

UNIVERSITY OF DELTA, AGBOR
DEPARTMENT OF CHEMICAL SCIENCE
LECTURE MATERIAL

COURSE TITLE: CO-ORDINATION CHEMISTRY

COURSE CODE: 415

Lecturer: UMUDI ESE QUEEN (Ph.D)

Introduction

Coordination Chemistry is a course of inorganic Chemistry, introduction of transition elements, separation of metals occurrence. Theories of coordination bonding, thermodynamics and kinetic mechanism. The course gives details of definition and application of coordination compounds. Some of the topics include nomenclature, formulae and isomerism of complexes. Rules and guidelines for naming these complexes. Students at the end of the lecture should be able to identify complexes, differences between a compound and a complex. Types of reactions occurring in coordination complexes. It will form the basis for their relating Chemistry (coordination) Chemistry to everyday life in different fields.

Module 1: Introduction to Transition elements

Unit 1: Extraction of Transition Elements

Unit 2: Definition of Transition Elements

Unit 3: Their Position in the Periodic Table

Unit 4: Physical and Chemical Properties

Module 2: Properties of Transition Elements

Unit 1: Distinguish Properties of Transition Elements

Unit 2: Definition of Coordination Complexes

Unit 3: Coordination Number

Module 3: Nomenclature

Unit 1: Rules of Naming Coordination Complex

Unit 2: Isomerism

Unit 3: Types of Isomerism

Unit 4: Theories of Structure and Bonding

Unit 5: Inner and Outer Orbital Complex

Summary

Transition elements were defined, their extraction, positions, properties, the origin of coordination Chemistry and coordination number was treated. At the end of the lesson, learners will be able to define transition elements, properties of transition elements, rules for naming coordination complexes and types of isomerism.

Module 1: Coordination Chemistry

1. Introduction
2. Learning Outcomes to be Achieved
3. Main Content
 - 3.1 Definitions of Coordination compounds
 - 3.2 Properties of Transition Elements/3d Orbital
 - 3.2.1 Coordination Number
 - 3.2.2 Rules for Naming Coordination Complexes
 - 3.2.3 Isomerism
 - 3.3 Types of Isomerism
 - 3.3.1 Theories of Structure and Bonding
 - 3.3.2 Spectrochemical Series
 - 3.3.3 The Nephelauxetic Series (Effect)
 - 3.3.4 John-Tellers Distortion/Square Planed Complex

3.3.5 Thermodynamic /Stability of Complex Compound

3.4 Chelate Effect

3.5 Kinetics and Mechanism

4. Exercises

5. Conclusion

6. Summary

7. Assignment

Introducing Coordination Compounds (Complexes)

In this unit, the learner will be acquainted with transition elements, definitions and how coordination complexes are formed. The unique properties of transition elements and the importance of the 3d orbitals. Therefore at the end of the lesson, the students should be able to

1. Explain how coordination complexes are formed.
2. Define transition elements.
3. List properties of transition elements.
4. Draw the shapes of the 3d orbitals that are degenerate.

3.1 What are Coordination Complexes?

Coordination compounds are compound formed between transition metals or elements and ligands. Ligands are groups of atoms, ions, radicals etc. possessing free pairs of electrons which could readily be donated to the metal atoms. The bond form is a co-ordinate or (dative) bond.



3.2

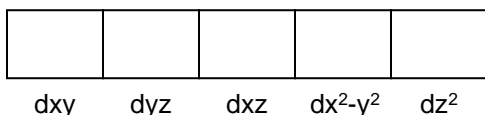
- The transition or d-block elements are so called because their position is between the S and P block elements and their properties are transitional between the highly reactive metallic elements of the S-block which form ionic compounds and the elements of the P-block which

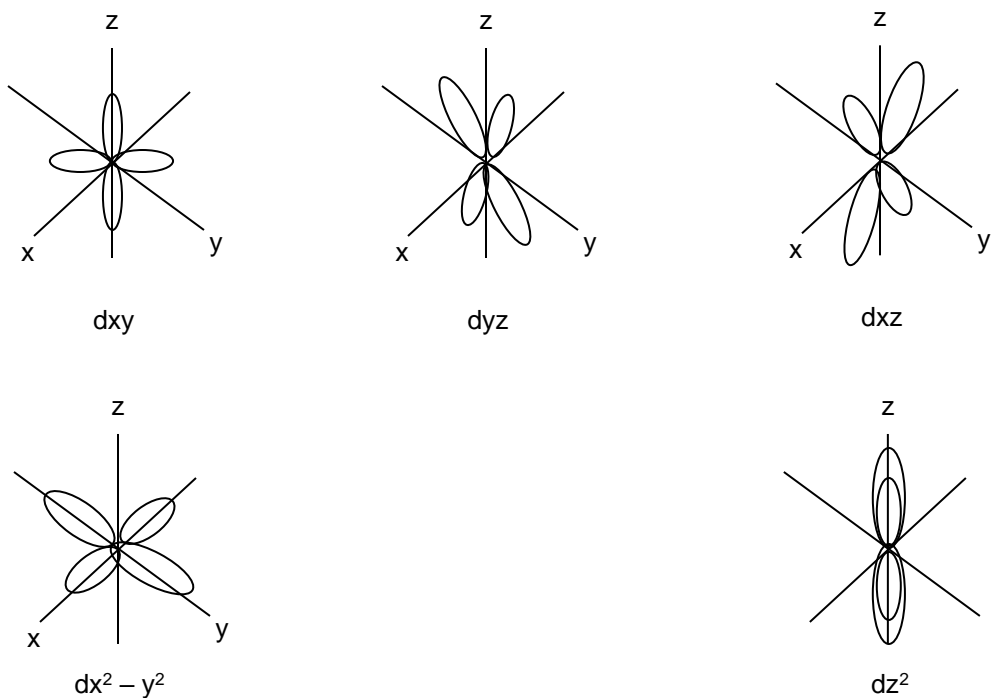
are largely covalent. The transition elements are defined as elements with partially filled d-orbitals.

- Properties of the transition elements

- i. All transition elements are metals, good conductors of heat and electricity.
- ii. They have variable valencies or oxidation states.
- iii. They show magnetic properties.
- iv. They have catalytic abilities i.e. they are used as homogeneous or heterogeneous catalysts since they provide good surface for reaction thereby facilitating the reaction of two different reactants.
- v. Variable colours. When the metal is in the free state, the colour is different from when it is in combined state, because the transition of electrons from lower to higher level. Colourless ions have completely empty sub-shell. These coloured transition metal ions which exhibit colours, absorb certain of the radiations from the white light falling on them and as a result the transmitted light is coloured.
- vi. Complex ions. Complex ion formation is not an exclusive property of transition elements, it does reach a maximum among these elements, not only the small size and comparatively high charge, the transition metal ions favour the acceptance of a lone pair of electrons from the ligand molecules or ions, but the special electronic configuration of these ions furnishes the necessary orbitals of appropriate energy to accommodate them.
- vii. Interstitial compounds. Small atoms like hydrogen, boron, carbon and nitrogen are able to fit into the interstices of the transition metal lattice, forming materials which are chemically similar to the metal themselves but frequently differ greatly in physical properties especially hardness. The composition of these “metals” are variable and cannot be expressed by a simple chemical formula - non stoichiometry. Interstitial alloys are of major importance in metallurgy.

- Shapes of the 3d orbitals



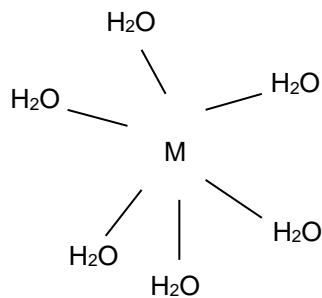


In the free undisturbed state, the orbitals have some energy and are said to be degenerate.

1. The groups with the lobes in between the axis d_{yz} , d_{xy} and d_{xz} .
2. Those whose lobes lie on the axis $d_{x^2 - y^2}$ and d_{z^2} .

3.2.1 Coordination Number

Each transition metal has a tendency of being surrounded by each number of ligands, which is referred to as its coordination number.

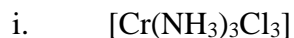


3.2.2 Rules for Naming Coordination Complex

1. Cationic species are named before anionic species e.g. NaCl.
2. Within a complex ion, the ligands are named first followed by the metal ion. $[\text{Co}(\text{NH}_3)]$ is named by specifying the ammine or ammonia first before the Cobalt.
 - i. Ligands whose name end in *-ide* have their suffix replaced by *-o-* e.g. Chloride to Chloro, Bromide to Bromo.
 - ii. Ligands whose names end in *-ite* and *-ate* become *-ito* and *-ato* respectively. Carbonate to Carbonato Oxalate to Oxalato.
3. Neutral ligands are given the same names as neutral molecules e.g. ethylenediamine as a ligand is called ethylenediamine, the only exceptions are H_2O – aquo, NH_3 to ammine.
4. The presence of more than one particular ligand is specified by di = 2, tri = 3, tetra = 4, penta = 5 etc.
5. Negative (anionic) complex ions always ends in the suffix *-ate*. $[\text{CrCl}_6]^{3-}$ – hexachlorochromate(III)ions. For those with Latin names, *-ate* is attached to them. Fe, Cu, Pb, Ag, Au, or Sn i.e. ferate, cuprate, plumbate, aurate etc. For neutral or positive charge complexes, the metal always appear in the English name of the first element.
6. The oxidation number in the complex is written in roman numbers in bracket followed by the name of the metal. $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3^-$ Hexaaquocobalt(III)chloride, when several types of ligands are coordinated around the central metal atoms named in different order
 - i. Negative first
 - ii. Organic anions.
 - iii. Neutral inorganic groups.
 - iv. Neutral organic group.

Exercise

v. Name the following complexes



3.2.3 Isomerism

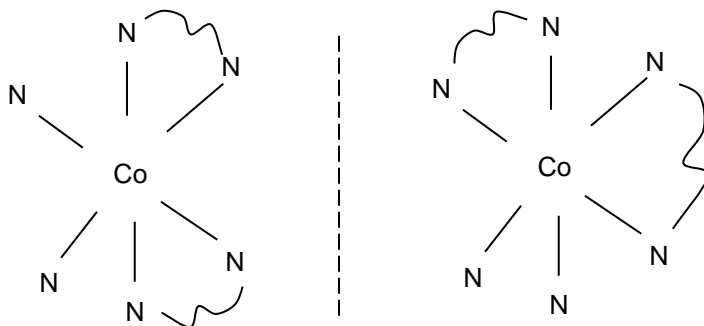
Compounds with same chemical formula but different structural arrangements are term isomers. Isomerism is exhibited by compounds with the same empirical formular but different special arrangement of atoms or groups within the molecule given rise to different physical and chemical properties. It is not only limited to coordination complexes.

3.3 Types of Isomerism

Different types of isomerisms encountered, these are:

i. Optical isomerism

This type of isomerism occurs when a molecule is asymmetric, it cannot be superimposed on its mirrow image. They have non-superimposable image of the left hand about to be fixed in the right hand of a glove. The two forms are optical isomers called either dextro or laevo (d or l form) depending on the direction they rotate polarimeter either to the left or right.



2. Geometric or Stereoisomerism

This gives rise to cis and trans formation $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{4+}$

6. Hydrate Isomerism – This differs in the placement of water molecules. The different positions of the water (aquo) ligands dictates the colour of the complex i.e. depending on the environment.

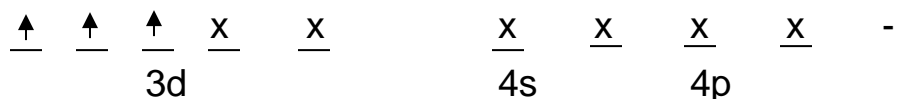
Exercise

1. Indicate the types of isomerism shown by the following complexes
 - a. $[\text{Co}(\text{CN})_5(\text{NCS})_3]$ and $\text{Co}(\text{CN})_5(\text{SCN})_3$
 - b. $[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{C}_2\text{O}_4)_3]$ and $[\text{Cr}(\text{NH}_3)] [\text{CoC}_2\text{O}_4)_3]$
 - c. $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{NO}_2\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$

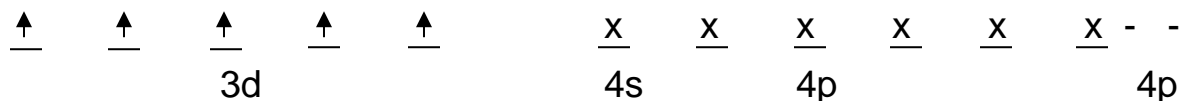
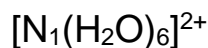
3.3.1 Theories of Structure and Bonding in coordination complexes

Valence Bond Theory

In coordination complexes (transition metals). This theory was developed by Pauling, that since coordination compounds contain complex ions with ligands forming coordinate bonds, these bonds are formed by the overlap of two orbitals and the sharing of electrons between the two atoms in the region of overlap.



$d^2 sp^3$ – inner orbital complex because of the usage of the 3d orbital.



$sp^3 d^2$ outer orbital complex because of the usage of the 4s orbital.

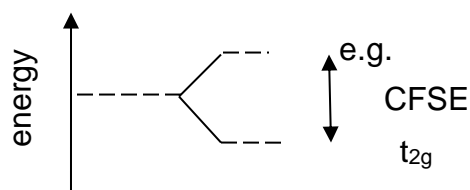
When 3d orbitals are used to form hybrid orbitals stronger metal-to-ligand bonds are formed. There is pairing and formation of inner orbital complexes. This theory successfully interpreted the main

features of coordination Chemistry and gives electronic structures, but it does not explain the phenomena of colour formation and the necessity to promote one 3d electron to some higher energy level for hybridization as in square planar complexes.

Crystal Field theory

This theory views the complex as held together by purely electrostatic attraction. It is concerned with the effect of the ligand on the energy degeneracy of the d-orbitals. The ligands point in the direction of the metal cation. The 3d degeneracy breakdown in the presence of a ligand, therefore all the ligands do not have same energy. The approach of a ligand creates an octahedron around the central metal atom. The d-orbital is split into two groups.

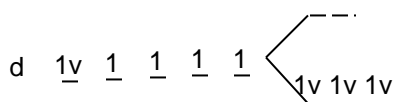
1. $dx^2 - y^2$ and dz^2 (higher energy) e.g. orbital.
2. dxy , dy^2 and dxz (lower energy) t_{2g} orbital.



If crystal field stabilization energy (CFSE) is weak, both e.g. and t_{2g} will be singly occupied before pairing but if high, electrons will pair up in the t_{2g} orbitals first.

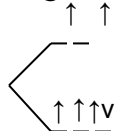
1v

e.g. $[\text{Fe}(\text{CN})_6]^{4-}$



Strong field, low spin

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



Weak field, high spin

3.3.2 Spectrochemical Series

The effect of ligand field on the splitting of the d orbital energy level results in absorption spectral that characterizes each transition metal cation, but the exact position of the bond depends on the ligand field and varies from ligand to ligand. Ligands can thus be arranged in order of increasing ligand field, the list thus produced is known as spectrochemical series.

$I < Br < Cl < F < OH < RCO_3 < H_2O < NH_3 < en < CN$ etc. when light is absorbed it promotes electrons from the t_{2g} to e_g level and its colour depends on the magnitude of the CFSE. As CFSE increases, more energy is required to raise electrons from t_{2g} to the e_g level hence light of high frequency must be used.

3.3.3 Nephelauxetic Effect

If the assumption that the states are exactly the same in a complex ion as in free gaseous ion (setting aside Δ as the variable parameter) and the energy levels (state) calculated with transition ions there are marked discrepancies. The separation due to repulsion between the d electrons. Therefore the energy decrease suggests the d electrons cloud has expanded in the complex. Distance between d electrons are increased and interelectronic repulsion decreases. Therefore, the d electron cloud expansion occurs partly because metal ion d orbitals overlap with ligand atoms and escape to some extent from metal ions. The result of ligand expansion of the d electrons cloud is called nephelauxetic effect – cloud expansion.

3.3.4 Jahn Tellers Effect

The Jahn – Tellers theorem states that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some sort of distortion to lower its symmetry and remove the degeneracy.”

If there is bonding in the d electrons are symmetrically arranged in the octahedral field, the repel all six electrons equally and form octahedral complex because the t_{2g} orbitals point in-between the ligands. On the other hand, the e_g orbitals point directly at the ligands hence asymmetric filling of the orbitals cause some ligands to be repelled more than the others resulting in significant distortion of its octahedral shape since the degeneracy is broken if filled asymmetrically in octahedral environment. To minimize the repulsion with the ligands, electrons go into the d_{z^2} before the $d_{x^2 - y^2}$ therefore the ligand along $+z$ and $-z$ are subjected to greater repulsion than the four ligands

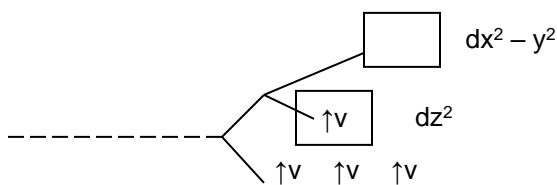
along +x, -x and +y and -y resulting in tetragonal distortion with four short bonds and two long bonds. This type of distortion is known as Jahn Tellers distortion.

- Importance of Jahn-Tellers Distortion

It is of practical help in understanding the structural Chemistry of certain transition – metal ions.

Square Planar Complexes

For d^8 complexes if the ligand field is strong, sufficiently, the two orbitals difference will be larger than the energy used or needed to pair them up. In such case, the two electrons pair up and occupy the lower energy dz^2 leaving $dx^2 - y^2$ empty.



Very strong octahedral field

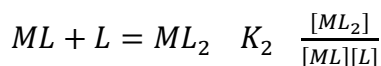
Therefore four ligands can approach directly since $dx^2 - y^2$ is empty. Ligand approaching +z and -z directions receive strong repulsive forces from the filled dz^2 orbital, In that case only four ligands will succeed in bonding to the metal and a square planar complex is formed.

3.3.5 Thermodynamic Stability of Complexes

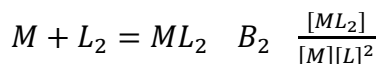
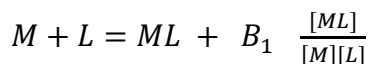
When metal ions dissolve in water, they form aquo ions, displacing a set of ligand by another one. How many water molecules are involved in direct contact with water; and time is involved. Most aquo ions are labile (react fast) and equilibration occurs, they are more or less acidic and dissociates as follows. Thermodynamic stability of specie is a measure of the extent to which this specie will form from or transform into when equilibrium is reached under certain conditions.

Kinetic stability of specie refers to the speed with which transformation leading to the attainment of equilibrium occurs. Solution of metal ion M and more dentate ligand L, its equilibrium is described thus





Or



Both K_1 s and B_1 s must be related, therefore from the expression B s multiplying both the numerator and denominator by $[ML]$ $[ML_2]$ and rearrange we have

$$\begin{aligned} & \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \\ &= \frac{[M]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_2]}{[ML_2][L]} \\ &= K_1 \quad K_2 \quad K_3 \\ & B_K = K_1 K_2 K_3 \end{aligned}$$

The K_1 s are called the step wise formation constants or stepwise stability constant and the B_1 s are called the overall formation constant (or overall stability constants).

3.4 Chelate Effect

Chelate effect refers to the stability that is enhanced in a system containing chelate rings as compared to systems with few or no rings. The greater the number of chelate rings, the greater the stability or the additional stability which a polydentate ligand confers on a complex is referred to as chelate effect. Chelation is a process whereby a polydentate ligand is co-ordinated to a central metal atom with the formation of a ring structure. In this case, there is steric hindrance if the ligands are bulky as compared to smaller chelate ligands, also the stability of a complex are more increased when ligands which coordinate to 2 or more positions replaces monodentate ligands.

Factors enhancing the stability of complexes.

The properties of the ligands and centre metal ion contributed to the stability of complex compounds.

i. Basicity of the ligand.

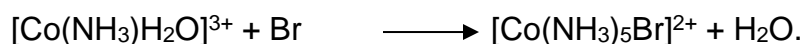
The log of stability constant should be a linear function of the stability constant i.e $\log k = a \log KH^+ + b$ where k = stability constant a and b are constants. If we have a ligand with similar structure but different basicity then the stability constant of the metal complex will increase in the same manner as their basicity.

- ii. The stability of complexes are more increased when ligands which coordinate to 2 or more positions replace monodentate ligands.
- iii. For charged ligands the greater the charge, the stronger the bond. $PO_4^{3-} > SO_4^{2-} > ClO^-$. For neutral ligands or molecules, the larger the permanent dipole, the more stable the complex.
- iv. Smaller ligands approach the central metal atom more than or more closely than bulky or large ones.

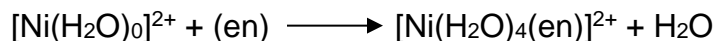
3.5 Kinetics and Mechanism of Reaction

- 1. Substitution reaction in octahedral complexes. The term lability refers to the rate at which replaceable anions moves from the metal ion it was coordinated to initially. There is a wide variation. In octahedral complexes two limiting rates are possible (fast rate and slow rate).
 - a. Replacement of coordinated solvent (water).

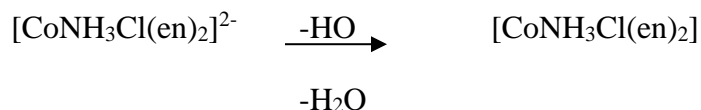
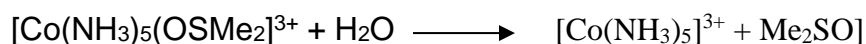
Complexes formed from hydrated metal ion in solution is given below

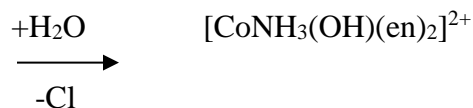


When an anion is the entering group it is called anation.



- b. Solvolysis – In this case, the reaction is carried out in aqueous solution (hydrolysis) either in acidic or basic medium.





- C. Octahedral complexes must first lose a coordinated anion through hydrolysis before being replaced by the new ligand.

Factors affecting rate of replacement of ligands.

- i. Size of the metal ion. Ionic size is important in ligand replacement, when ions are smaller, the substitution rate slows down since ligands are held tightly.
- ii. The higher the charge on the metal ion the more inert the complex.
- iii. d – electron configuration. If a metal complex has electrons in the antibonding e.g. orbitals, the ligands are expected to be relatively weakly bonded and to be easily displaced.
- iv. Electrostatic crystal field theory. The change in crystal field stabilization energy on going from reactant complex to the activated complex corresponds to the crystal field contribution to the activation energy of the reactant. However two factors act as limiting agents.
 - a. The formation of a five coordinate square pyramidal activated complex and
 - b. The formation of a 7-coordinate pentagonal activated complex.

4. Exercises

1. How does the crystal field theory explain the phenomenon of colour?
2. Which of the following is more stable and why? $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$
3. Describe and explain Jahn-Teller's effect in octahedral complexes of Cu^{2+}
4. In a step-wise formation, account for the thermodynamic of complex ions in aqueous solution.

5. Conclusion

From the entire course content, the learner can conclude that transition elements and their compounds formed with ligands which are coordination compounds are of importance in various aspects of life ie foods, medicine photography, chemical industries etc and it is of practical help in understanding the structural chemistry of certain transition-metal ions.

6. Summary

At the end of this course, the learners should be able to

- Define transition element, state coordination compounds and their reactions,
- Explain isomerism,
- List spectrochemical series,
- Enumerate importance of coordination compounds,
- Explain bonding in coordination complexes and its mechanism
- Identify coordination complex
- Name them correctly,
- State the importance of the 3d orbitals.

7. Assignment

Read up organometallic compounds and bonding in metal carbonyls.

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