Coordination Chemistry

For

3rd Students

(Chem./Zoology group)

By

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COORDINATION COMPOUNDS

Contents

1. INTRODUCTION

You have already studied in your earlier classes that there are two types of compounds. The compounds that can easily dissociate into their constituent ions in aqueous medium are called simple salts and double salts such as NaCl, $MgCl_2$, $FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, etc. On the other hand, the compounds which do not dissociate into their constituent ions in any solvent are known as coordination or complex compounds such as $[Cu(NH_3)_4]^{2+}$. Transition metals have an ability to form a number of coordination compounds due to their small size, high charge and presence of empty d orbitals on the metal ion. A compound formed from the union of metal ion (an electron deficient species, central metal atom/ion; Lewis acid) and electron rich species (ligand; Lewis base) which can donate one electron pair is called coordination compound or complex compound. The coordination compounds can

be represented by the general formula, $[MLn]^{\pm m}$, where M is a metal ion, L is electron rich species; n is the number of L attached to the metal atom/ion and m is the charge on complex ion.

Some metal complexes were prepared and used in the eighteenth century in the form of metal salts and vegetable extracts as paints.

In 1798, $CoCl_3.6NH_3$ was discovered. Werner gave a theory to understand the bonding in such compounds about a century later in 1893. We are studying chemistry of coordination compounds because they have many applications in analytical / environmental chemistry, metallurgy, biological systems, industries and medicine.

A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:-

a) Simple salt

b) Molecular (or) addition compounds

a) **Simple salt**

A simple salt is formed by the neutralization of an acid by a base. KOH + HCl → KCl + H2O

Normally, a simple salt ionizes in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b) **Molecular (or) addition compounds**

i**) Double salts**

These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt.

Double salts retain their properties only in solid state.

They are also called as lattice compounds.

Example

Mohr's salt

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$

The double salts give the test of all their constituent ions in solution.

ii) **Coordination (or complex) compounds**

Coordination compound is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

Example

$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2 \cdot 4KCN$ (or) $K_4[Fe(CN)_6]$

Ferrous cyanide

$Fe(CN)_2 \cdot 4KCN \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

Complex anion

In $K_4[Fe(CN)_6]$ the individual components lose their identity.

The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

i) An anionic complex compound contains a complex anion and simple cation.

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

simple cation complex anion

ii) A cationic complex contains complex cation and simple anion

$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

Complex cation simple anion

iii) A neutral complex , In the case of a complex compound,

$[Cr(NH_3)_6][Co(CN)_6]$, it gives both complex cation and complex anion

$[Cr(NH_3)_6][Co(CN)_6] \rightarrow [Cr(NH_3)_6]^{3+} + [Co(CN)_6]^{3-}$

complex cation complex anion

TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) **Lewis Acid**

All electron acceptors are Lewis acids.

(b) **Lewis Base**

All electron donors are Lewis base.

(c) **Central metal ion**

In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation.

Hence, central metal cation in a complex serves as a lewis acid.

(d) **Ligand** (Latin word meaning to bind)

A ligand is an ion (or) a molecule capable of functioning as an electron donor. Therefore the neutral molecules or ions which are directly attached to the central metal ion are called as ligand (or) coordination

groups. These coordination groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewis bases.

Examples:

$[Ni(NH_3)_6]^{2+}$: Ligand = NH_3 molecule and Central metal ion = Ni^{2+}

$[Co(NH_3)_5Cl]^{2+}$: Ligands = NH_3 molecule and Cl^- ion

(e) **Coordination number**

The total number of coordinate bonds through which the central metal ion is attached with ligand is known as coordination number. Coordination number may be two, three, four, five, six, seven, eight, nine or even higher in case of lanthanides and actinides . Coordination number depends on size, charge and electronic configuration and nature of meal/ion and ligands

For example

– large metal atoms show high CN

– bulky ligands reduce coordination number

-Lewis bases easily donate electrons to metals and metals with lesser number of electrons can easily accept electrons

Examples $K_4[Fe(CN)_6]$ the coordination number of Fe(II) is 6 and in $[Cu(NH_3)_4]SO_4$ the coordination number of Cu(II) is 4.

(f) Coordination sphere

the central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called coordination sphere or first sphere of attraction

(g) Oxidation number or Oxidation state of central metal atom/ ion

It is the number that represent an electric charge with an atom or ion actually has or appears to have when combined with other atom

(h) Counter ions

The ions excluding the coordination sphere are called as counter ions. In $K_4[Fe(CN)_6]$ compound, K^+ is the counter ion.

Ligands and their types

The electron rich species, which may be charged species, e.g. Cl^-, CN^-, NO_2^-, etc or neutral species e.g. H_2O, NH_3, $NH_2CH_2CH_2NH_2$, CO, NO, etc., that can donate an electron pair to the metal atom/ion are called ligands.

Types of ligands

The ligands can be classified in the following ways:

Type I- Based on electron accepter/donor properties of the ligand

- σ (sigma) donor ligands are those ligands which can only donate electron pair to the meal ion, e.g. H_2O, NH_3, F^-. These ligands are also known as weak field ligands.
- σ (sigma) donor and Π (pi) accepter ligands are those ligands which can donate electron pair and also have a tendency to accept electron in

their empty antibonding π molecular orbitals (MO). Such ligands can involve in backbonding (π bond) with the metal ion. For example, CO, CN^-, NO, etc. These ligands are also known as strong field ligands.

- Π (pi) donor ligands are those ligands like benzene and ethylene, which do not have lone pair of electrons but only π electrons for donation to the metal atom/ion.

Type II- Based on the basis of number of donor atoms in the ligand

- Monodentate or unidentate ligands

The ligands that bound to a metal ion through a single donor atom are called as monodentate or unidentate ligands, e.g. Cl^-, H_2O or NH_3. These ligands can be further divided into the following subclasses on the basis of charge (Figure 1).

- Ambidentate ligands

Some ligands have two or more than two different donor atoms. These ligands can attach through any of the donor atoms. They are given different names depending upon nature of the donor atom linked to the metal atom. These ligands are known as ambidentate ligands e.g. NO_2 (donor atom may be either N or O), SCN^- (donor atom may be either S or N), CN^- (donor atom may be either C or N), $S_2O_3^{2-}$ (donor atom may be either S or N). These are also monodentate ligands.

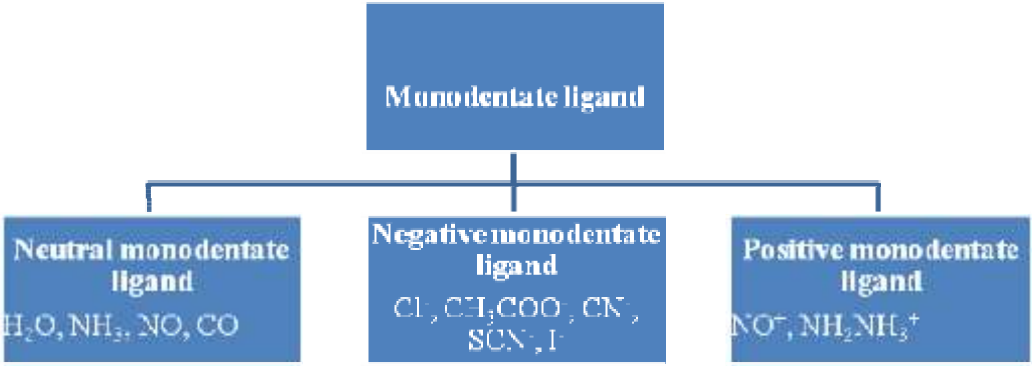

Figure1: Classification of monodentate ligands

2. WERNER’S COORDINATION THEORY AND ITS EXPERIMENTAL VERIFICATION

Alfred Werner in 1893 suggested a new theory for explaining the nature of bonding in coordination compounds known as Werner’s theory. According to this theory, there are two kinds of valences of metal atom/ion in coordination compounds: primary and secondary valences

Postulates of Werner’s theory

1) Every metal atom has two types of valencies

i) Primary valency or ionisable valency

ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature where as the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

Werner's theory can be explained on the basis of experimental evidences

- Molar conductivity measurement method

Compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ show decreasing order of conductivity due to the formation of 4 ions, 3 ions, 2 ions and no ions, respectively in solution.

$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$ (1 complex ion + 3 chloride ions)

$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$ (1complex ion +2chloride ions)

$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2] + +Cl^-$ (1 complex ion+1chloride ion)

$[Co(NH_3)_3Cl_3] \longrightarrow [Co(NH_3)_3Cl_3]$ (No ions)

- <u>Precipitation method</u>

  When cobalt ammine chloride complexes react with $AgNO_3$, some of the Cl^- ions get precipitated with $AgNO_3$ to form AgCl. The number of Cl^- ions that are ionisable and present outside the coordination sphere can react with $AgNO_3$. Thus, coordination compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ react with 3, 2 and 1 mole of $AgNO_3$ to form 3, 2 and 1 mole of AgCl, respectively as there are 3, 2 and 1 ionisable Cl^- ions, respectively.

Defects of Werner’s theory

- Although the theory describes the structure of many compounds, it can’t explain the nature of bonding between metal atom/ion and ligands.
- Werner’s theory was unable to explain why 4- and 6-coordination numbers are the preferred coordination numbers.

EFFECTIVE ATOMIC NUMBER CONCEPT (EAN CONCEPT)

- This rule is given by English Chemist Nevil V. Sidgwick. Effective atomic number (EAN) is the total number of electrons in metal atom/ion (atomic number) plus the electrons gained from ligands. This EAN is the atomic number of a noble gas. Therefore, EAN decides stability of coordination compound. If a coordination compound follow EAN rule, than it is stable one.
  - EAN= Atomic number of metal atom/ion + number of e- donated by ligands or 2 x number of ligands (as each ligand can donate two electrons to metal atom/ion).
  - **For $[Co(NH_3)_6]^{3+}$**
  - Atomic number of Co=27; Atomic number of Co^{3+}=24; there are six ligands hence electrons donated by 6 ligands = 6 x 2

- EAN = 24 + (6 x 2) = 36 (atomic number of Krypton; Kr)

- **For [Ni(CO)$_4$]**
- Atomic number of Ni=28; there are four ligands hence electrons donated by 4 ligands = 4 x 2
- EAN = 28 + (4 x 2) = 36 (atomic number of Krypton; Kr)

- **For [Fe(CN)$_6$]$^{4-}$**
- Atomic number of Fe=26; Atomic number of Fe^{2+}=24; there are six ligands hence electrons donated 6 ligands = 6 x 2
- EAN = 24 + (6 x 2) = 36 (atomic number of Krypton;

- **For $[Ag(NH_3)_4]^+$**
  - Atomic number of Ag=47; Atomic number of Ag^+=46; there are four ligands, hence electrons donated by 4 ligands = 4 x 2
  - EAN = 46 + (4 x 2) = 54 (atomic number of Xenon; Xe)

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- **For $[V(CO)_6]^-$**
  - Atomic number of V=23; Atomic number of V^- = 24; there are six ligands hence electrons donated 6 ligands = 6 x 2
  - EAN = 24 + (6 x 2)

    = 36 (atomic number of Krypton; Kr)

- **For $[Mn(CN)_4]^{2-}$**
  - Atomic number of Mn=25; Atomic number of Mn^{2+} = 23; there are four ligands hence electrons donated 4 ligands = 4 x 2

EAN = 23 + (4 x 2) = 31

Not obeying EAN rule as 31 is not the atomic number of any noble gas

NOMENCLATURE OF COORDINATION COMPOUNDS

Rules for writing formula of coordination compounds

Formula of the cation whether simple or complex must be written first followed by anion.

The coordination sphere the sequence of symbols is :

First metal name followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically

Polyatomic ligands are enclosed in parentheses

e.g In $Na[PtBrCl(NO^{+2})_2NH_3(NO)]$ sequence in coordination sphere is metal atom, alphabetical sequence of anionic ligand Br^-, Cl^-, NO^{2-}, followed by neutral ligand NH_3 and then cationic ligand NO^+

IUPAC nomenclature of coordination compounds

steps suggested by IUPAC (International Union of Pure and Applied Chemistry)

The rules are outlined below:

- In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.
- Name of non-ionic or molecular complexes are written as one word without any gap.
- In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).
- Ligand names generally end with ‘O’ if the ligand is negative (‘chloro’ for Cl^-, ‘cyano’ for CN^-, ‘hydrido’ for H^-) and unmodified if the ligand is neutral (‘methylamine’ for $MeNH_2$). Special ligand names are ‘aqua’ for water, ‘ammine’ for ammonia, ‘carbonyl’ for CO,ni trosyl’ for NO.

- A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, like triphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

For example, $[Ni(PPh_3)_2Cl_2]$ is named dichlorobis(triphenylphosphine)nickel(II).

- A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.
- If the complex ion is negative, the name of the metal ends in 'ate' for example, ferrate, cuprate, nickelate, cobaltate etc.
- If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each.

For example, NH_3 (ammine) would be considered as 'a' ligand and come before Cl^-(chloro).

- Some additional notes

Some metals in anions have special names

B Borate ,Au Aurate, Ag Argentate, Fe Ferrate, Pb Plumbate, Sn Stannate, Cu Cuprate, Ni Nickelate

- Use of brackets or enclosing marks. Square brackets are used to enclose a complex ion or neutral coordination species.

Examples

$[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(III) chloride

$[Co(NH_3)_3(NO_2)_3]$ triamminetrinitrocobalt (III)

$K_2[CoCl_4]$ potassium tetrachlorocobaltate(II)

note that it is not necessary to enclose the halogens in brackets.

Name of Negative ligands

Ligand	Name	Ligand	Name
H^-	Hydrido	HS^-	Mercapto
O^{2-}	Oxo	NH_2^-	Amido
O_2^{2-}	Peroxo	NH^{2-}	Imido
O_2H^-	Perhydroxo	NO_3^-	Nitrato
OH^-	Hydroxo	ONO^-	Nitrito
F^-	Fluoro	NO_2^-	Nitro
Cl^-	Chloro	N^{-3}	Nitride
Br^-	Bromo	P^{3-}	Phosphido
I^-	Iodo	N_3^-	Azido
CO_3^-	Carbonato	CNO^-	Cyanato
$C_2O_4^-$	Oxalate	NCO^-	Cyanato
$CH_3CO_2^-$	Acetate	SCN^-	Thiocyanato
SO_4^{2-}	Sulphato	HCO_3^-	Hydrogencarbonato
SO_3^{2-}	Sulphito	$S_4O_6^{2-}$	Tetrathionato
S^{2-}	Sulphido	HSO_3^-	Hydrogensulphito
$NH_2CH_2CO_2^-$	glycinato	$C_5H_5^-$	Cyclopentadienyl
$(OCCH_2)_2NCH_2CH_2CH_2$ $N(CH_2CO_2^-)_2$	Ethylenediammine tetraacetato (EDTA)	$S_2O_3^{2-}$	Thiosulpahato

Name of neutral ligands

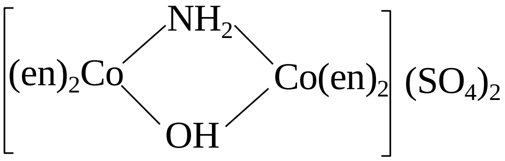
Ligand	Name	Ligand	Name
C_5H_5N (py)	pyridine	$NH_2(CH_2)_2NH_2$ (en)	ethlenediammine
NH_3	Ammine	CH_3NH_2	Methylamine
H_2O	Aqua/aquo	CO	Carbonyl
C_6H_6	Benzene	NO	Nitrosyl
N_2	Dinitrogen	CS	Thiocarbonyl
O_2	Dioxygen	NS	Thionitrosyl
Ph_3P	Triphenylphosphine	CH_3COCH_3	Acetone

Name of Positive ligands

Ligand	Name
NO^+	Nitosonium
NO_2^+	Nitronium
$NH_2NH_3^+$	hydrazinium

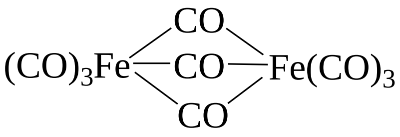
These rules are illustrated by the following examples:

COMPOUNDS	SYSTEMATIC NAMES
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(II) chloride
$[Co(NH_3)_5Cl]^{2+}$	Chloropentamminecobalt(III) ion
$[Co(NH_3)_4SO_4]NO_3$	Sulphatotetramminecobalt(III) nitrate
$[Co(NH_3)_3(NO_2)_3]$	Trinitrotriamminecobalt(III)
$[Co(NH_3)_3NO_2.Cl.CN]$	Chlorocyanonitrotriamminecobalt(III)
$[Cr(en)_3]Cl_3$	Tris(ethylenediamine)chromium(III) chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Pt(py)_4][PtCl_4]$	Tetrapyridineplatinum(II)tetrachloroplatinate(II)
$[(NH_3)_5Co.NH.Co(NH_3)_5](NO_3)_5$	Decammine-μ-amidodicobalt(III) nitrate



$$\left[(en)_2Co\langle{}^{NH_2}_{OH}\rangle Co(en)_2\right](SO_4)_2$$

Tetrakis(ethylenediamine)-μ-amido-μ-hydroxo-dicobalt(III) sulphate



Tri-μ-carbonylbis(tricarbonyliron(III))
OR
Hexacarbonyltri-m-carbonyl-diiron(III)

$AlCl_3.(EtOH)_4$ Aluminum(III)chloride-4-ethanol.

Name the following complexes:

(a) $[Cu(NH_3)_4]SO_4$; (b) $K_2[CoCl_4]$;

(c) $Co(phen)_2Cl_2$; (d) $[Co(en)_2(H_2O)Cl]Cl_2$

ISOMERISM OF COORDINATION COMPOUNDS

INTRODUCTION

The objectives of this unit are to familiarize you with the isomerism in coordination compounds and its types. The coordination compounds which have the same chemical formula but different ways of attachment of ligands are called as isomers. These isomers have different physical and chemical properties. The phenomenon that gives rise to the isomers is known as isomerism. There are two main types of isomerism in coordination compounds; structural and stereo- isomerism. Our focus will be on both structural isomerism and stereoisomerism. Structural isomerism is due to the different bond arrangement of atoms in coordination compound around the central metal atom/ ion while stereoisomerism arises due to different three-dimensional arrangement of atoms in space.

Isomerism in coordination compounds

The coordination compounds having the same molecular formula but different arrangement of atoms/ groups around the central metal/ ion are called isomers and the phenomenon which gives rise to isomers is called as isomerism. The isomers have different physical and chemical properties.

Coordination compounds exhibit two major types of isomerism, namely (A) structural isomerism and (B) stereoisomerism (space isomerism). Each of these is further classified as shown below.

A) Structural isomerism

i) Coordination isomerism ii) Ionization isomerism

iii) Hydrate or Solvate isomerism iv) Linkage isomerism

B) Stereoisomerism

i) Geometrical isomerism ii) Optical isomerism

A) Structural isomerism

Structural isomerism is also known as constitutional isomerism. The molecules have same number of atoms which differ in their structure or bonding. The different chemical formulae of structural isomers are either due to difference in ligands that are bonded to the central atoms or the mode of bonding of individual ligand (which atom of the ligand is bonded to the central atom). Now we will discuss the various types of structural isomerism one by one in brief.

i) Coordination isomerism

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centers.

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

$[PtII(NH_3)_4]$ $[CuCl_4]$ and $[Cu(NH_3)_4]$ $[PtCl_4]$

$[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centers.

The coordination compounds in which both the cationic and anionic species are complex ions, show coordination isomerism. This isomerism occurs by the interchange of ligands in between the cationic part and the anionic part. In another words, you can define the coordination isomers as the isomers in which the complex anion and complex cation of a coordination compound exchange one or more ligands

ii) **Ionization Isomerism**

This is the phenomenon by which ligands present inside the coordination sphere and anion or neutral molecule present outside the coordination sphere can exchange their place. The central metal / ion and the other ligands except one that is exchangeable are similar in both the isomers. Thus, ionization isomerism is the exchange of ions between coordination sphere and ionization sphere. The physical and chemical properties of the two isomers are entirely different as they give different ions on dissolving in suitable solvent. Two octahedral ionization isomers will have five identical ligands while the sixth ligand will be different. In case of tetra coordinated isomers, three ligands will be identical and the fourth one will be the different one. The different ligand in one isomer may be outside of the coordination sphere in the other isomer. The oxidation state of the central ion would not be changed in the two isomers

Coordination compounds having the same molecular formula but forming different ions in solution are called ionization isomers. This property is known as ionization isomerism.

An example of this type of isomerism is furnished by the red-violet, $[Co(NH_3)_5Br]SO_4$ $[Co(NH_3)_5SO_4]Br$

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.

$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4NO_2Cl]Cl$

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

iii) Hydrate isomerism

In hydrate isomerism, there is exchange between water molecule inside the coordination sphere and ions present in the ionization sphere. Composition of hydrate isomers is the same but the number of water molecules inside the coordination sphere is different . For example, $CrCl_3.6H_2O$ has the following three hydrate isomers:

A. $[Cr(H_2O)_6]Cl_3$ (violet)
B. $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (blue green)
C. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (green)

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 3,2, and 1 Cl^- ions in solution respectively.

iv) Linkage Isomerism

Complexes having ambidentate ligands like SCN^- / NCS^-, CN^-/NC^- and NO_2^-/ ONO^- (capable of coordinating in more than one way) show linkage isomerism. The two isomers differ from each other by the linkage atom attachment to the central atom/ ion. The ligand can have more than two donor atoms but should be joined to the central atom/ ion via only one atom (unidentate ligand). The formula of the compound is same but their properties are entirely different. The name of the ligands is also changed according to their donor atom. When donor atom is N, NO_2^- is called as nitro, while it is called nitrito if the donor atom is O atom.

For example

$[Co(NH_3)_5ONO]Cl_2$ the nitrito isomer -
red colour - O attached

$[Co(NH_3)_5NO_2]Cl_2$ the nitro isomer -
yellow colour - N attached

B) Stereoisomerism (space isomerism)

Consider two compounds containing the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism.

Compounds which have the same atoms/groups, same position of atoms/groups and same sets of bonds, but differ in their spatial arrangement around the central atom/ ion are called as stereoisomers and the phenomenon is known as stereoisomers

There are two different types of stereoisomerism.

i) Geometrical isomerism or ii) Optical isomerism.

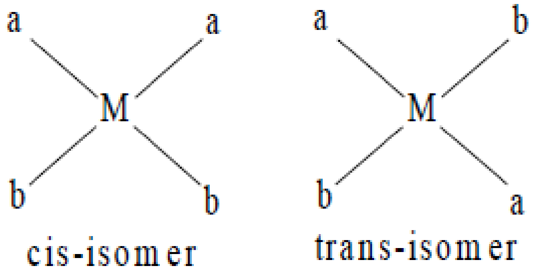
i) Geometrical isomerism (or) cis-trans isomerism

The compounds with differences in geometrical arrangement of the ligands around the central atom/ ion are known as geometrical isomers and the phenomenon as geometrical isomerism. This is also called as cis-trans isomerism. The geometrical isomers have the same empirical formula but different physical and chemical properties due to different arrangement of the ligands in space. The geometrical isomers can be easily separated from each other. When similar atoms/ groups (ligands) are adjacent to each other, the isomer is called cis-isomer (Latin, cis= same). In trans-isomer, the similar ligands are present diagonally opposite to each other (Latin, trans = across). It is common in di-substituted square planar and octahedral complexes with co-ordination number of 4 and 6, respectively. Tetrahedral (coordination number 4) complexes do not show geometrical isomerism because in this geometry, all the ligands are present in cis- position (adjacent) with respect to each other (all bond angles are same).

Geometrical isomerism is due to ligands occupying different position around the central ion. The ligands occupy position either adjacent to one another or opposite to one another. These are referred to as cis-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism. Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral

Geometrial isomerism in 4-coordinate complex

(1) **[Ma2b2] type complexes Square planar**

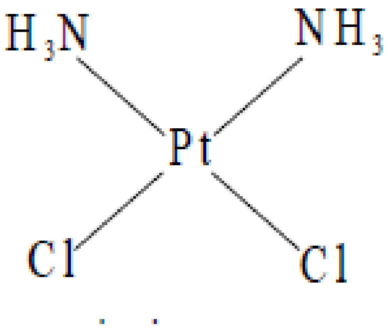


In a cis-isomer two identical (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

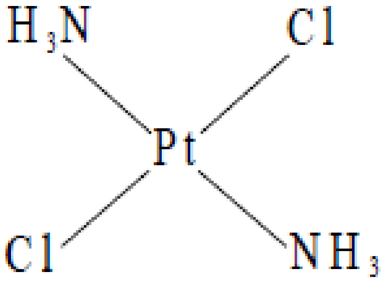
Square planar complexes of the type [Ma2b2]n+ where a and b are monodentate ligands, exist as cis and trans-isomers as shown

Example of this type of complexes are

$[Pt(NH_3)_2Cl_2]$ and $[Pd(NH_3)_2(NO_2)_2]$



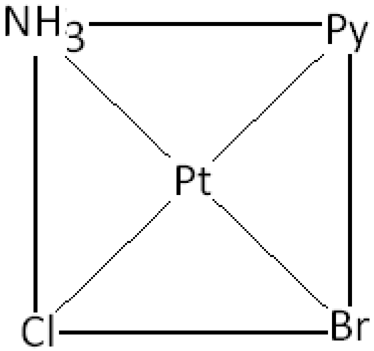
cis-isomer

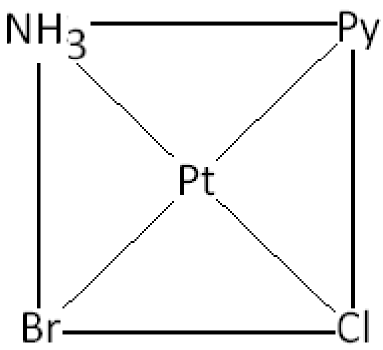


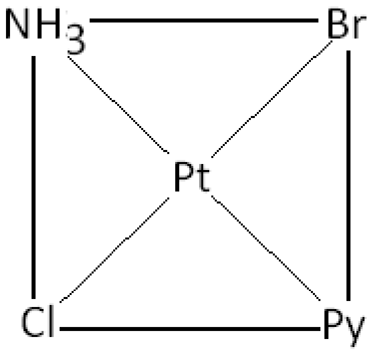
trans-isomer

(2) [Mabcd] type complexs

Square planar complex of this type exist in three isomeric forms for example [Pt(NH_3)(Py)(Cl)(Br)] exist in the following structures

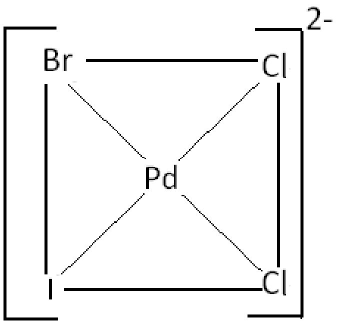




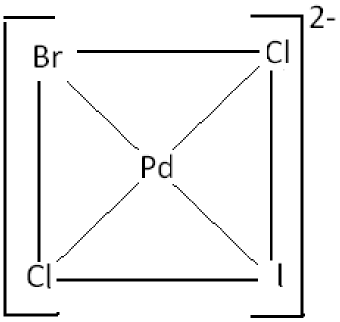


(3) [Ma2bc] type complexes

Square planar complexes of this type also shows cis-trans isomerism. For example [Pd $(Cl)_2BrI]^{2-}$ exists in the following cis-trans



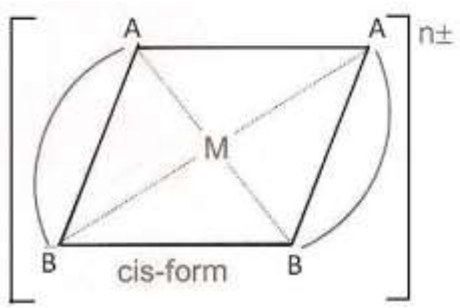
cis-isomer

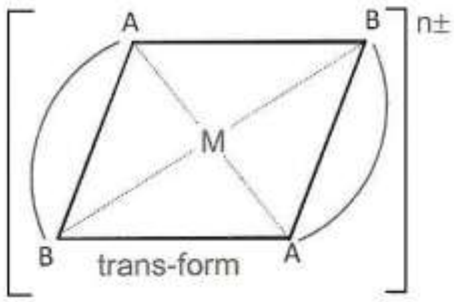


trans-isomer

(4) [M(AB)2]n± type complex

Here m is the central metal ion and (AB) represents an unsymmetrical bidentate ligand(A) and (B) arethe two ends (i.e. coordinating atoms) of the bidentates ligands such type of complexes also show trans and cis isomerism

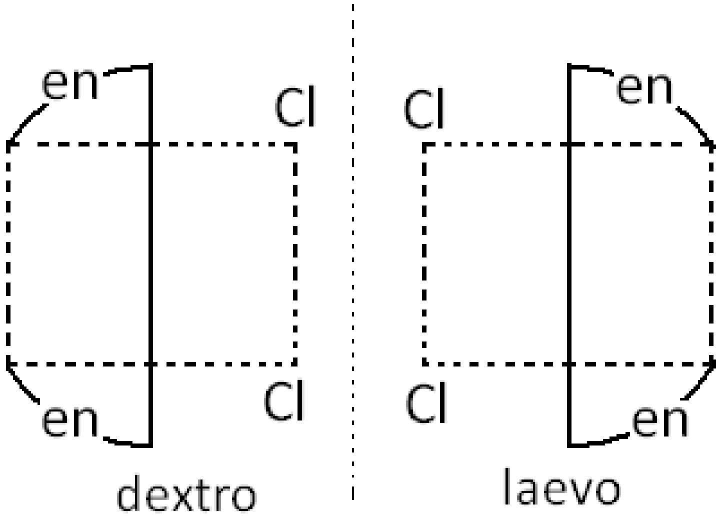




a) Optical Isomerism

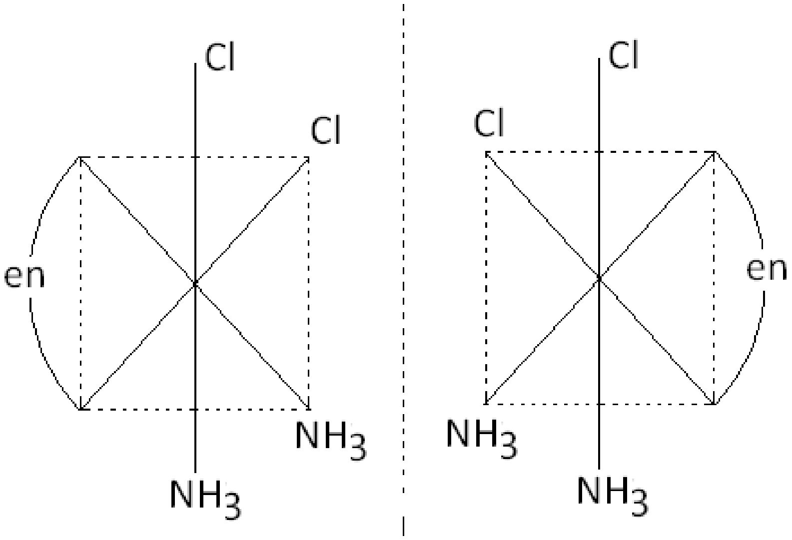
This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarized light. The compounds which exhibit this property are called optical isomers. The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is that the isomers rotate the plane of polarized light either to the left or right. If the rotation is on the left side, then that isomer is levo and if on right side, then isomer is dextro. The equal proportion of levo and dextro mixture is called racemic mixture

It is generally found octahedral chelate ions. The two isomers of this type of complex are mirror image of each other and cannot super impose on each other, hence they possess chirality character.



coordination compound of type $[PtCl_2(en)_2]^{2+}$ two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optical activity because the whole molecule is asymmetric.

The optical isomers of $[CoCl_2(en)(NH_3)_2]^+$ are as follows



Importance and applications of Coordination Compounds

Coordination compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.

These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.

Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes

Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

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

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B12, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the un decomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry.

  An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis–platin and related compounds.

List of References:

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E.S. Gilreath

2- Coordination Compounds

S. F. A. Kettle

3- Advanced Inorganic Chemistry: A Comprehensive Text

Cotton and Wilkinson