

Introduction to Coordination Chemistry

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Coordination chemistry of transition metals is very important as it helps students to understand various industrial, chemical and biological processes. Hemoglobin and chlorophyll are the two most important compounds found in nature containing Fe^{2+} and Mg^{2+} , respectively. They are responsible for the existence of life on earth. Vitamin B_{12} contains a cobalt center. Cisplatin, *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$, is used for the treatment of cancer.

Coordination compounds

When a **metal** (M) is bonded to n number of **ligands** (L), then the resultant compound can be represented as $[\text{ML}_n]$. A coordination compound consists of a central metal center surrounded by one or more ligands (molecules or ions) containing a donor atom(s) such as N, O, C, P and S. Some examples are $[\text{CoCl}_3(\text{NH}_3)_3]$, $[\text{Fe}(\text{CO})_5]$, $[\text{PtCl}_4(\text{NH}_3)_2]$ & $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$. The formula of a compound (or complex ion) should be always written inside a **square bracket**. The constituents in the square bracket (*e.g.*, NH_3) belong to the **inner-coordination sphere**. The molecules and ions written outside the square bracket belong to the **outer-coordination sphere**, *e.g.*, Cl^- in the salt $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$. Generally, a ligand donates an electron pair to the metal center. To accept these electrons the metal center should contain vacant orbitals of appropriate energy.

d-Electron configuration of a metal center

The *d*-electron configuration of V^+ , V^{2+} , V^{3+} and V^{4+} ions are $[\text{Ar}]3d^4$, $[\text{Ar}]3d^3$, $[\text{Ar}]3d^2$ and $[\text{Ar}]3d^1$, respectively. Note that 4s electrons are removed before the removal of 3*d*-electrons. The reason for this is that in a **metal cation** the energy of 3*d*-orbitals is lower than the energy of the 4s-orbital. In the **free metal**, the energy level of the 4s-orbital is lower than that of the 3*d*-orbitals.

Group Number of a metal center

The Group number of a *d*-block element is equal to the

sum of *s*- and *d*-electrons in the *free metal* (*i.e.*, zerovalent metal or M^0). For example, the electron configuration of Sc is $[\text{Ar}]3d^14s^2$, thus, the Group number of Sc is 3. Thus, the elements Sc, Y and La belong to Group 3.

Coordination number of a metal center

The number of monodentate ligands (or electron pairs) coordinated (or donated) to a central atom/ion is called the **coordination number** (C.N.). It depends on, (i) the **oxidation number** (O.N.) of the metal center, (ii) the nature of the coordinated ligands, and (iii) the size of the metal center and ligands (steric factors).

The most common coordination numbers in transition metal complexes are **four** and **six**, although coordination numbers from **two** to **twelve** have been reported.

Types of coordination complexes

There are three types of complexes called neutral, cationic and anionic depending on the charge of the complex or the complex ion; $[\text{Fe}(\text{CN})_6]^{4-}$ is an anionic **homoleptic** complex anion, $[\text{CoCl}_2(\text{NH}_3)_4]^+$ is a cationic **heteroleptic** ion, and $[\text{CoCl}_3(\text{NH}_3)_3]$ is a neutral compound. The coordinated ligands within a complex or complex ion do not easily dissociate when dissolved in a solvent: *e.g.*, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{CoCl}_2(\text{NH}_3)_4]^+$ ions and $[\text{CoCl}_3(\text{NH}_3)_3]$ remain intact upon dissolution. In a neutral complex, $[\text{CoCl}_3(\text{NH}_3)_3]$, the number of monoanionic ligands coordinated to the metal center is equal to its oxidation number, *i.e.*, +3.

Mononuclear complexes are those with one metal center while complexes with two, three or more metal centers are called bi-, tri-, or poly-nuclear complexes, respectively.

Ligands

Ligands are simply anionic or neutral molecules bonded to a metal center *via* a coordinate bond. They can either be neutral or anionic. Each ligand has at least one pair of unshared electrons, which can be donated to the metal

center. Some examples for anionic and neutral ligands are given below.

| | |
|---------|--|
| Anionic | Cl^- , CN^- , HO^- , SCN^- , SO_4^{2-} |
| Neutral | H_2O , NH_3 , CO , PPh_3 , NO , O_2 |

Ligands are classified according to the number of coordinating atoms within the ligand as given in Table 1.

Table 1: Classification of ligands

| Ligand Type | C.N. | Example |
|--------------|------|--|
| Monodentate | 1 | NH_3 , H_2O , CO , Cl^- , PPh_3 |
| Bidentate | 2 | Ethylenediamine (en), bipyridine (bipy), CO_3^{2-} , oxalate (ox^{2-}), acetyl acetate (acac^-) |
| Tridentate | 3 | Diethylenetriamine (dien) |
| Tetradentate | 4 | Triethylenetetraamine (trien) |
| Hexadentate | 6 | Ethylenediamine tetraacetate (EDTA^{4-}) |

The process of metal center being bonded by more than one coordinating (or ligating) atoms to form a **ring structure** is called **chelation**. Such ligands are called **chelating ligands**, e.g., $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (en), oxalate (ox^{2-}). Hydrazine (H_2NNH_2) is a bidentate ligand but two nitrogen atoms are not sufficiently far apart to form a stable chelate. Bridging (μ) ligands (Cl^- , SCN^- , H_2N , CO etc.) can link two or more metals.

Some ligands contain **more than one atom or group** capable of donating electrons to a metal center. Ligands which can form more than two points of attachment to the metal center are termed **polydentate** (Figure 1 and Table 1).

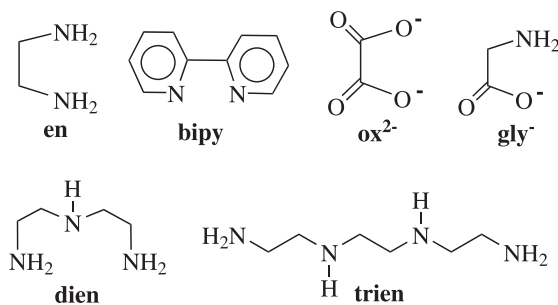


Figure 1: Some polydentate Ligands

Some simple ligands have two different coordinating atoms where only one can bind with the metal center at a

time. They are called **ambidentate ligands**. For example, SCN^- ligand can bind *via* nitrogen or sulfur.

Geometry of coordination compounds

The **spatial arrangement of ligands** around a metal center defines the geometry of a compound. The geometry varies with the **number** and **type** of ligands attached to the central atom. The common geometries of coordination compounds are given in Table 2.

Table 2: Geometries of complexes

| C.N. | Geometry | Example |
|------|----------------------|---------------------------------------|
| 2 | Linear | $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ |
| 3 | Trigonal planar | $[\text{Cu}(\text{PPh}_3)_3]^+$ |
| 4 | Tetrahedral | $[\text{FeBr}_4]^-$ |
| | Square planar | $[\text{Ni}(\text{CN})_4]^{2-}$ |
| 5 | Trigonal bipyramidal | $[\text{Fe}(\text{CO})_5]$ |
| | Square pyramidal | $[\text{NiBr}_3(\text{PPh}_3)_2]$ |
| 6 | Octahedral | $[\text{Mo}(\text{CO})_6]$ |

Note - d^6 metal centers prefer **octahedral**; d^8 metal centers prefer **square-planar**; d^{10} metal centers prefer **tetrahedral** geometries.

Structures of some compounds or ions are shown in Figure 2.

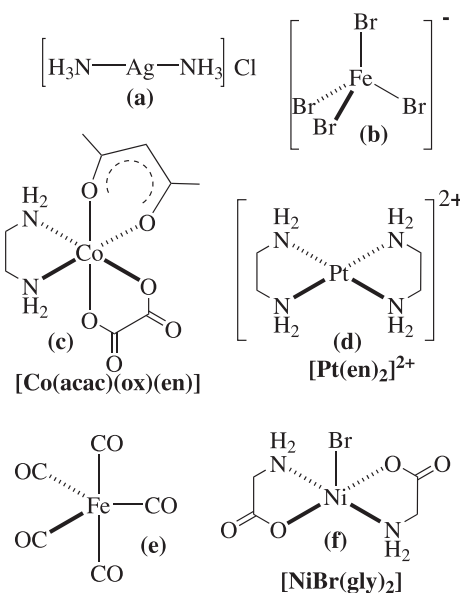


Figure 2: (a) Linear; (b) tetrahedral; (c) octahedral; (d) square-planar; (e) trigonal bipyramidal; (f) square-pyramidal geometry

Sometimes the energy difference between two isomers can be quite small and the compounds can interconvert between them (e.g., square pyramidal \rightleftharpoons trigonal bipyramidal). These molecules are known as fluxional molecules.

Werner's Theory

This theory describes the binding of ligands in coordination compounds. According to Werner's coordination theory, a metal has two different types of valencies, which are primary valency and secondary valency. The primary valency is the oxidation number of the metal center. The number of ligand atoms bound to the metal center or the coordination number is defined as the secondary valency. The primary and secondary valencies of Co in $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$ are +3 and 6, respectively.

The Effective Atomic Number

The electron pairs from ligands can be added to the central metal until the metal center has the same number of electrons as in the next noble gas. The total number of electrons on the central metal center including those gained from ligands is called the Effective Atomic Number (EAN) of the central metal center. In many cases, the EAN is equal to the atomic number (Z) of the next noble gas. The EAN of Co(III) in $[\text{Co}(\text{NH}_3)_6]^{3+} = 27 - 3 + 2 \times 6 = 36$; which is equal to the atomic number (Z) of Kr. However, there are few compounds which do not obey this rule.

The valence electron count (VEC) and the 18e rule

The valence electron count is equal to the sum of *d*-electrons in the metal center (i.e., the Group number of metal) and the electrons donated by the ligands.

For example, the VEC of $[\text{Ni}(\text{CO})_4]$ is equal to 18e (= 10 + 2x4).

The 18e-rule says that any transition metal center would form a stable compound if the VEC of the metal is 18. Thus, these complexes are **coordinationally saturated**. The complexes with incompletely filled valence shells (i.e., VEC < 18e) are called **coordinationally unsaturated** complexes. A metal center would prefer to take up a ligand(s) in order to fulfill the 18e-rule.

Molar conductivity of compounds

Werner prepared a series of cobalt-ammine complexes, and studied their properties. He found that when CoCl_3 was reacted with different amounts of NH_3 yielded a set of new compounds with different compositions :- $\text{CoCl}_3 \cdot 6\text{NH}_3$ (A), $\text{CoCl}_3 \cdot 5\text{NH}_3$ (B), $\text{CoCl}_3 \cdot 4\text{NH}_3$ (C), $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ (D) and $\text{CoCl}_3 \cdot 3\text{NH}_3$ (E). He studied the molar conductivity and the number of Cl^- ions given by each of these complexes. His observations are presented in Table 3.

Table 3: Characterizing data for (A) - (E)

| | X | Y | Z | Ionic information |
|-----|---|-----|---|--|
| (A) | 3 | 430 | 4 | $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$ |
| (B) | 3 | 430 | 4 | $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}(\text{Cl}^-)_3$ |
| (C) | 2 | 250 | 3 | $[\text{CoCl}(\text{NH}_3)_5]^{2+}(\text{Cl}^-)_2$ |
| (D) | 1 | 100 | 2 | $[\text{CoCl}_2(\text{NH}_3)_4]^+(\text{Cl}^-)$ |
| (E) | 0 | 0 | * | $[\text{CoCl}_3(\text{NH}_3)_3]$ |

X = Number of Cl^- ions precipitated as AgCl

Y = Molar conductivity in $\text{m}^2 \Omega^{-1} \text{mol}^{-1}$

Z = Total number of ions present in the solution

* = non electrolyte

The characterizing data suggest complexes (A) - (D) to be salts and (E) a neutral compound. The molar conductivity values are in good agreement with the ionizable chloride ions present in (A) - (D). In all of these complexes, cobalt shows the primary valency (oxidation number) of +3 and the secondary valency (C.N.) of 6.

Nomenclature of coordination compounds

You have learnt nomenclature of coordination compounds for the A/L examination. Some names of the ligands and compounds are given below.

- $[\text{CoCl}(\text{NH}_3)_5]^{2+}$
= Pentaamminechloridocobalt(III) ion
- $\text{K}_4[\text{Fe}(\text{CN})_6]$
= Potassium hexacyanidoferrate(II)
- $[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$
= Dichloridodi(methylamine)copper(II)
- cis*- $[\text{Pt}(\text{gly})_2]$
= *cis*-Diglycinatoplatinum(II)

5. $[\text{Pt}(\text{acac})(\text{py})_2]^+$
= Acetylacetonatodi(pyridine)platinum(II)
6. $[\text{Os}(\text{C}_2\text{O}_4)_3]^{2-}$
= Trioxalatoosmate(IV)
7. *fac*- $[\text{Mo}(\text{CO})_3(\text{PMe}_3)_3]$
= *fac*-Tricarbonyltris(trimethylphosphine)
molybdenum(0)

Problems

- What is the oxidation number of Fe in $[\text{FeSO}_4(\text{gly})(\text{bipy})]$ (A)?
 - Give the IUPAC name of (A).
 - What is the coordination number of Fe in (A)?
 - Determine the Effective Atomic Number (EAN) of Fe in (A).
(Atomic number of Fe is 26)
- Write the chemical formula of glycenatodicarbonyldichloridocobalt(III)
- The substance with the composition $\text{FeCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ has a molar conductivity of $430 \text{ m}^2\text{ohm}^{-1}\text{mol}^{-1}$ (i.e., 1:3 electrolyte). Write the molecular formula of it?
 - A neutral mononuclear 16e-complex (B) containing a Co(I) center is coordinated only to chloride and CO ligands.
 - What is the molecular formula of (B)?
 - Comment on the geometry of (B) and draw the structure of (B).
- What is the molecular formula of diamminebromidocarbonyloxalatocobalt(III).
- Give the IUPAC name of $[\text{Co}_2(\mu\text{-Cl})_2(\text{CO})_4]$ (C).
 - (C) is a symmetrical molecule without a metal-metal bond. Draw the structure of (C).

Student Corner

Introduction to Polymer Chemistry

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Polymers play an important role in our day-to-day life. In Greek, poly means “many” and mer means “parts”. Polysaccharides, proteins and nucleic acids are the main **bio-polymers/macromolecules**. A large number of industries (e.g., packaging, textile, automobile, paper etc.) are based on **synthetic polymers** such as polyethylene (PE), poly(vinylchloride) (PVC), polyesters, nylon, etc., and **natural polymers** such as rubber, cellulose, etc. Joseph Priestly discovered “**natural rubber**”, a natural **polymer** derived from the **monomer** 1,3-*cis*-isoprene. **Bakelite** was the 1st **synthetic polymer** prepared by Leo Baekeland in 1907 from **phenol** and **HCHO**.

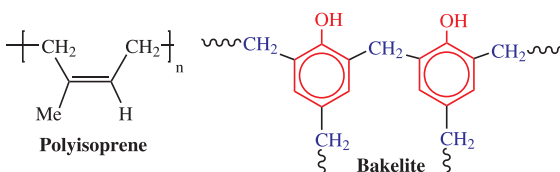
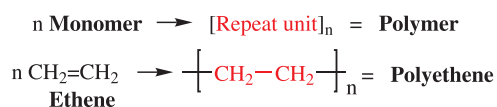


Figure 1: Natural rubber and Bakelite

Polymerization is the process which makes macromolecules by chemically bonding a large number of monomer units, consisting of two or more functional

groups or reactive sites such as acid (-COOH), alcohol (-OH), amino (-NH₂) groups, halide, -SH, -NCO, C=C, C≡C, etc.



Ethene has two reactive sites (two radicals or cation and anion); it produces **linear** polymers.

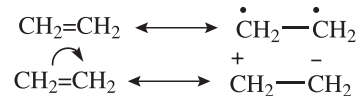


Figure 2: Reactive sites of ethene

Poly(pent-1-ene) $-\text{[CH}_2\text{CHR]}_n-$ can be considered as a **branched polymer** {R = (CH₂)₂Me}. **Hydroxy acids** (e.g., lactic acid, HOCH(Me)COOH) and amino acids (e.g., glycine, H₂NCH₂COOH) are bi-functional monomers, and *via* **condensation**, they produce linear polymers $-\text{[OCH(Me)CO]}_n-$ / $-\text{[CH(Me)COO]}_n-$ and $-\text{[HNCH}_2\text{CO]}_n-$ / $-\text{[CH}_2\text{CONH]}_n-$. 1,3-Diisocyanatobenzene is also a bi-functional