
Coordination Compounds - Part 1

Objectives

After going through this lesson, the learners will be able to understand the following

- Appreciate the postulates of Werner's theory of coordination compounds
- Know the meaning of the terms: coordination entity, number, sphere, polyhedron and homoleptic, heteroleptic
- Learn the rules of nomenclature of coordination compounds and write formulas and names of mononuclear coordination compounds
- Understand different types of isomerism in coordination compound
- Understand the nature of bonding

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- Introduction
- Werner's Theory of Coordination Compounds
- Definition of Some Important Terms of Coordination Compounds
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- Summary

Introduction

The transition metals form a large number of complex compounds in which the metal atoms are bound to a number of anions or neutral molecules through a coordinate bond. In modern terminology such compounds are called coordination compounds. These are addition or molecular compounds which retain their identity in dissolved state as well as in solid state. They differ from double salts because double salts dissociate into constituent ions in solution whereas the coordination compounds do not completely dissociate in solutions. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. Chlorophyll, hemoglobin and vitamin B₁₂ are coordination compounds of magnesium, iron and cobalt respectively. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in medicinal chemistry, chemical analysis, chemical industry, metallurgical processes etc. The challenging field of bioinorganic chemistry, i.e.

application of inorganic chemistry to the living system also deals with coordination compounds.

Werner's Theory of Coordination Compounds

Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques. As his work preceded the discovery of the electron, the electronic theory of valence was not known. Werner proposed the concept of primary valence and secondary valence for a metal ion. Binary compounds such as CrCl_3 , CoCl_2 or PdCl_2 have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained bound to the metal.

1 mol $\text{CoCl}_3 \cdot 6\text{NH}_3$ (Yellow) gave 3 mol AgCl

1 mol $\text{CoCl}_3 \cdot 5\text{NH}_3$ (Purple) gave 2 mol AgCl

1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$ (Green) gave 1 mol AgCl

1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$ (Violet) gave 1 mol AgCl

These observations, together with the results of conductivity measurements in solution can be explained if

- six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and
- the compounds are formulated as shown in Table 1, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions.

Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six. Note that the last two compounds in Table 1 have identical empirical formula, $\text{CoCl}_3 \cdot 4\text{NH}_3$, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds.

Table 1: Formulation of Cobalt(III) Chloride-Ammonia Complexes

Colour	Formula	Solution conductivity corresponds to
Yellow	$[\text{Co}(\text{NH}_3)_6]^{3+}3\text{Cl}^-$	1:3 electrolyte
Purple	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}2\text{Cl}^-$	1:2 electrolyte
Green	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+\text{Cl}^-$	1:1 electrolyte
Violet	$[\text{CoCl}_2(\text{NH}_3)_4]^+\text{Cl}^-$	1:1 electrolyte

The main postulates of Werner's theory of coordination compounds are:

- In coordination compounds metals show two types of linkages (valency)-primary and secondary.
- The primary valencies are normally ionisable and are satisfied by negative ions.
- The secondary valencies are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

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 bracket are called counter ions. He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and $[\text{CoCl}_2(\text{NH}_3)_4]^+$ are octahedral entities, while $[\text{Ni}(\text{CO})_4]$ and $[\text{PtCl}_4]^{2-}$ are tetrahedral and square planar, respectively.

Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, potash alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[\text{Fe}(\text{CN})_6]^{4-}$ of $\text{K}_4[\text{Fe}(\text{CN})_6]$ do not dissociate into Fe^{2+} and CN^- ions.

Problem 1: On the basis of the following observations made with aqueous silver nitrate solutions, assign secondary valencies to metals in the following compounds:

Formula	Moles of AgCl precipitated per mole of the compounds with excess AgNO ₃
i) PdCl ₂ .4NH ₃	2
ii) NiCl ₂ .6H ₂ O	2
iii) PtCl ₄ .2HCl	0
iv) CoCl ₃ .4NH ₃	1
v) PtCl ₂ .2NH ₃	0

Solution: i) Secondary 4, ii) Secondary, 6, iii) Secondary, 6 iv) Secondary, 6
v) Secondary 4



Werner was born on December 12, 1866, in Mülhouse, a small community in the French province of Alsace. His study of chemistry began in Karlsruhe (Germany) and continued in Zurich Switzerland, where in his doctoral thesis in 1890, he explained the difference in properties of certain nitrogen containing organic substances on the basis of isomerism. He extended van't Hoff's theory of tetrahedral carbon atom and modified it for nitrogen.

Werner showed optical and electrical differences between complex compounds based on physical measurements. In fact, Werner was the first to discover optical activity in certain coordination compounds. He, at the age of 29 years became a full professor at Technische Hochschule in Zurich in 1895. His accomplishments included the development of the theory of coordination compounds. This theory, in which Werner proposed revolutionary ideas about how atoms and molecules are linked together, was formulated in a span of only three years, from 1890 to 1893. The remainder of his career was spent gathering the experimental support required to validate his new ideas. Werner became the first Swiss chemist to win the Nobel Prize in 1913 for his work on the linkage of atoms and the coordination theory.

Definitions of Some Important Terms Pertaining to Coordination Compounds

- Coordination entity

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[\text{CoCl}_3(\text{NH}_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[\text{Ni}(\text{CO})_4]$, $[\text{PtCl}_2(\text{NH}_3)_2]$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$.

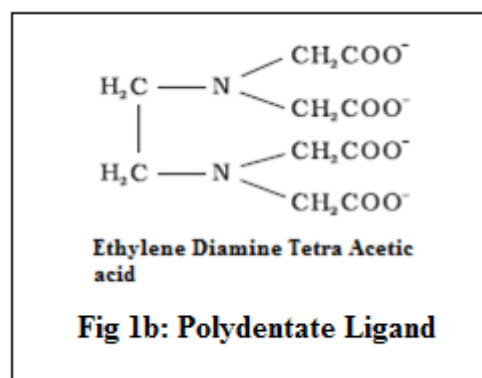
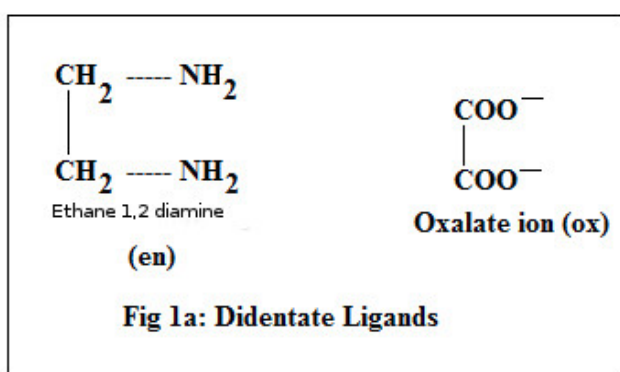
- **Central atom/ion**

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[\text{Ni}(\text{H}_2\text{O})_4\text{Cl}_2]$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are Ni^{2+} , Co^{3+} and Fe^{3+} , respectively. These central atoms/ions are also referred to as Lewis acids as they act as electron pair acceptors in forming coordinate bonds.

- **Ligands**

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules, such as proteins. When a ligand is bound to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be uni-dentate.

When a ligand can bind through two donor atoms as in $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1,2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be di-dentate (Fig 1a) and when several donor atoms are present in a single ligand as in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, the ligand is said to be poly-dentate. When a di- or poly-dentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelating ligand as the resultant coordination compound has a ring structure called a chelate.



Ethylene diamine tetra acetate ion (EDTA⁴⁻) (Fig 1b) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion. It has many uses in everyday life such as:

- chelates with Ca²⁺ ion in bathroom cleaners and shower sprays,
- helps prevent blood clots,
- removes heavy metals from the body in case of metal poisoning
- helps to dissolve iron in plant fertilizer,
- helps to remove traces of iron from mayonnaise.

The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Some ligands may have two different ligating atoms but use one of them at a time. They are called ambidentate ligand (Fig 1c). Examples of such ligands are the NO₂⁻ and SCN⁻ ions. NO₂⁻ ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN⁻ ion can coordinate through sulphur or nitrogen atom.

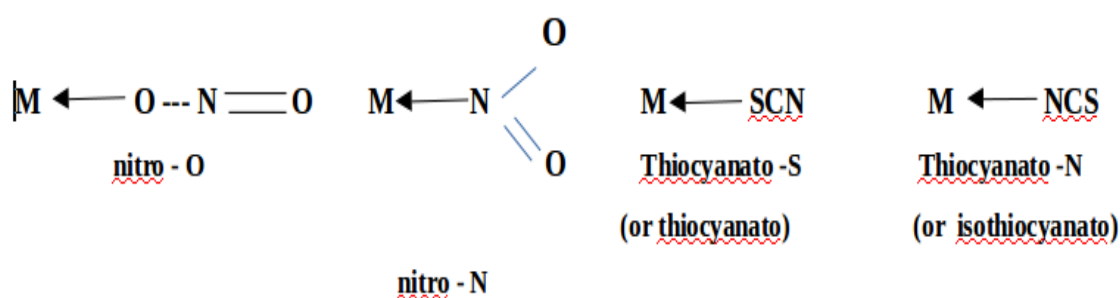


Fig 1c: Ambidentate ligand

Some Features of Chelating Ligands

- Chelating ligands give higher values of formation constants or stability constants due to which such coordination complexes are highly stable even though these are large complex molecules.
- Chelating agents are used to remove unwanted metal ions from various mixtures, these are called sequestering agents.
- Sequestering agents find good use in medicine to selectively remove toxic metal ions like Hg²⁺ and Pb²⁺, and not affect the biologically important metals.

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- The heme unit in haemoglobin, important in the human respiratory process, is a chelate of iron(II).
 - Chlorophyll is an important constituent of photosynthesis in plants and is a chelate of magnesium(II).

- **Coordination Number**

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[\text{PtCl}_6]^{2-}$ and $[\text{Ni}(\text{NH}_3)_4]^{2+}$, the coordination numbers of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $\text{C}_2\text{O}_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands. It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion; pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

- **Coordination Sphere**

The central atom/ion and the ligands attached to it are enclosed in square brackets and are collectively termed as the coordination sphere. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $\text{K}_4[\text{Fe}(\text{CN})_6]$, the coordination sphere is $[\text{Fe}(\text{CN})_6]^{4-}$ and the counter ion is K^+ .

- **Coordination Polyhedron**

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is octahedral, $[\text{Ni}(\text{CO})_4]$ is tetrahedral and $[\text{PtCl}_4]^{2-}$ is square planar. Fig. 2 shows the shapes of different coordination polyhedra.

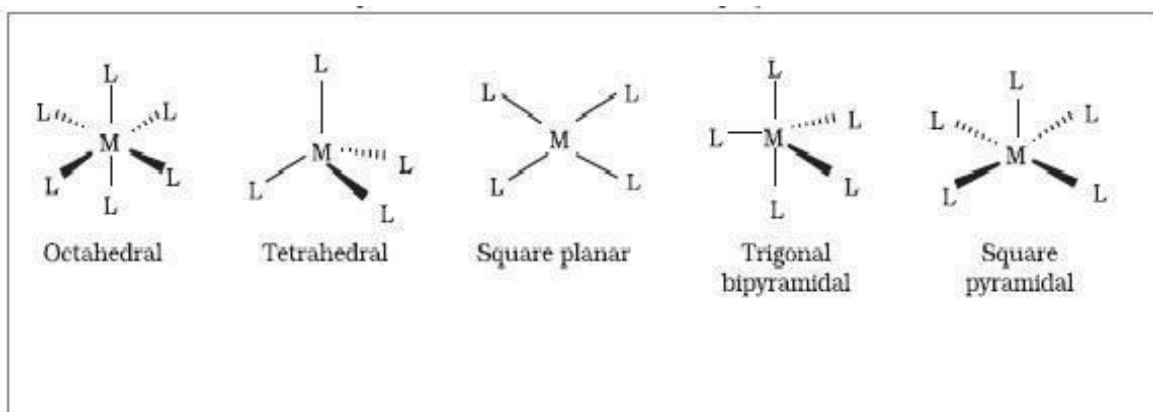


Fig 2: Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand

- **Oxidation Number of Central Atom**

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parentheses following the name of the coordination entity. For example, the oxidation number of copper in $[\text{Cu}(\text{CN})_4]^{3-}$ is +1 and it is written as Cu(I).

- **Homoleptic and Heteroleptic Complexes**

Complexes in which a metal is bound to only one kind of donor group, *e.g.*, $[\text{Co}(\text{NH}_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor group, *e.g.*, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, are known as heteroleptic.

Effective Atomic Number: This concept was proposed by Sidgwick and the EAN of a metal atom is equal to the total number of electrons present in it in the compound. The EAN of cobalt in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is calculated as;

Co(III) has $27 - 3 = 24$ electrons

6 NH_3 molecules donate $2 \times 6 = 12$ electrons

EAN = $24 + 12 = 36$.

A handy formula is :EAN = $Z - \text{ON of metal} + 2 \times \text{CN}$

(where, Z = atomic number of metal atom,

ON = oxidation number of metal atom,

CN = coordination number of metal in the complex)

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

Nomenclature of Coordination Compounds

Nomenclature is important in coordination compounds because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

• Formulas of Mononuclear Coordination Entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:

- The central atom is listed first.
- The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- Polydentate ligands are also listed alphabetically. In the case of an abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- There should be no space between the ligands and the metal within a coordination sphere.
- When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, etc.
- The charge of the cation(s) is balanced by the charge of the anion(s).

Note: The 2004 IUPAC draft recommends that ligands will be sorted alphabetically, irrespective of charge.

• Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the

name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

- The cation is named first in both positively and negatively charged coordination entities.
- The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from the writing formula).
- Names of the anionic ligands end in -o, those of neutral and cationic ligands are the same except aqua for H₂O, ammine for NH₃, carbonyl for CO and nitrosyl for NO. These are placed within enclosing marks () when written in the formula of coordination entity.
- Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, [NiCl₂(PPh₃)₂] is named as dichloridobis(triphenylphosphine) nickel (II).
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
- If the complex ion is a cation, the metal is named the same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example, Co in a complex anion, [Co(SCN)₄]²⁻ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe, cuprate for Cu, stannate for Sn and plumbate for Pb.
- The neutral complex molecule is named similarly to that of the complex cation.

[Note: *The 2004 IUPAC draft recommends that anionic ligands will end with -ido so that chloro used earlier would become chlorido, etc].*

The following examples illustrate the nomenclature for coordination compounds.

- [Cr(NH₃)₃(H₂O)₃]Cl₃ is named as: tri-ammine tri-aqua chromium(III) chloride

Explanation: The complex cation is inside the square bracket. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically

neutral). From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules, therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

- $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2(\text{SO}_4)_3$ is named as: tris (ethane-1,2–diamine) cobalt(III) sulphate

Explanation: The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2–diamine is a neutral molecule, so the oxidation number of cobalt in the complex ion must be +3. *Remember that you never have to indicate the number of cations and anions in the name of anionic compound.*

- $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$ is named as: diammine silver(I) dicyanoargentate (I)

[Notice how the name of the metal differs in cation and anion even though they contain the same metal ions.]

Problem 2: Write the formulas for the following coordination compounds:

- Tetraammineaquachlorocobalt(III) chloride
- Potassium tetrahydrozincate (II)
- Potassium trioxalatoaluminate (III)
- Dichlorobis (ethane-1,2-diamine) cobalt(III)
- Tetracarbonylnickel(0)
- Tetraamminedichlorocobalt (III) chloride
- Sodium Tetracyanonickelate (II)
- Tris(ethane-1,2-diamine) platinum (II) nitrate
- Ammine Bromido Chlorido Nitrito-N-palladate (II)
- Dichlorobis (ethane-1,2-diamine)platinum (IV) nitrate
- Iron (III) hexacyanoferrate (II)

Solution:

- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
- $\text{K}_2[\text{Zn}(\text{OH})_4]$
- $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
- $[\text{CoCl}_2(\text{en})_2]^+$

- (e) $[\text{Ni}(\text{CO})_4]$
- (f) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$
- (g) $\text{Na}_2[\text{Ni}(\text{CN})_4]$
- (h) $[\text{Cr}(\text{en})_3](\text{NO}_3)_3$
- (i) $[\text{Pd}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^-$
- (j) $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$
- (k) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

Problem 3: Write the IUPAC names of the following coordination compounds:

- (a) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
- (b) $\text{K}_3[\text{Cr}(\text{SO}_4)_3]$
- (c) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
- (d) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
- (e) $\text{Hg}[\text{Co}(\text{SCN})_4]$
- (f) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- (g) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$
- (h) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (i) $\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
- (j) $\text{K}_2[\text{PdCl}_4]$
- (k) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$.

Solution:

- (a) Diammine chloridonitrito-N-platinum (II)
- (b) Potassium trisulphatochromate(III)
- (c) Dichloridobis (ethane-1,2-diamine) cobalt (III) chloride
- (d) Pentaamminecarbonatocobalt (III) chloride
- (e) Mercury tetrathiocyanato-S-cobaltate (III)
- (f) Hexaamminecobalt (III)chloride
- (g) Pentaammine bromidocobalt (III) bromide
- (h) Potassium hexacyanoferrate (III)
- (i) Sodium tris oxalato chromate (III)
- (j) Potassium tetrachloridopalladate (II)
- (k) Diamminechlorido (methylamine) platinum (II) chloride.

Problem 4: Explain the term ‘Ambidentate ligand’ giving two examples for each.

Solution: Ambidentate ligands are those ligands that can attach to the central metal atom through two different atoms present within itself.

Example; Nitro group can attach to the central metal atom through nitrogen (N) or through oxygen (O) Thiocyanate group can attach to the central metal atom through sulphur (S) or through nitrogen (N) as shown in fig below.

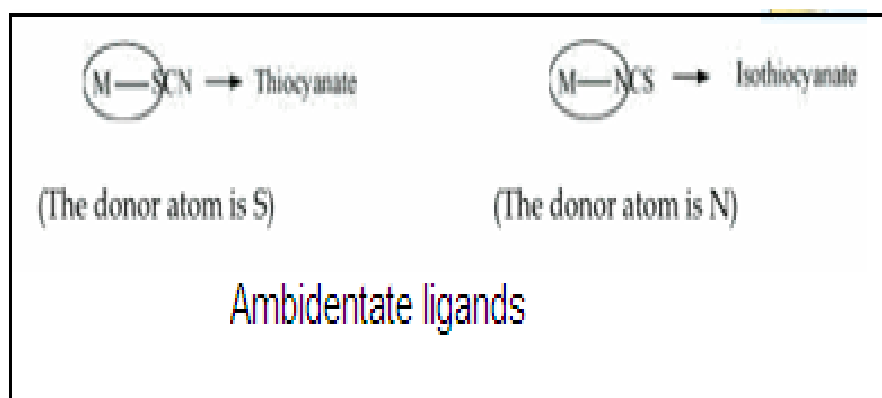
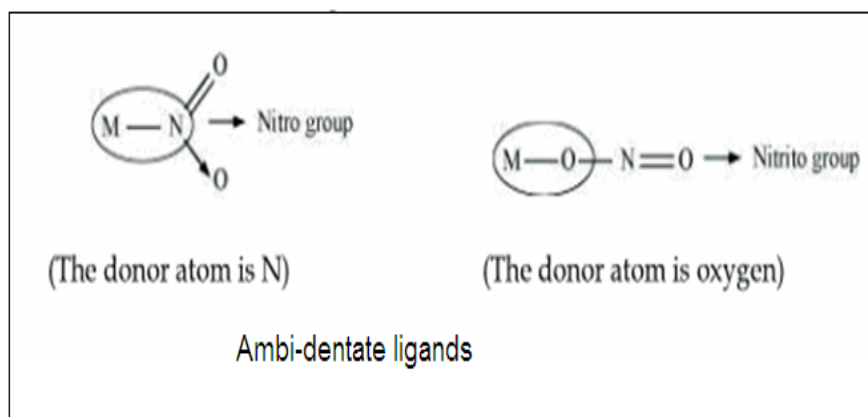


Fig 3: Ambidentate ligands

Summary

Transition metal ions form a unique type of compounds called coordination compounds. The important distinguishing feature is the presence of two, four, five, six and sometimes more chemical groups placed geometrically around the central metal ion and linked by coordinate bond. These groups could be neutral molecules, cations or anions and are called ligands. These coordinating groups affect the chemical properties of the metal atom. A comprehensive system of nomenclature of the coordination compounds has been formulated by IUPAC. It is

a set of simple rules that need to be followed to name a coordination compound. The different types of isomerism shown by various coordination compounds and theories of bonding are discussed in the second module.