
HISTORY OF COORDINATION CHEMISTRY COMPOUNDS GENERAL TERMINOLOGY

Dr.Ravindra Singh Yadav

Associate Professor

Department of Chemistry

M.M.H.College, Ghaziabad (U.P.) India

ABSTRACT

Chemistry of coordination is the topic of this study. In coordination compounds, groups referred to as ligands are frequently present around metals. The concept of coordination complexes, or ligands around a core metal ion, was introduced by Werner, and he also discovered the geometrical forms of numerous compounds. The primary topic of inorganic and physical inorganic chemistry critical surveys will be Coordination Chemistry Reviews.

Keywords:coordination,chemistry,geometrical.

INTRODUCTION

The coordination theory in chemistry examines and describes the structure of a complex (coordination compound), which consists of a core atom connected to surrounding atoms or molecules.

There is widespread use of the term "coordination chemistry," which encompasses aspects of theoretical, bioinorganic, and organometallic chemistry. Reviews frequently analyse recent developments in a certain subject or highlight the results of a particular strategy. On occasion, important and well-liked topics are the focus of special issues. The contributions from a specific country or area of the globe may also be highlighted in these special issues, which may also contain the transcripts of invited speakers at key international conferences. There is also the uncommon full-length piece. Additionally, the journal offers specialised volumes with yearly reviews of organometallic, transition metal group, and main group chemistry.

HISTORY OF COORDINATION CHEMISTRY

Today's coordination chemistry is built on research from the late nineteenth and early twentieth century. The work of Alfred Werner, a Frenchman who spent most of his career in Zurich, Switzerland, is what, as was already mentioned, laid the groundwork for the field because it was he who realized that there was no necessary connection between the number of ligands attached and the metal's oxidation state. He defined the very stable complex of cobalt (III) (or Co^{3+}) and six ammonia molecules as consisting of a central metal ion and its bound surrounds by placing six bound ammonia molecules symmetrically and as far apart as feasible at each of the six corners of an octahedron.

The apparent constant number of donor atoms in the metal ion, commonly known as its "coordination number," turned out to be the answer to the puzzle, not its fundamental valency. Werner received the Nobel Prize in 1913 as a consequence of his work demonstrating the 'magic number' of six for cobalt (III) in several experiments. Modern research has made it feasible to make and analyse a limited number of cobalt (III) compounds with coordination numbers of five or even four, yet his conclusions remain true. Recently, cobalt (III)-containing metalloenzymes with active sites have been discovered. These enzymes' strong reactivity is a result of the low coordination number they have around the metal. Depending on the formal oxidation state of a metal, it may exhibit a range of preferred coordination numbers that vary not just from metal to metal but also for a given metal.

Cu (II) has a larger tendency toward four coordination as opposed to Mn (II), which favours six coordination. In contrast to six-coordinate Mn, Mn (VII) favours four-coordination. The behaviour in the solid form may be different from that in solution due to the availability of several possible donors as a result of the solvent itself frequently functioning as a potential ligand. Six Cl ions, each of which is shared by two metal centres in the solid state, are arranged octahedrally around the Fe (III) centres to form FeCl_3 .

However, ' FeCl_3 ' is most frequently seen as separate $[\text{Fe}(\text{OH}_2)_6]^{3+}$ and Cl ions in an aqueous acidic solution. Whether a coordination complex has metal or metalloid components, the fundamental concept is the same. However, one aspect of the chemistry of the majority of metal complexes is an often-incomplete d or f electron shell (for lanthanoids and actinoids).

These coordination complexes have attracted attention and found utility in a variety of fields because the spectroscopic and magnetic properties of their components are particularly indicative of the molecule under investigation. The market is extremely diversified and, dare we say it, challenging. It could be challenging to determine the formal oxidation state of the central metal ion in specific metal complexes because electron density might be present on some ligands to the point that it influences the physical behaviour. We may infer that the study of metal coordination chemistry is a difficult area that will test your scientific knowledge. In contrast, all stable carbon compounds have four bonds surrounding each carbon centre, making the chemistry of carbon very simple. Metals can have formal oxidation states ranging from zero to eight, and their coordination numbers can be between two and fourteen. For the given metal, there may be (and typically are) a range of oxidation states, coordination numbers, and distinctive spectroscopic and chemical behaviours. As the chemistry of the great majority of the metals and metalloids in the Periodic Table, coordination chemistry is crucial to the right understanding of chemistry. Since many coordination compounds contain organic molecules as ligands, which may impact their reactivity and behaviour, understanding organic chemistry is also crucial in this area. Additionally, since coordination molecules' spectroscopic and magnetic properties are essential to a thorough understanding, knowing a number of physical and analytical techniques is essential.

Coordination compounds

Molecules that have one or more metal centres bonded to ligands are known as coordination compounds (atoms, ions, or molecules that donate electrons to the metal). These complexes may have a charge or be neutral. The complex is stabilized by nearby counter-ions when it is charged. A metal ion is located in the middle of a complex ion, which is surrounded by several other molecules or ions. These can be thought of as being joined to the core ion by coordinate (dative covalent) connections, however the bonding may be more intricate in some instances. Ligands are the ions or molecules that surround the metal ion in the centre. This unique research involves interactions between main group elements, transition metals, and f-elements as coordination centres with organic or inorganic ligands. Coordination chemistry is a broad topic. This section will include cover research of these systems from the fields of biology and medicine. The synthesis, structure, bonding, optical, physical-chemical, kinetic, and thermochemical features of coordination compounds are all given special attention. In addition, papers that focus on practical applications of the most recent discoveries in new materials, such as catalysts, magnets, optical materials, solvatochromic-, thermochromic-, or other chromotropic coordination compounds, are highly encouraged. We value research on solvent-solute interactions and mutual Lewis's acid-base interactions.

Werner's Theory of Coordination Compounds

The capacity of metallic elements to function as Lewis acids and form complexes with various Lewis bases is one of their most crucial characteristics. A metal complex is made up of a core metal atom or ion that is joined to one or more ligands, which are ions or molecules that have one or more pairs of electrons that the metal can share. The word ligand comes from the Latin verb ligare, which means "to bind." Metal complexes can have three different charges: neutral $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ positively charged $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$ or negatively charged $[\text{UF}_6]^{4-}$. Complex ions are the name for electrically charged metal complexes. One or more metal complexes can be found in a coordination compound.

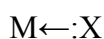
Coordination compounds are important for at least three reasons.

The chemistry of more than half the elements includes metal complexes because, first, the majority of the elements in the periodic table are metals and practically all metals form complexes. Second, a lot of industrial catalysts are metal complexes, and these catalysts are slowly playing a bigger role in terms of reactivity control. For instance, the majority of the polyethylene and polypropylene "plastic" things we use on a daily basis are produced using a catalyst made of a titanium complex and an organometallic compound of aluminum. Last but not least, transition-metal compounds are crucial to biochemistry. Examples include cytochromes, which are iron complexes that transfer electrons in our cells, hemoglobin, an iron complex that transports oxygen in our blood, and complexes of Fe, Zn, Cu, and Mo that are essential parts of several enzymes, which serve as the catalysts for all biological events.

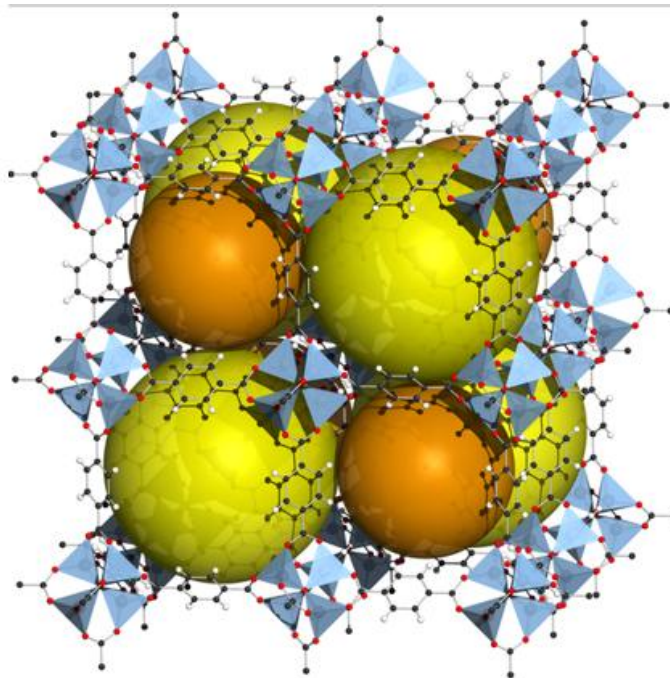
Introduction to Crystal Field Theory and Coordination Chemistry

Coordination compounds are extended solids and molecules with bonds between a transition metal ion and one or more ligands (or complexes). In the creation of these coordinate covalent connections, the metal ions act as Lewis bases and the ligands as Lewis acids. The bond is formed by overlapping the ligand's molecular orbital with the metal ion's d-orbitals, and the ligand typically has one pair of electrons. Neutral molecules (H_2O , NH_3 , organic bases like pyridine, CO , NO , H_2 , and phosphines PR_3) and anions (halides, CN^- , SCN^- , cyclopentadienone (C_5H_5^-), H^- , etc.) are the most frequent ligands in coordination complexes. The resultant complexes can be neutral such as ($[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$), cationic such as ($[\text{Cu}(\text{NH}_3)_4]^{2+}$), or anionic such as ($[\text{Fe}(\text{CN})_6]^{4-}$). Weak or insignificant Brnsted base ligands, such as CO , CN^- , H_2O , and Cl^- , can still be effective Lewis bases in the formation of transition metal complexes, as we shall show in the sections that follow.

When the ligands are Lewis bases, coordinate covalent bonds, also known as dative bonds, are often shown by lines or sporadically by arrows to indicate that the electron pair "belongs" to the ligand X.



The convention is to attribute both electrons in the dative bond to the ligand when counting electrons on the metal, even though the bonds are often polar covalent and the metal and ligand share electrons (explained below).



$\text{Zn}_4\text{O}(\text{BDC})_3$, commonly known as MOF-5, is a metal-organic framework in which cationic Zn_4O clusters are connected by 1,4-benzenedicarboxylate (BDC) anions. Large voids are shown as orange spheres and are present in the stiff structure. MOFs are being created for use in the practical storage of gases, particularly H_2 and CO_2 , and may be

created from a variety of transition metal ions and bridging ligands. The volumetric storage density of MOF-5 is 66g H₂/L, which is similar to the density of liquid H₂.

We enclose the metal ions and ligands that are directly bound to one another in square brackets [...] when putting up the formulae of coordination compounds. Consequently, [Co (NH₃)₅Cl]. The octahedral [Co (NH₃)₅Cl] is found in Cl₂. Two Cl⁻ anions that are not coordinated to the metal and two 2⁺ ions with five ammonia molecules and one chloride ion directly bound to the metal.

Basic Concept of Coordination Chemistry

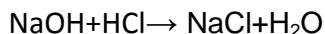
initial valencies They are unmotivated. Frequently, the compound appears as a positive ion. Its main valency is determined by the number of charges on the complex ion.

These secondary valencies' directed nature may be noticed. The number of ligand atoms coupled to the metal ion equals the number of secondary valencies. The coordination number is that. Known as ligands, groups are typically found surrounding metals in coordination compounds. Werner identified the geometrical shapes of many compounds and proposed the idea of coordination complexes, or ligands surrounding a core metal ion. He is awarded the 1913 Nobel Prize in Chemistry for his work in coordination chemistry.

Basic terms to comprehend coordination chemistry

Simple Salts:

Salt and water are produced when an acid and an alkali interact. Neutralization reactions are the term for these kinds of reactions. e.g.



Such salts produce ions in solution when they are dissolved in water. The degree of neutralisation determines the kind of salt—acid, basic, or normal. Multiple acidic or basic radicals can be found in mixed salts, for example. NaKSO₄.

Molecular or Addition compounds:

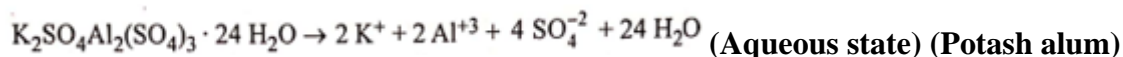
We create crystals of novel compounds known as molecular or addition compounds when solutions containing two or more types of salts (simple molecules) in stoichiometric proportions are evaporated.

There are two types of compounds depending on their behaviour in aqueous solution.

(a) Lattice compounds or double salts: Double salts are addition compounds with the following properties.

They are crystallised and present. They create ions after dissolving in water that are identical to the parts of the double salts individually. e.g.

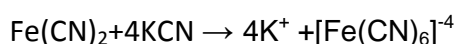




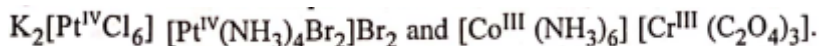
Double salts test their individual constituents in aqueous solution while retaining their identity.

(b) Complex coordination compounds:

$\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$ is produced when a solution of $\text{Fe}(\text{CN})_2$ and KCN is combined and evaporated to dryness (Potassium ferrocyanide). Water causes it to dissociate, but it does not exhibit the test for Fe^{+2} and CN^- ions; instead, it exhibits the test for K^+ and $[\text{Fe}(\text{CN})_6]^{4-}$ ions.



It has been noted that the unique features of the molecular complex $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$, are lost. Coordination (or complex) compounds are the name given to such molecules. Simple cations and complex anion are found in coordination compounds, as are complex cations and simple anion or complex cations and complex anion, for example.



The ions in the complicated compounds mentioned above $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{-2}$, $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Br}_2]^{+2}$, and

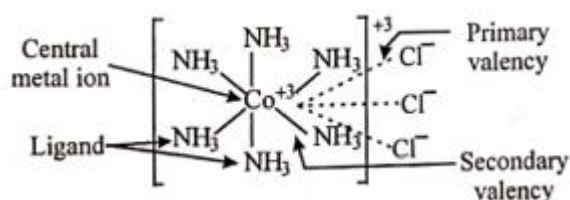
$[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{+3}$ and $[\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{-3}$ referred to as complex ions.

(II) ion complex:

An electrically charged radical is created when a metal cation joins forces with one or more neutral molecules or anions, such as, $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{-2}$, $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{+3}$ etc.

(iv) Coordination compound:

The compound in which the central metal atom or ion is attached to neutral molecules and / or ions in number exceeding the charge or oxidation number of atom or ion is called coordination compound e.g. $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$.



The main and secondary valencies of the central metal atom or ion are divided into two categories. The central metal atom or ion is connected to a specific number of ligands by secondary valencies, and it has a specific orientation. The coordination number is another name for the secondary valencies.

(v) Ligands:

The initial coordination sphere's ligands are the neutral molecules or ions (anions) connected to the metal ion at its centre by coordinate bonds. such as $[\text{Fe}(\text{CN})_6]^{-3}$. The ligands in this case are six CN^- ions. Ligand typically serves as a donor partner, giving the central metal ion one or more pairs of electrons. However, the CO molecule in metallic carbonyl serves as both a donor and an acceptor $(\text{M} \rightleftharpoons \text{CO})$. Inside the first sphere of attraction, ligands are placed around the metal ion according to chosen geometries. Linear, equilateral triangular, tetrahedral, square planar, trigonal bipyramidal, square pyramidal, and octahedral geometries are examples of frequent shapes.

(vi) Ligancy or the coordination number (C.N.)

Coordination number is the total number of donor atoms (coordinating atoms) that are directly bound to the central atom/ion. It shows the total number of chemical bonds that have been created between the donor atoms in the ligands and the central metal ion. e.g.,

The C. N. of Fe^{+3} in $[\text{Fe}^{\text{III}}(\text{CN})_6]^{-3}$ is six. Likewise, in $[\text{Ni}(\text{en})_3]^{+2}$ "Since each ethylene diamine molecule $(\text{NH}_2 - \text{CH}_2\text{CH}_2 - \text{NH}_2)_3$ contains two donor nitrogen atoms, Ni^{+2} 's C.N. is also six. Amount of ligands in $[\text{Ni}^{\text{II}}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{+2}$. "There are only three.

Coordinating atom:

An atom of a ligand is referred to as a coordinating atom if it is connected to a central metal atom or ion through that atom. A ligand, such as e.g. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is connected to the central metal atom by means of its nitrogen (N) atom. Thus, the coordinating atom of NH_3 is the nitrogen (N) atom. There are six atoms that coordinate.

Coordination sphere:

The core metal ion and one or more ligands that are immediately connected to it are found in this structure, which Werner referred to as the coordination sphere or initial sphere of attraction. The square bracket, sometimes referred to by Werner as the "coordie bracket," creates the second sphere of attraction. For instance, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ anions outside the square frame create the second sphere of attraction. In this case, Cl atoms are outside the square bracket. Because the atoms are outside the square bracket, there is a second sphere of attraction.

Chelation:

When a multidentate (polydentate) ligand uses more than one of its coordinating atoms to form two or more coordinate bonds with the same central metal atom, the result is a complex with closed rings known as a chelate. The process is called chelation. The increased stability of complexes containing chelated ligands is referred to as the "chelate effect." Because they interact to form chelate complexes, multidentate ligands are known as chelating ligands. Not all multidentate ligands are chelating ligands, it should be noted. It is possible for the coordinated atoms of the ligand to be arranged such that they cannot

coordinate to the same metal atom to produce a ring structure. $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ is a chelating ligand as a result.

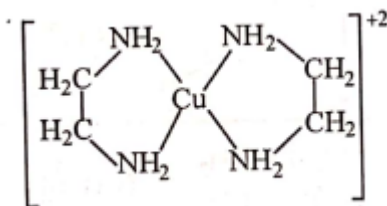


Fig 1. Bis (ethylenediamine) copper (II)ion.

Chelate effect:

The chelation effect refers to the differential in stability between a metal chelate and an equivalent simple complex.

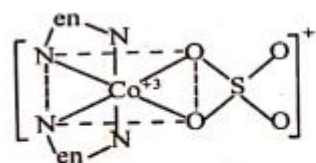
Flex dentate character of polydentate ligands:

Polydentate ligands have the flex dentate characteristic. It alludes to the possibility that it may not use all of its donor atoms to attach to the metal ion.

For instance, in the compounds, EDTA serves as a hexadentate ligand. $[\text{Cr}^{\text{III}}(\text{OH})(\text{HEDTA})]^{-2}$ and $[\text{Co}^{\text{III}}(\text{Br})(\text{HEDTA})]^{-2}$, as well as a pentadentate ligand in $[\text{Pd}^{\text{II}}(\text{H}_2\text{EDTA})]^0$ in

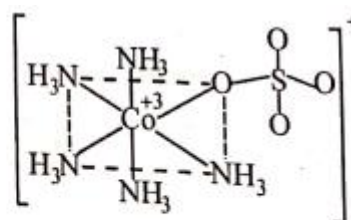
$[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{SO}_4]^+$ and $[\text{Co}^{\text{III}}(\text{en})_2\text{SO}_4]^+$.

Complex sulphate group exhibits six and eight absorption bands due to S-O vibrations, respectively, when acting as a monodentate or bidentate ligand. Sulfate group functions as a bidentate group in Figure 1.2 (a). The oxygen atom of the sulphate group is covalently joined to Co^{+3} in Figure 1.2 (b). Figures (a) and (b) therefore demonstrate the flex dentate property of SO_4^{-2} ion.



(a)

$[\text{Co}^{\text{III}}(\text{en})_2\text{SO}_4]^+$ ion



(b)

$[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{SO}_4]^+$ ion

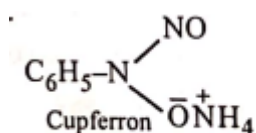
Fig.1.2 (a) and(b) $[\text{Co}^{\text{III}}(\text{en})_2\text{SO}_4]^+$ and $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{SO}_4]^+$

Classification of chelates:

The polydentate ligands can be connected to the central metal ion through two distinct kinds of functional groups, such as an acidic group and a coordinating group, to form covalent bonds and coordinate bonds, respectively. According to the number and kind of bonds that their ligands establish with metal ions, chelates are divided into several categories. To form covalent bonds, the metal atom swaps out one or more H-atoms from acidic groups in the ligand. The most prevalent acidic groups are =NOH, -COOH, -SO₃H, and -OH (oxime). Coordinating bond (e.g., -NH₂, -NH, -N:, -NOH (oxime), -OH, CEO, and -S-O-thio ether) generated by donation of an electron pair from the ligand without replacement of the H-atom. Chelates are used in medical science and daily life.

Uses of chelates:

- (i) In analytical chemistry, some ions may be quantitatively recognized by the production of chelates that are stable and colorful, such as Al⁺³, Ni⁺² and Mg⁺². Certain metal ions are titrated using chelate agents.
- (ii) When softening water Water hardness (Ca⁺² and Mg⁺² ions) causes soap to precipitate as a sticky precipitate and waste. However, we may avoid the precipitation of soap with Ca⁺² and Mg⁺² ions by complexing the metal ions. Therefore, too many complexing substances, such polyphosphates and polydentate amino acids, might stop precipitation in hard water. This efficiently softens hard water.
- (iii) Sequestration is the suppression of the precipitation process of the ions Ca⁺² and Mg⁺², which are in charge of the water's hardness.
- (iv) When hazardous radioactive elements are eliminated from the body:



Since EDTA (ethylene diamine tetra acetic acid) is the best chelating agent, it is employed in the body's removal of dangerous radioactive elements.

When used in solvent extraction, several neutral chelates have poor water solubility but high Cupferron ONHA solubility. Thus, several metals, including Zr and Hf, may be extracted into a water-impermeable organic phase in the presence of ligands that can form inner complexes. Trifluoro acetylacetone, for instance, is a crucial organic solvent for the extraction of the metals Zr and Hf. Additionally, cupferron is employed in the refining of many metals.

- (v) Fruit, fruit juices, food items, etc. are preserved with the aid of certain chelating chemicals in food preservation.

CONCLUSION

The chemistry of carbon is fairly straightforward since all stable carbon compounds have four bonds encircling each carbon centre. Formal oxidation states for metals can range from 0 to 8, while their coordination numbers can range from 2 to 14. There may be (and frequently are) a variety of oxidation states, coordination numbers, and unique spectroscopic and chemical behaviours for the given metal. Coordination chemistry is essential to a proper understanding of chemistry since it describes the chemistry of the vast majority of metals and metalloids in the Periodic. Knowing organic chemistry is also essential in this subject because many coordination compounds contain organic molecules as ligands, which may affect their reactivity and behaviour.

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