. Strong field ligands are those in which donor atoms are C, N or P.

For example - $CN^-$, $NC^-$, CO, $NH_3$, EDTA, en (ethylenediammine) etc.

ii. **Weak field ligands**

Those ligands which cause lower splitting of Cl - orbitals. In this case $\Delta_0$ parameter is smaller compared to the energy required for the pairing of electrons are called weak field ligands. Weak field ligands contains halogens O and S as donor atoms.

For example- $F^-$, $Cl^-$, $Br^-$, $I^-$, $SCN^-$, and $C_2O_4^{2-}$ etc.

**Q.89 What are high spin and low spin complexes?**

**Ans:**

i. **High –spin complexes:**

When crystal field splitting energy is greater than electron pairing energy. The complexes formed are called high – spin complexes.

ii. **Low – spin complexes:**

When crystal field splitting energy is smaller than electron pairing energy. The complexes formed are low-spin complexes.

**Q.90 Explain the splitting of Cl-orbitals and formation of octahedral complexes.**

**Ans**

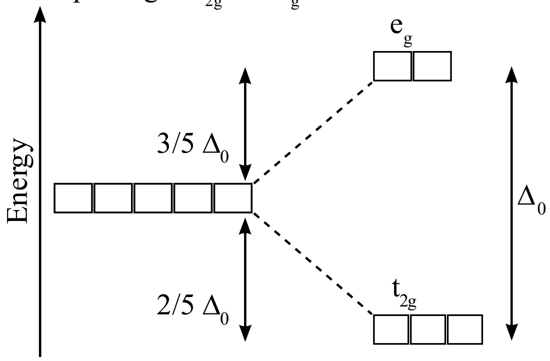
**i.** In octahedral environment the central metal ion is surrounded by six ligands.

ii. Ligands approach the metal ion along the x, y, z axes. As the ligands approach the metal ion the degeneracy of d orbitals is resolved.

iii. With closer approach of ligands along the axes, the doubly degenerate $d_{x^2-y^2}, d_{z^2}$ $(e_g)$ orbitals experience larger repulsion than the triply degenerate $t_{2g}$ orbitals.

iv. The $e_g$ set has higher energy than the $t_{2g}$ set by the amount $\Delta_0$.

v. The $\Delta_0$ parameter is equal to 10 Dq units of splitting of $t_{2g}$ and $e_g$ levels.



$e_g$ - The higher energy set of orbitals ($d_{z2}$ and $d_{x2-y2}$)
$t_{2g}$ -The lower energy set of orbitals ($d_{xy,}d_{yz}$and $d_{zx}$)
$\Delta_0$or 10 Dq - The energy separation between the two levels
The $e_g$ orbitals are repelled by an amount of 0.6 $\Delta_0$.
The $t_{2g}$ orbitals to be stabilized to the extend of 0.4 $\Delta_0$.

**Crystal field Splitting in an octahedral complex**

**Q.91 Why the electronic configurations $d^1$, $d^2$, $d^3$, the high spin and low spin complex cannot be distinguished.**

**Ans:**

i. For electron configurations $d^1$, $d^2$, $d^3$ the electrons occupy $t_{2g}$ orbitals and obey the Hund's rules.

ii. For electronic configurations $d^1$, $d^2$, $d^3$ and $d^8$, $d^9$, $d^{10}$ the high spin and low spin configurations cannot be distinguished.

iii. Only the electronic configurations $d^4$ and $d^7$

render the high and low spin complexes.

iv. These are dipiciated in the table below.

| d orbital electronic configuration | | High spin | Low spin |
|---|---|---|---|
| $d^4$ | $e_g$ | ↑ — — | — — |
| | $t_{2g}$ | ↑ ↑ ↑ | ↑↓ ↑ ↑ |
| $d^5$ | $e_g$ | ↑ ↑ | — — — |
| | $t_{2g}$ | ↑ ↑ ↑ | ↑↓ ↑↓ ↑ |
| $d^6$ | $e_g$ | ↑ ↑ | — — — |
| | $t_{2g}$ | ↑↓ ↑ ↑ | ↑↓ ↑↓ ↑↓ |
| $d^7$ | $e_g$ | ↑ ↑ | ↑ — |
| | $t_{2g}$ | ↑↓ ↑↓ ↑ | ↑↓ ↑↓ ↑↓ |

**d orbital diagrams for high spin and low spin complexes.**

**Q.92 Explain the factors effecting crystal field splitting Energy.**

**Ans:** Factors affecting Crystal field splitting parameter( $\Delta_0$ )

i. **Strength of ligand :**
the magnitude of crystal field splitting depends on strength of the ligands. The strong ligands those appear in spectrochemical series approach closer to the central metal which results in a large crystal splitting.

ii. **Oxidation state of the metal :**
A metal with the higher positive charge is able to draw ligands closer to it than that with the lower one. Thus the metal in higher oxidation state results in larger separation of $t_{2g}$ and $e_g$ set of orbitals. The trivalent metal ions cause larger crystal field splitting than corresponidng divalent ones.

**+Q.93 Sketch qualitatively crystal field d orbital energy level diagrams for each of the following complexes.**

**i. $[Ni(en)_3]^{2+}$ ii. $[Mn(CN)_6]^{3-}$**
**iii. $[Fe(H_2O)_6]^{2+}$**
**Predict whether each of the complexes is diamagnetic or paramagnetic.**

**Ans :**

i. **$[Ni(en)_3]^{2+}$**

**a.** (en) Ethylenediammine is a strong field ligand. The metal ion is $Ni^{2+}$ and its d-orbital electronic configuration is $d^8$.

b. Crystal field d orbital energy level diagram for $[Ni(en)_3]^{2+}$ is.

$d^8$ $e_g$ ↿ ↿

$r_{2g}$ ⇅ ⇅ ⇅

There are two unpaired electrons. The complex $[Ni(en)_3]^{2+}$is paramagnetic.

ii. **$[Mn(CN)_6]^{3-}$**

The crystal field d-orbital energy level diagram $[Mn(CN)_6]^{3-}$ is

$d^4$ $e_g$ — —

$t_{2g}$ ⇅ ⇅ ⇅

There are two unpaired electrons. The complex $[Mn(CN)_6]^{3-}$ is paramagnetic.

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

**a.** $H_2O$ is a weak ligand. The metal ion is $Fe^{2+}$ and its d–orbital electronic configuration is $d^6$

$d^6$ eg ↿ ↿

$r_{2g}$ ⇅ ⇅ ↿

c. There are four unpaired electrons in $[Fe(H_2O)_6]^{2+}$ is paramagnetic.

**Q.94 Write a short note on colour in coordination compound.**

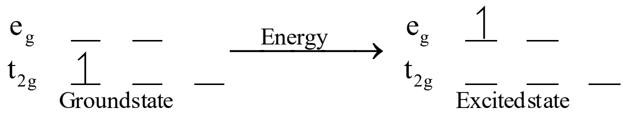
**Ans:**

i. The formation of on octahedral complex is accompanied by splitting of d orbitals into $t_{2g}$ and $e_g$ sets. A separation of these two sets of orbitals is $\Delta_0$, which can be measured from experiments.

ii. The $\Delta_0$ corresponds to a certain frequency of electromagnetic radiation usually in the visible region. A colour complementary to the absorbed frequency is thus observed.

iv. Consider the $[Ti(H_2O)_6]^{3+}$ complex. The central metal ion titanium has electronic configuration 3d and the electron occupies one of the

$t_{2g}$ orbitals



d-d transition in d' system

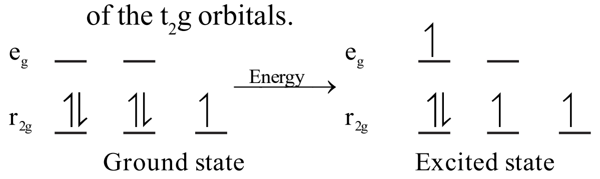
v. The absorption of the wavelength of light corresponding to $\Delta_0$ parameter promotes an electron from the $t_{2g}$ level.

vi. Such energy gap in case of the $[Ti(H_2O)_6]^{3+}$ complex is 20,300 $cm^{-1}$ (520 nm, 243kJ/mol) and a complimentary colour to this is imparted to the complex. A violet colour of the $[Ti(H_2O)_6]^{3+}$ complex arises from such d – d transition.

**Q.95 With the help of crystal field energy level diagram explain why the complex $[Cr(en)_3]^{3+}$ is coloured.**

**Ans:**

i The central metal ion chromium has electronic configuration $3d^3$ and the electron occupy one of the $t_2$g orbitals.

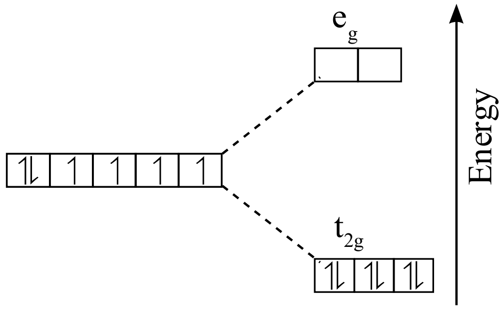


ii. The absorption of the wavelength of light excites electron from $t_{2g}$ level to eg level. Therefore d-d transition in complex $[Cr(en)_3]^{3+}$ is possible. Hence, the complex is coloured.

**★ Q.96 Draw qualitatively energy level diagram showing d-orbital splitting in the octahedral environment. Predict the number of unpaired electrons in the complex $[Fe(CN)_6]^{4-}$. Is the complex diamagnetic or paramagnetic? It is coloured? Explain.**

**Ans:**

i.



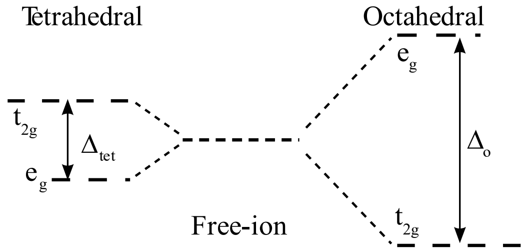
ii. There is no unpaired electrons in $t_{2g}$ orbital, hence the complex is diamagnetic

iii. In this complex d-d transition does not occur, hence it is colourless.

**Q.97 Write a short note on the formation of tetrahedral complexes using crystal field theory.**

**Ans:**

i. The tetrahedral structure having the metal atom M at centre and four ligands occupying the corners.



**Splitting of d orbitals in tetrahedral and octahedral complexes**

ii. The $d_{xy}$, $d_{yz}$, $d_{zx}$ orbitals with their lobes lying in between the axes point toward the ligands. On the other hand, $d_{x^2-y^2}$ and $d_{z^2}$ orbitals lie in between metal-ligand bond axes. The $d_{xy}$, $d_{yz}$ and $d_{zx}$ orbitals experience more repulsion from the ligands compared to that by $d_{x^2-y^2}$ and $d_{z^2}$ orbitals.

iii. Due to larger such repulsions the $d_{xy}$, $d_{yz}$, and $d_{zx}$ orbitals are of higher energy while the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are of relatively lower energy.

iv. Each electron entering in one of the $d_{xy}$, $d_{yz}$, and $d_{zx}$ orbitals raises the energy by 4Dq whereas that occupying $d_{x^2-y^2}$ and $d_{z^2}$ orbitals lowers it by 6 Dq compared to the energy of hypothetical degenerate d orbitals in the ligand field.

v. A splitting of d orbitals in tetrahedral crystal fields (assumed to be 10 Dq) thus is much less (typically 4/9) compared to that for the octahedral environment. The crystal field splitting of d orbitals in a tetrahedral ligand field is compared with the octahedral one.

vi. Thus the pairing of electrons is not favoured in tetrahedral structure. For example, in $d^4$ configuration an electron would occupy one of the $t_{2g}$ orbitals. The low spin tetrahedral complexes thus are not found.

vii. Typically metal complexes possessing the central metal ion with $d^8$ electronic configuration, for example, $Ni(CO)_4$, favours the tetrahedral structure.

## 9.10 Application of coordination compounds

**Q.98 Write the applications of coordination compounds.**

**Ans:**

i. In biology :
  - a. Several biologically important natural compounds are metal complexes.
  - b. They play important role in a number of processes occuring in plants and animals.
  - c. For example, chlorophy ll present in plants is a complex of Mg.
  - d. Haemoglobin present in blood is a complex of iron.

ii. In medicines
  - a. Pt complex cisplatin is used in the treatment of cancer.
  - b. EDTA is used for treatment of lead poisoning.

iii. To estimate hardness of water:
  - a. Hardness of water is due to the presence of $Ca^{2+}$ and $Mg^{2+}$ ions.
  - b. The ligand EDTA forms stable complexes with $Ca^{2+}$ and $Mg^{2+}$
  - c. It can, therefore, be used to estimate hardness.

iv. In electroplating :
  - a. Usually stable coordination complexes on dissolution dissociate to small extent and furnish a controlled supply of metal ions.
  - b. The metal ions when reduced clump together to form the clusters or nanoparticles.
  - c. When the coordination complexes are used the ligands in the complex keep the metal atoms well separated from each other.
  - d. These metal atoms tend to form a protective layer on the surface. Certain cyanide complexes $K[Ag(CN)_2]$ and $K[Au(CN)]_2$ find applications in the electroplating of these noble metals.

**★ Q.99 Mention two applications of coordination compounds.**

**Ans:** *Refer Q. no. 95*

**★ Q.100 Activity :**

**The reaction of chromium metal with $H_2SO_4$ in the absence of air gives blue solution of chromium ion.**

$$\mathbf{Cr_{(s)} + 2H^{+}_{(aq)} \longrightarrow Cr^{2+}_{(aq)} + H_{2(g)}}$$

**$Cr^{2+}$ forms octahedral complex with $H_2O$ ligands.**

**i. Write the formula of the complex.**

**ii. Describe bonding in the complex using CFT and VBT.**

**Draw crystal field spiltting and valence bond orbital diagrams.**

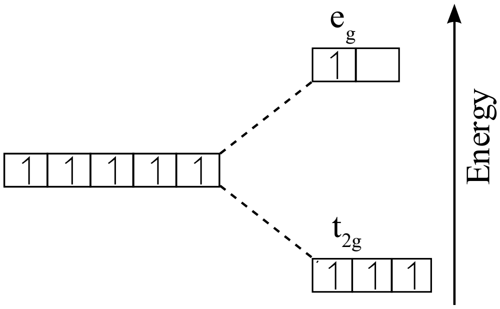
**Ans:**

1 Since chromium forms octahedral complex with water ligands. The formula of complex is $[Cr(H_2O)_6]^{2+}$

2. i. Bonding in $[Cr(H_2O)_6]^{2+}$ using CFT theory
  - a. The metal ion $Cr^{2+}$ and ligand $H_2O$ act as point charges and there is electrostatic interaction between the two.
  - b. When ligands approach the metal ion they create crystal–field around the metal ion and the degeneracy of d–orbitals is destroyed with $d_{x^2-y^2}$ and $d_{z^2}$ $(e_g)$ orbitals experiencing larger repulsion and has greater energy than $d_{xy}$, $d_{y^2}$, $d_{zx}$ $(t_{2g})$ orbitals by an amount $\Delta_0$.

  iii. Since $H_2O$ is a weak field ligand, hence, crystal field splitting energy $\Delta_0$ is smaller than the pairing up energy and high spin complexes are formed.

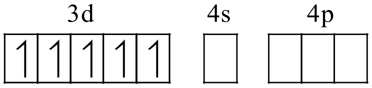
  iv. The crystal field splitting energy diagram for $[Cr(H_2O)_6]^{2+}$ is shown as:



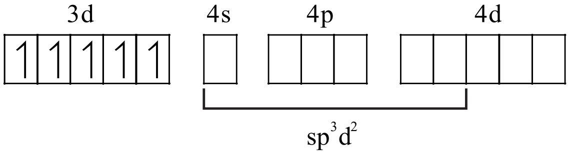
e. Bonding in $[Cr(H_2O)_6]^{2+}$ using VBT

f. Oxidation state of chromium is +2

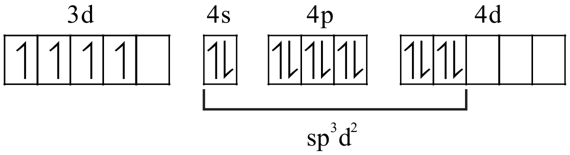
2. Valence shell electronic configuration of $Cr^{2+}$



3. Number of $H_2O$ ligands is 6. Therefore, the number of vacant metal ion orbitals required for bonding with ligands must be six.
4. $H_2O$ is weak field ligand and hence, complex is high spin.
5. Six orbitals on metal available for hybridisation are two 3d, one 4s and three 4p. The complex is octahedral.

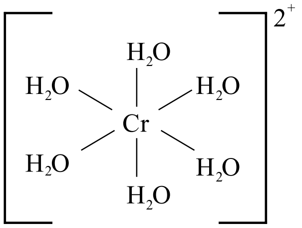


6. The six metal ion orbitals for bonding with $H_2O$ ligands are derived from $sp^3d^2$ hybridization. Six vacant $sp^3d^2$ hybrid orbital of $Cr^{2+}$ overlap with six orbitals of $H_2O$ molecules.
7. Configuration after complex formation would be



8. The complex has four unpaired electrons and hence, paramagnetic.

   The structure of $[Cr(H_2O)_6]^{2+}$ is



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