Index

Chapter 1 Introduction to Coordination Chemistry		
1.1.	Introduction	1
1.2.	Double Salt and Coordination Compounds	2
1.3.	Some important terminologies of coordination compounds	3
1.4.	Classification of ligands	5
1.5.	Nomenclature of the coordination complexes	7
Chapter 2 Isomerism of the coordination compounds		
2.1.	Introduction	9
2.2	Structural isomerization	9
2.3.	Steroisomerism	13
Chapter 3 Theories of coordination chemistry		
3.1	Early theories to explain bonding in coordination compounds	33
3.2.	Later theories to explain bonding in coordination compounds	35
Chapter 4 Term symbol and electronic spectra of the coordination compounds		
4.1.	Term Symbols	76
4.2.	Electronic Spectra of the Coordination Complexes	92
4.3	Charge Transfer Spectra	125
129		
Chapter 5 Magnetism of the coordination complexes		
5.1.	Introduction	130
5.2.	Origins of Magnetic Behavior	130
5.3.	Types of Magnetism	131
5.4.	Temperature Dependence of Magnetic Susceptibilities	132
5.5.	Deviations from Spin-Only Behavior	133
Chapter 6 Stability and the reaction mechanism of the coordination complexes		
6.1.	Stability of the coordination compounds	141
6.2.	Inorganic Reaction Mechanism	151
6.3.	Summary	183
6.4	HOTS-High order thinking skills	187
212		
Chapter – 7 Introduction to organometallic compounds and their stability		
7.1.	Introduction of Organometallic Compounds	213
7.2.	Classification of Organometallic Compounds	213
7.3	Electron Rule	215

Chapter 8 Interaction of metal with carbonyl & nitrosyl ligand		
8.1.	Metal Carbonyl Clusters	221
8.2.	Zintl Ions	229
8.3.	Isolobal Species	230
8.4.	Metal carbonyls	243
8.5.	Phosphine Ligand	259
8.6.	Metal Nitrosyls	260
8.7.	Fluxional Behaviour of the Organometallic Compounds	263
8.8.	HOTS- High Order Thinking Skills	267

Chapter 9 Reactions of the organometallic compounds & metal carbenes		
9.1.	Reaction in Organometallic Chemistry	275
9.2.	Metal Carbenes	284
9.3.	Metal Alkyl, Alkene and Allyl Complexes	287
9.4.	Organometallic Compounds of Main Group Elements	296

Chapter 10 New Generation Of Organometallic Chemistry : Metallocene Compounds		
10.1.	Introduction to Metallocenes	299
10.2.	Cyclopentadienyl (Cp) Complexes	299
10.3.	Bent Sandwich Compounds	304
10.4.	Half Sandwich Compounds	305
10.5.	Cycloheptatriene Complexes	306
10.6.	Cyclooctatetraene Complexes	308

Chapter 11 Applications of organometallic compounds: homogeneous catalysis		
11.1.	Homogeneous Catalysis	312
11.2.	Hydrogenation of Alkenes by Wilkinson's Catalyst	314
11.3.	Hydroformylation or Oxo Process	317
11.4.	Wacker Process of Alkenes	320
11.5.	Monsanto Acetic Acid Process	322
11.6.	Alkene Polymerization: Ziegler-Natta Catalyst	323
11.7.	Water Gas Reaction: Fischer-Tropsch Process	324
11.8	Catalytic Deuteration	325
11.9	Olfien Metathesis	326
11.10	Summary	334
11.11.	HOTS- High Order Thinking Skills	336

Chapter 1

Introduction to Coordination Chemistry

1.1. Introduction

The transition elements comprise of elements present in groups 3 to 12 of the long form of the periodic table. These elements are found in the central region of the standard periodic table. These elements are termed as 'transition elements' as they show transition in their properties as we move across the periodic table from metallic elements of groups 1 and 2 and the predominantly non-metallic elements of groups 13 to 18. Nevertheless, the transition elements still show metallic character to a greater extent. The chemistry of the transition elements has been investigated for two centuries, and in the past fifty years these elements and their compounds have proved to be a nearly ideal touchstone for many of the models which have been developed to understand structure and bonding. The elements range from the widespread to the extremely rare; iron is the fourth most abundant element (by weight) in the earth's crust, technetium does not occur naturally. Elements such as gold and silver have been known in the native state since antiquity, whereas technetium was first prepared in 1937. Most of the elements exhibit a typical silvery metallic appearance, but gold and copper are unique in their reddish coloration and mercury is the only metal which is liquid at ambient temperatures. Compounds of the transition elements account for the majority of colored inorganic materials, and many pigments are relatively simple derivatives of these elements; however, not all transition-element compounds are colored. What are the common features that unite these elements? It is surprisingly difficult to find a single definition which satisfactorily encompasses all of the transition elements. The elements occur at that point in the periodic table where the d orbitals are being filled. The first-row transition elements coincide with the filling of the 3d, the second row with the filling of the 4d, and the third row with the filling of the 5d orbitals. We define a transition element as elements possessing filled or partially filled valence d orbitals in one or more of its oxidation states. This definition excludes the elements in groups 13 to 18. It is well known that, the 3d orbitals lie at higher energies than the 4s orbitals. On the other hand, the configurations of the M2+ ions listed, in literature reveal the loss of electrons from the 4s shell in preference to the 3d, so that in these species the 4s orbitals are the higher in energy.

The systematic investigation of the chemistry of the transition elements began in the nineteenth century, and it rapidly became apparent that many of the compounds were somewhat different from those with which chemists were then familiar. There was a clear difference between the behavior of simple ionic compounds such as sodium chloride and typical transition-element compounds such as $FeCl_2.4H_2O$. It was also obvious that the compounds did not resemble the typically covalent compounds of organic chemistry. It was considered that many of the compounds formed by transition metals were of a complex constitution, and they were accordingly known as complexes.The transition metals can be broadly defined as those elements in which either as elements or as ions has partly filled d orbitals. These elements are also called as d block elements as the last differentiating electroenters in the d orbital

.Table 1.1: Electronic configuration of transition elements

Scandium	[Ar] $3d^1\ 4s^2$	**Yttrium**	[Kr] $4d^1\ 5s^2$	**Lanthanum**	[Xe] $5d^1\ 6s^2$
Titanium	[Ar] $3d^2\ 4s^2$	**Zirconium**	[Kr] $4d^2\ 5s^2$	**Hafnium**	[Xe] $4f^{14}\ 5d^2\ 6s^2$
Vanadium	[Ar] $3d^3\ 4s^2$	**Niobium**	[Kr] $4d^4\ 5s^1$	**Tantalum**	[Xe] $4f^{14}5d^3\ 6s^2$
Chromium	[Ar] $3d^5\ 4s^2$	**Molybdenum**	[Kr] $4d^5\ 5s^1$	**Tungsten**	[Xe] $4f^{14}\ 5d^4\ 6s^2$
Manganese	[Ar] $3d^5\ 4s^1$	**Technetium**	[Kr] $4d^5\ 5s^2$	**Rhenium**	[Xe] $4f^{14}\ 5d^5\ 6s^2$
Iron	[Ar] $3d^6\ 4s^2$	**Ruthenium**	[Kr] $4d^7\ 5s^1$	**Osmium**	[Xe] $4f^{14}\ 5d^6\ 6s^2$
Cobalt	[Ar] $3d^7\ 4s^2$	**Rhodium**	[Kr] $4d^8\ 5s^1$	**Iridium**	[Xe] $4f^{14}\ 5d^7\ 6s^2$
Nickel	[Ar] $3d^8\ 4s^2$	**Palladium**	[Kr] $4d^{10}\ 5s^0$	**Platinum**	[Xe] $4f^{14}\ 5d^9\ 6s^1$
Copper	[Ar] $3d^{10}\ 4s^1$	**Silver**	[Kr] $4d^{10}\ 5s^1$	**Gold**	[Xe] $4f^{14}\ 5d^{10}\ 6s^1$
Zinc	[Ar] $3d^{10}\ 4s^2$	**Cadmium**	[Kr] $4d^{10}\ 5s^2$	**Mercury**	[Xe] $4f^{14}\ 5d^{10}\ 6s^2$

The cations of the metals have greater tendency to form the complexes with several donating molecules or atoms called *ligands.* The metal ions and the ligand are linked to each other by a special type of covalent bond called as coordinate bond or dative bond. These complexes give rise to the special type of the chemistry called as coordination chemistry. In this chapter, we are going to study these complexes of the transition metals, their isomerism, electronic and other spectral properties of the coordination compounds, and magnetic properties of the coordination compounds and most importantly the reaction mechanism of the coordination compounds.

1.2. Double Salt and Coordination Compounds

Firstly, let us get acquainted with coordination compounds. Are double salts and coordination compounds the same?

Table 1.2: Difference between double salt and coordination compounds

DOUBLE SALT	COORDINATION COMPOUNDS
Compound prepared by the mixing of the two different types of the salt compounds.	Compound composed of the central metal atom surrounded by the ligands around it
They exist only in the solid state. When they are put into the liquid form, they break down into their constituent atoms.	They exist into both solid as well as in liquid form. Also, they retain their identity when dissolved into water and any other solvent.
Their properties are same as their constituents.	Their properties differ from their constituents.
These compounds are of ionic type and don't contain any coordinate bond.	These compounds may or may not be ionic but thecomplex part always contains coordinate bond.
Metal ion shows normal valency in these compounds	In these compounds, the metal atom shows two types of valencies: primary valency and secondary valency
A double salt loses its identity in the solution.	Coordination compound retain their identity in the solution
e.g. Potash alum ($K_2SO_1.Al_2SO_1.24H_2O$)Carnallite ($KCl.MgCl_2.6H_2O$)	e.g. $K_3[Fe(CN)_6]$, $Ni(CO)_4$

NOTE: -

When double salts are dissolved in the water, it gives tests for each and every constituent. Thus, Potash alum ($K_2SO_1.Al_2SO_1.24H_2O$) gives positive tests for K^+, SO_4^{2-} and Al^{3+}.On the other hand, when coordination complexes are dissolved in the water, each and every constituent can't be detected. Thus, $K_3[Fe(CN)_6]$, this compound does not give the positive test for the Fe and CN ions. Actually, these ions are present the form of a new ion called complex ion. Upon dissociation it gives

$$K_3[Fe(CN)_6] = 3\,K^+ + [Fe(CN)_6]^{2-}$$

1.3. Some important terminologies of coordination compounds

1.3.1. Central ion or centre of coordination: -

The cations to which one or more neutral molecules or anions are attached are called the centre of coordination. This cation being electropositive in nature acts as a Lewis acid by accepting the electrons. For this purpose of accepting the pair of electrons, the central metal must have the vacant d orbitals and this explains why the transition metals having empty d orbital's forms the coordination compounds very readily.

e.g. In $K_3[Fe(CN)_6]$ and $Ni(CO)_4$, Fe^{3+} and Ni^{2+} acts as a central metal ions.**1.3.2. Ligands or coordinating groups: -**

Any molecule, atom or ion which is capable of donating pair of electrons to the central metal ion is called a ligand or coordinating groups. These ligands are nucleophilic and act as a Lewis base by donating the electron(s). Further in ligand, the particular atom which donates the electrons is called as the donor atom. The common donor atoms are N, O, S and halogens.**1.3.3. Coordination number: -**

The total number of ligands that is directly attached to the central metal atom is called as the coordination number. Coordination number states the actual arrangement of the ligand around the central metal atom, Thus, in other words coordination number defines the geometry of the coordination complex.**Table 1.3: Coordination numbers and general geometries associated with that number**

Coordination Number	Arrangement of donor atoms around metal centre	Less common arrangements
2	Linear	
3	Trigonal planar	
4	Tetrahedral; Square planer	Trigonal pyramidal
5	Trigonalbipyramidal;square based pyramidal	
6	Octahedral	Trigonal prismatic
7	Pentagonal bipyramidal	Monocappedtrigonal prismatic; monocapped octahedral
8	Dodecahedral;Square antiprismatic; hexagonal bipyramidal	Cube; bicappedtrigonal prismatic
9	Tricappedtrigonal prismatic	

***Note that for some coordination numbers; more than one possible arrangement of donor atoms exists.**

1.3.4. Coordination sphere:

The central metal atom and the ligand directly attached to it are collectively called as the coordination sphere. Coordination sphere is written inside the square bracket. The point to be noted that, the central metal atom and the ligands inside the square bracket behave as the single entity.**1.3.5. Oxidation state:**

It is the number which represents the formal charge on the central metal atom of a complex ion.

e.g. the oxidation number of Fe, Ni and Co in $[Fe(CN)_6]^{3-,}$ $[Ni(CO)_4]$ and $[Co(NH_3)_6]^{3+}$ is +2, zero and 3+ respectively.**a.Determination of the oxidation number of any compound: -**

i. $K_3[Fe(CN)_6]$

As the complex has three monovalent cations outside the coordination sphere, the complex must carry a negative charge and hence

$K_3[Fe(CN)_6] \leftrightarrow 3K^+ + [Fe(CN)_6]^{3-}$

Now consider, the complex ion as $[Fe(CN)_6]^{3-}$

The formal charge on CN anion is -1. Therefore, mathematically oxidation state is calculated as;

$x + (-6) = -3$

$x = 3$

Thus, the iron is present as Fe^{3+} or Fe (III).**ii. $[Ni(CO)_4]$**

As the complex has no any ion as well as no any charge, the complex must carry no charge hence it is a neutral species.

Now consider, the complex ion as $[Ni(CO)_4]$

The formal charge on CO anion is 0. Therefore, mathematically oxidation state is calculated as;

$x + 4(0) = 0$

$x = 0$

Thus the nickel is present as Ni(0)

1.3.6. Complex ion: -

An electrically charged or a neutral species formed by a combination of the central cation with one or more ligand species. $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ are the examples of the complex ions that we have already seen in the above part. Complex ions are able to produce the electrolytic solution in the water but the neutral complexes can't produce the electrolytic solutions because *ions present outside the square bracket only are ionizable.* Thus $K_3[Fe(CN)_6]$ is an electrolyte but $[Co(NH_3)_3Cl_3]$ is a non-electrolyte.

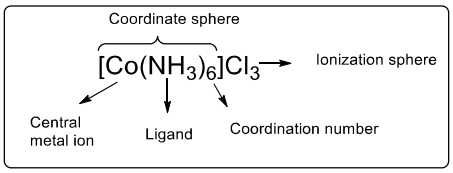


Fig 1.1: General representation of molecular formula of coordination complexes

1.4. Classification of Ligands

Ligands are classified as monodentate or polydentate (bi-, tri-, tetra- etc.) depending upon the number of the donor atoms that are present in the ligand.

1.4.1 Monodentate Ligands: -

These ligands use only one atom at a time as their donor atom, this fills only one coordination site at a time. They are also called as unidentate ligands. The ligands such as halogens are necessarily monodentate. Some of the monodentate ligands are tabulated in the table.

Table 1.4: List of monodentate ligands

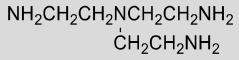
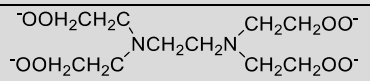
IUPAC name of the ligand	Formula
Fluro	F^-
Chloro	Cl^-
Bromo	Br^-
Iodo	I^-
Azido	N_3^-
Cyano	CN^-
Thiocyanato-S	SCN^-
Thiocyanato-N	NCS^-
Hydroxo	OH^-
Aqua	H_2O
Carbonyl	CO
Thiocarbonyl	SC
Nitrosyl	NO^+
Nitrito-N	NO_2^-
Nitrito-O	ONO^-
Methylisocyanide	CH_3NC
Phosphane	PR_3
Pyridine	Py
Ammine	NH_3
Methylamine	$MeNH_2$
Amido	NH_2^-

1.4.2 Polydentate ligands: -

These ligands use more than one atom at a time as their donor atom, this fills more than one coordination site at a time. If two donor atoms are used then the ligand is called as bidentate ligand, if three donor atoms are used then the ligand is called as tridentate ligand, and so on. Some of the polydentate ligands are tabulated in the table.

When the polydentate ligand is bound to the central atom , the resulting complex has a ring structure, such complex is called as “chelate.”

Common chelating amines

Chelating Points	Common name	IUPAC name	Abbreviation	Formula
Monodentate	Ammine, methylamine	Ammine, methylamine		NH_3, CH_3NH_2
Bidentate	Ethylenediamine	1,2-ethanediamine	en	$NH_2CH_2CH_2NH_2$
Tridentate	diethylenetriamine	2,2'-diaminodiethylamine or 1,4,7-triazaheptane	dien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
Tetradentate	Triethylenetetraamineβ,β',β'' —triaminotriethylamine	1,4,7,10-tetraazadexane β,β',β'' —tris(2-aminoethyl) amine.	trien	
Pentadentate	Tetraethylene pentamine	1,4,710,13-pentaazatridecane	tren	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
Hexadentate	Ethylenediamine tetraacetate	1,2-ethanediyl(dinitrito) tetraacetate	EDTA	

Common multidentate ligands

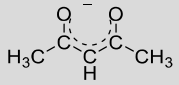
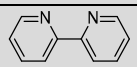
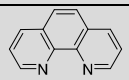
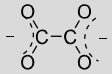
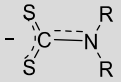
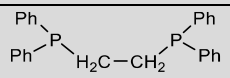
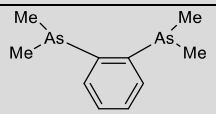
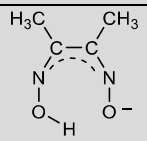
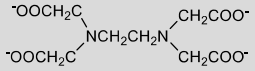
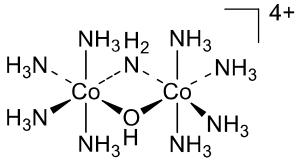
Common name	IUPAC name	Abbreviation	Formula	structure
acetylacetonato	2,4-pentanediono	acac	$CH_3COCHCOCH_3^-$	
2,2'-bipyridine	2,2'-bipyridyl	bipy	$C_{10}H_8N_2$	
1,10-phenanthroline	1,10-diaminophenanthrene	Phen, 0-phen	$C_{12}H_8N_2$	
oxalato	oxalato	ox	$C_2O_4^{2-}$	
Dialkyldithiocarbamato	Dialkylcarbamo dithioato	dtc	$S_2CNR_2^-$	
1,2-bis(diphenylphosphino) ethane	1,2-ethanediylbis (diphenylphosphane)	dppe	$Ph_2C_2H_4PPh_2$	
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethylarsane)	diars	$C_6H_4(As(CH_3)_2)_2$	
dimethylglyoximato	Butanedienedioxime	DMG	$HONCC(CH_3)C(CH_3)NO^-$	
ethylenediaminetetraacetato	1,2-ethanediyl(dinitrilo) tetraacetato	EDTA	$(^-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$	

Table 1.5: List of polydentate ligands

1.4.3. Bridging ligands:

The ligand that binds with two atoms simultaneously, it forms a bridge between the two atoms and acts as a ligand for two metals simultaneously.

e.g. NH_2 and OH in this example are the bridging ligands for both the Co atoms



1.4.4. Ambidentate ligands:

These ligands are capable of bonding through one type of donor atom in one complex but through a different donor atom in another complex. Such a ligand has two binder atoms.

e. g $[(NH_3)_5Co\text{-}ONO]\ Cl_2$ Red colored complex

$[(NH_3)_5Co\text{-}NO_2]\ Cl_2$ Yellow colored complex