

ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-12) TOPIC-COORDINATION COMPOUNDS PREPARED BY: MR. ARNAB PAUL CHOWDHURY SET NUMBER-06 DATE: 21.11.2020



Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds, the central metal atom or ion is linked by ions or molecules with coordinate bonds, e.g., Potassium ferrocyanide, K_4 [Fe(CN)₆].

 $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$ Central metal atom - Ligand K4[Fe(CN)6] - Coordination number Counter ion Coordinate sphere (entity)

Double Salts

These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr'S salt, $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot (H_2O_4)_2SO_4 \cdot ($

Terms Related to Coordination Compounds

1. Complex ion or Coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

(i) Cationic complex entity It is the complex ion which carries positive charge. e.g., $[Pt(NH_3)_4]^{2+}$

(ii) Anionic complex entity It is the complex ion which carries negative charge. e.g., [Fe(CN)₆]⁴

2. Central Atom or Ion

The atom or ion to which a fixed number of ions or groups are bound is .ned central atom or ion. It is also referred as Lewis acid. e.g., in $(NiCI_2(H_2O)_4]$. Ni is central metal atom. It is generally transition element or inner-transition element.

3. Ligands

Ligands is electron donating species (ions or molecules) bound to the Central atom in the coordination entity.

These may be charged or neutral. LIgands are of the following types :

(i) **Unidentate** It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. e.g., H_2O , NH_3 , etc.

(ii) **Didentate** It is the ligand. which have two donor sites.



(iii) **Polydentate** It is the ligand, which have several donor sites. e.g., [EDTA]⁴ is hexadentate ligand.



(iv) **Ambidentate ligands** These are the monodentate ligands which can ligate through two different sites, e.g., NO², SCN⁻, etc.

(v) Chelating ligands Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate IS, Such ligands USes two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings, more is the stability of complex.

The stabilisation of coordination compounds due to chelation is known as **chelate effect**. π – acid ligands are those ligands which can form π – bond and n-bond by accepting an appreciable amount of 1t electron density from metal atom to empty π or π – orbitals.

4. Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g., in [PtCl₆]², Pt has coordination number 6. In case of monodentate ligands,

Coordination number = number of ligands

In polydentate ligands.

Coordination number = number of ligands * denticity

5. Coordination Sphere

The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions.

6. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called coordination polyhedron around the central atom or ion.

7. Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom.

e.g., $[CU(CN_4)_{3.}, oxidation number of copper is +1, and represented as Cu(I).$

Types of Complexes

1. Homoleptic complexes

Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g., $[Co(NH_3)_6]^{3+}$

2. Heteroleptic complexes

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[Co(NH_3)_4CI_2]^2$

3. Labile and Inert complexes

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

Effective Atomic Number (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of metal atom is equal to the total number of electrons present in it.

EAN = Z - ON of metal + 2 * CN

(where, Z = atomic number of metal atom

ON = oxidation number of metal

and CN = coordination number of complex)

An ion with central metal atom having EAN equal to next inert gas will be more stable.

IUPAC Naming of Complex Compounds

Naming is based on set of rules given by IUPAC.

1. Name of the compound is written in two parts (i) name of cation, and (ii) name of anion.

2. The cation is named first in both positively and negatively charged coordination complexes.

3. The dissimilar ligands are named in au alphabetical order before the name of central metal atom or ion.

4. For more then one similar ligands. the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.

5. If the complex part is anion, the name of the central metal ends with suffix 'ate'.

6. Names of the anionic ligands end in '0', names of positive ligands end with 'ium' and names of neutral ligands remains as such. But exception are there as we use aqua for H_2O , ammine for NH₃, carbonyl for CO and nitrosyl for NO.

7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.

8. The name of the complex part is written as one word.

9. If the complex ion is a cation, the metal is named same as the element.

10. The neutral complex molecule is named similar to that of the complex cation.

Some examples are

(i) [Cr(NH₃)₃(H₂O)₃]Cl₃ triamminetrichlorochromium (III) chloride

(ii) [Co(H₂CH₂CH₂H₂)₃]₂(SO₄)₃ tris (ethane-I,2-diamine) cobalt (III) sulphate

(iii) [Ag(NH₃)₂] [Ag(CN)₂] diamminesilver (I) dicyanoargentate(I)

(iv) K₄ [Fe(CN)₆] potassiumhexacyanoferrate (II)

Isomerism in Coordination Compounds Coordination compounds exhibit the following types of isomerism:

1.Structural Isomerism

In this isomerism. isomers have different bonding pattern. Different types of structural isomers are

(i) **Linkage isomerism** This type of isomerism is shown by the coordination compounds having ambidentate ligands. e.g.,

[Co(NH₃)₅(NO₂)]Cl and [Co(NH₃)₅(ONO)]Cl or pentaamminenitrito- N Cobalt (III) chloride and pentaamminenitrito-O'Cobalt (III) chloride.

(ii) **Coordination isomerism** This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex, e.g.,

 $[Cr(NH_3)_6)$ $[CO(CN)_6]$ and $[CO(NH_3)_6]$ $[Cr(CN)_6]$

(iii) **Ionisation isomerism** This isomerism arise due to exchange of ionisable anion with anionic ligand. e.g..

[Co(NH₃)₅SO₄]Br and [Co(NH₃)₅Br]SO₄ (red) (violet)

(iv) **Solvate isomerism** This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside it. e.g..

 $[Co(H_2O)_6]CI_3, [Co(H_2O)_4C1_2]CI \cdot 2H_2O, [Co(H_2O)_3CI_3]. 3H_2O$

2. Stereoisomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types :

(i) Geometrical isomerism Geometrical isomers are of two types i.e., cis and trans isomers. This isomensm is common in complexes with coordination number 4 and 6.
Geometrical isomerism in complexes with coordination number 4
(i) Tetrahedral complexes do not show geometrical isomerism.

(ii) Square planar complexes of formula [MX₂L₂] (X and L are unidentate) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer, e.g.,



(iii) Square planar complex of the type [MABXL] (where A, B, X, L, are unidentate ligands) shows three isomers, two cis and one trans.

e.g., [Pt(NH₃) (Br)(Cl)(Py)].

Geometrical isomerism in complexes with coordination number 6

Octahedral complexes of formula $[MX_2L_4]$, in which the two X ligands may be oriented cis or trans to each other, e.g., $[Co(NH_3)_4Cl_2)^2$.



Octahedral complexes of formula $[MX_2A_2]$, where X are unidentate ligands and A are bidentate ligand. form cis and trans isomers, e.g., $[CoC1_2(en)_2]'$

In octahedral complexes of formula $[MA_3X_3]$, if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face. it is known as facial (fae) isomer, when the positions are around the meridian of the octahedron, it is known as meridional (mer) isomer. e.g., $[Co(NH_3)_3(NO_2)_3]$



(ii) **Optical isomerism** These are the complexes which have chiral structures. It arises when mirror images cannot be superimposed on one another. These mirror images are called enantiomers. The two forms are called dextro (d) and laevo (l) forms. Tetrahedral complexes with formula [M(AB)₂] show optical isomers and octahedral complexes (cis form) exhibit optical isomerism.

Bonding in Coordination Compounds

Werner's Theory

Metals exhibit two types of valencies in the formation of complexes.

These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.

2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Valence Bond Theory (VBT)

This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. Coordination number shows the number of such empty orbitals, i.e., number of empty orbitals is equal to the coordination number. These empty orbitals hybridised before participation in bonding and the nature of hybridisation depends on the nature of metal and on the nature of approaching ligand.

Inner orbital complexes or outer orbital complexes

When outer d-orbital are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is sp³d². They have octahedral shape.

When d-orbitals of (n - 1) shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3 . They are also octahedral in shape.

1. 6 - ligands (unidentate), octahedral entity.

(i) Inner orbital complex $[Co(NH_3)_6]^{3+}$



All electrons are paired, therefore complex will be diamagnetic in nature.



Complex has unpaired electrons, therefore, it will be paramagnetic in nature.

2. 4-ligands (unidentate) tetrahedral entity.

| S.No. | Inner orbital complexes | | Outer orbital complexes |
|-------|---|---|-------------------------|
| (a) | Strong field or low spin ligands | Weak field or high spin ligands Hybridisation is sp^3 (where one orbital of 4s and three orbitals of $4p$) | |
| (b) | Hybridisation is dsp^2 (where one orbital of 3d, one orbital of 4s and two orbitals of 4p)/ | | |
| (c) | Square planar shape | Tetrahedral shape | |

(i) Inner orbital complex, $[Ni(CN)_4]^{2-}$



All electrons are paired so complex will be diamagnetic in nature.

(ii) Outer orbital complex, [CoCl₄]-



Since, complex has unpaired electrons. so it will be paramagnetic in nature.

Limitations of VBT

This theory could not explain the quantisation of the magnetic data, existence of inner orbital and outer orbital complex, change of magnetic moment with temperature and colour of complexes.

Crystal Field Theory (eFT)

This theory was proposed by H. Bethe and van Vleck. Orgel. in 1952, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five d-orbitals are classified as

(i) Three d-orbitals i.e., d_{xy} , d_{yz} and d_{zx} are oriented in between the coordinate axes and are called t_{2g} – orbitals.

(ii) The other two d-orbitals, i.e., $d_{x^2-y^2}$ and d_{z^2} oriented along the x - y % axes are called e_g – orbitals.

Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t_{2g} and e_g level is designated by Δ and is called **crystal** field splitting energy.]

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series

$$\label{eq:relation} \begin{split} I^- &< Br^- < SCN^- < CI^- < S^{2-} < F^- < OH^- \\ &< C_2 O_4^{2-} < H_2 O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO. \end{split}$$

Crystal field splitting in octahedral complexes

In case of octahedral complexes, energy separation is denoted by Δ_{\circ} (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of d $_{x^2-y^2}^2$ and d $_{z^2}^2$ orbitals.

Energy of e_{g} set of orbitals > energy of t_{2g} set of orbitals.

The energy of e_s orbitals will increase by (3/5) Δ_o and t_{2g} will decrease by (2/5) Δ_o . If $\Delta_o < P$, the fourth electron enters one of the e_s orbitals giving the configuration $t_{2g}^3 e_s^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes. If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^2$. (where, P = energy required for e- pairing in an orbital). Ligands which produce this effect are known as strong field ligands and form low spin complexes.



Crystal field splitting in tetrahedral complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate comers of the cube and the metal ion at the center of the cube.

Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals. In such complexes d – orbital splitting is inverted and is smaller as compared to the

octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons are not possible so these are high spin complexes.



Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds to dod transition of the electron, i.e., electron jump from $t_{2\epsilon}$ level to higher e_{ϵ} level. In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.

$[Ti(H_2O]_6]^{3+}$ — Violet in colour $[Cu(H_2O)_4]^{2+}$ — Blue in colour, etc.

Limitations of CFT

1. It does not consider the formation of 7t bonding in complexes.

2. It is also unable to account satisfactorily for the relative strengths of ligands e.g., it does not explain why H_2O is stronger ligand than OH_2 .

3. It gives no account of the partly covalent nature of metal-metal bonds.

Ligand Field or Molecular Orbital Theory

This theory was put forward by Hund and Mulliken. According to this theory, all the atomic orbitals of the atom participating in molecule formation get mixed to give rise an equivalent number of new orbitals, called the molecular orbitals. The electrons are now under the influence of all the nuclei.

Stability of Coordination Compounds

The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).

 $e.g., \qquad M^+ + nL^{x-} \rightleftharpoons [ML_n]^{y-};$

 $K = \frac{[(ML_n)^{y^-}]}{[M^+] [L^{x^-}]^n}$

The factors on which stability of the complex depends :

(i) Charge on the central metal atom As the magnitude of charge on metal atom increases, stability of the complex increases.

(ii) Nature of metal ion The stability order is 3d < 4d < 5d series.

(iii) Basic nature of ligands Strong field ligands form stable complex.

The instability constant or the dissociation constant of compounds is defined as the reciprocal of the formation or stability Constant.

Importance and Applications of Coordination Compounds

1. They are used in many qualitative and quantitative analysis.

2. Hardness of water is estimated by simple titration with Na₂ EDTA.

3. Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

4. They have great importance in biological systems.

5. They are used as catalyst for many industrial processes.

6. In medicinal chemistry, there is a growing interest of chelating therapy.

Organometallic Compounds

They contain one or more metal-carbon bond in their molecules. They are of the following types:

1. Sigma (σ) bonded compounds

Metal-carbon bond is sigma bond, e.g., $(C_2H_5)_4$ Pb, $Zn(C_2H_5)_2$ R – Mg – X, etc.

2. $Pi(\pi)$ bonded compounds

In which molecules/ions containing π bonds act as a ligand. e.g., Ferrocene, Dibenzene chromium and Zeise's salt.

Zeise's salts is K[PtCl₃($\eta^2 - C_2H_4$)] In which ethylene acts as a ligand which do not have a lone pair oi electron.

In ferrocene, $Fe(\eta^{s} - C_{s}H_{s})_{2}$ represents the number of carbon atoms with which metal ion is directly attached.

3. σ and π bonded compounds

Metal carbonyls are their examples. Metal-carbon bond of metal carbonyls have both σ and π – bond character. They have CO molecule as ligand, e.g.,



Wilkinson's catalyst (Rh(PPh₃)₃CI] is used as homogeneous catalyst in the hydrogenation of alkenes. Zeigler-Natta catalyst

[Ti Cl₄ + ($C_2H_3 >_3AI$] acts as heterogeneous catalyst in the polymerisation of ethylene

Till now, we have come across many complex compounds that contain carbonyl ligands only. These compounds are better termed as homoleptic carbonyls or metal carbonyls. Most of the transition metals are known to form homoleptic carbonyls or metal carbonyls which have simple, well-defined structures. For example tetrahedral, octahedral etc. In a metal carbonyl, the metal-carbon bond possesses both σ and π character. The bond between the carbonyl molecule and the metal is further strengthened by the synergic effect produced by the metal-ligand bond. The two types of bonding that exist in metal carbonyls are explained below:

Structure of Metal Carbonyls:

- Due to the donation of <u>electrons</u> by the carbonyl molecules to the vacant orbitals of the metal, a metal-carbon σ bond is formed.
- Due to the donation of a pair of electrons from a filled d orbital metal into the vacant anti bonding π^* orbital of carbonyl ligand, a metal-carbon π bond is formed.



Stability of Coordination Compounds:

Coordination compounds are found to dissociate in various solutions. The stability of a coordination compound in a solution mainly depends on upon the degree of association between the two species involved in the state of equilibrium. Quantitatively the stability of any complex is given by the magnitude of the equilibrium constant for the formation of the compound. A general example is given below:

$$A + 4B {\rightarrow} AB_{\scriptscriptstyle 4}$$

Thus, the amount of AB_4 molecule in the solution depends on upon the value of the <u>equilibrium</u> constant, k. This is also known as stability constant. On the other hand, the instability constant or the dissociation constant of complexes is given by the reciprocal of the equilibrium constant of the formation reaction.

GLOSSARY

1. Coordination compounds contain a central atom (or cation) which is coordinated to a suitable number of anions or neutral molecules and usually retain their identity in solution as well as in solid state. These may be a positively charged, negatively charged or a neutral species,

[Co(NH₃)₆]³⁺, [NiCl₄]², [Ni(CO)₄] etc.

2. In 1893, Werner proposed a theory to explain the structure and bonding in coordination compounds:

(a) In coordination compounds, metals show two types of valencies : Primary valency and secondary valency.

(b) Primary valencies are ionisable.

(c) Secondary valencies are not ionisable.

(d) This theory was successful to very limited extent and could not explain many aspects of coordination compounds.

3. In modern formulations, such spatial, arrangements are called coordination polyhedra.

The species within the square bracket are coordination entities or complexes and the ions outside the square brackets are called counter ions.

4. The compounds which have the same molecular formula but differ in their structural arrangements are known as isomers.

5. The types of isomerism shown by coordination compounds are :

(a) Geometrical (or cis-trans) isomerism: Two coordination compounds are said to be geometrical isomers, when they differ in the arrangement of their ligands in space. When two identical ligands occupy adjacent position, the isomer is called 'cis-form' and when they arranged opposite to one another, the isomer is called 'trans-form'.

(b) Optical isomerism shown by the chiral molecule, i.e., the molecules which do not have plane of symmetry e.g., $[Cr(ox)_3]^3$.

(c) Linkage isomerism occurs in complexes when an ambidentate ligand is present in the coordination sphere, e.g., $[CO(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5(-ONO)]^{2+}$.

(d) Coordination isomerism occurs in those complexes which are made of cationic and anionic coordination entities due to the interchange of ligands between the cation and anion entities, e.g., $[CO(NH_3)_6]$ $[Cr(CN)_6]$ and $[Co(CN)_6]$ $[Cr(NH_3)_6]$.

(e) lonisation isomerism, is due to the exchange of ions in coordination sphere of metal ion and the ions outside the coordination sphere. These two isomers give different ions in aqueous solution, e.g,

 $[Co(NH_3)_5Br]^{2+} SO_4^{2-}$ and $[Co(NH_3)_5(SO_4)]^+ Br^-$

(f) Solvate or hydrate isomerism occurs when water is a part of coordination entity or is outside it, e.g., CrCl₃-6H₂0 has three isomers.

[Cr(H₂O)₆]Cl₃(violet)

hexaaquachromium(III)chloride

 $[Cr(H_2O)_5Cl]Cl_2.H_2O(blue green) \\ Pentaaquachloridochromium(lll)chloride monohydrate \\ \label{eq:cr}$

tetra aquadichloridochromium(III)chloridedihydrate

6. Magnetic properties:

(i) Inner orbital (low spin) complexes are those complexes in which hybrid orbitals of metal are formed by hybridisation of (n-1) d, ns and np-orbitals, e.g., $[Fe(CN)_6]^4$, $[CO(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$, $[(MnCCN)_6]^{3-}$, etc.

(ii) Outer orbital (high spin) complexes are those comp lexes in which the hybrid orbitals of metal are formed by hybridisation ns, np and nd-vacant orbitals, e.g., $[MnF_6]^3$, $[FeF_6]^3$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_20)_6]^{2+}$, etc.

7. Assumptions of Crystal Field Theory:

(a) The ligands are assumed to be point charges.

(b) The interaction between the point charges and the electrons of the central metal are electrostatic in nature.

(c) The 5d-orbitals in an isolated gaseous metal ion have the same energy, i.e., they are degenerate.

8. The stability of a coordination compound [MLn] is measured in terms, of its stability constant

For overall reaction,

$$[M(H_2O)_n] + nL \iff [ML_n] + nH_2O$$

Stability constant, $\beta = \frac{[ML_n]}{[M(H_2O)_n](H_2O)}$

$$= \frac{[M(H_2O)_n][L]^n}{[M(H_2O)_n][L]^n}$$

9. Drawbacks of Crystal Field Splitting:

(a) From the assumption that ligands are point charges, it follows that anionic ligands should exert greatest splitting effect. But anionic ligands actually are found at the low end of the spectro chemical series.

(b) It does not take into account for the covalent character of bonding between the ligand and the central atom.

10. Bonding in metal carbonyls: In metal carbonyl, the metal carbon (M – C) bond possesses both the σ - and π -bond character.

11. Importance and applications of coordination compounds:

(a) In many quantitative and qualitative chemical analysis.

(b) In extraction processes of metals, like silver and gold.

(c) Purification of metals like Ni can be achieved through formation and subsequent decomposition of their coordination compounds.

(d) In biological systems the pigment responsible for photosynthesis is chlorophyll, is a coordination compound of magnesium. Haemoglobin, coordination compound, of Fe, acts as a oxygen carrier.

(e) Case of chelate therapy in medicinal chemistry.

PREPARED BY: MR. ARNAB PAUL CHOWDHURY