



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 423

COURSE TITLE: COORDINATION CHEMISTRY

CHM 423
COORDINATION CHEMISTRY

COURSE DEVELOPER:

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COURSE GUIDE

INTRODUCTION

Coordination Chemistry involves the study of coordination compounds, their structures, properties and applications. The term 'Coordination' used to describe these compounds stems from the nature of chemical bond that leads to the formation of these compounds. This chemical bond called coordinate covalent bond involves donation of electron pair(s) by a molecule or negatively charged ion, a Lewis base, to a neutral metal or positively charged ion, a Lewis acid. These compounds are known, from spectroscopic studies, to exist in various structures based on the number of ligand i.e. Lewis base that coordinates to the metal.

The unique ability of the coordination compounds to exist in diverse shapes provides them to exhibit properties which make them to be useful in living systems (e.g. Haemoglobin, an important biological molecule in transportation of oxygen), medicine (e.g. Cisplatin, used in treatment of cancer) and in industries (e.g. Petroleum Industry where a number of coordination compounds are used as catalysts involved in chemical processes such as hydrogenation, aromatization etc).

Many coordination compounds have been in use before their classification and characterization for example Prussian blue, $[\text{Fe}(\text{CN})_6]^{3-}$, a coordination compound, have been used for decades in textile industry as a pigment before the chemistry of coordination compounds began historically with Alfred Werner (1866-1919). The contributions of Alfred Werner to coordination chemistry served as the foundation upon which other Chemists build to explain the nature, structures, properties and application of these compounds.

COURSE DESCRIPTION

Coordination Chemistry provides the information on the mode of action of biological molecules based on their structural studies. With such knowledge, scientists have been able to design and modify several important biological molecules. This course will expose students to the applications of previous knowledge acquired in spectroscopic techniques, Chemical kinetics, thermodynamics and reaction mechanisms. The course will open a new world to students with interest in medicine, where knowledge of coordination chemistry is employed in the extraction of metal poison in living systems, and petrochemical industry, where the knowledge of coordination chemistry is important in catalyst design and application.

LEARNING OUTCOMES

In coordination chemistry, students will acquire knowledge on the nomenclature, preparation, classification, stereochemistry, reaction kinetics and mechanisms, chemical equilibrium and thermodynamics of reactions of metal complexes. Also in this course, students are expected to know how various spectroscopic techniques (such as Absorption and Vibrational spectroscopy) and other physical methods (such as Magnetic properties) are employed in characterization of metal complexes.

AIMS OF THIS COURSE

The aims of this Course include;

- i. introduction of students to the chemistry of coordination compounds (Definition, Recognition, Preparation and Application),
- ii. to provide students with knowledge on how to; name coordination compounds using IUPAC system of naming (Nomenclature), classify coordination compounds based on their coordination numbers (Coordination formula) and identify number and types of various isomers possible with each coordination compound (Isomerism)
- iii. to enable students to identify various structures and hybridization(s) possible with each coordination compound based on its coordination number (Stereochemistry)
- iv. to expose students to physical methods (Magnetic properties, Vibrational and Electronic Spectroscopy) used in structural analysis of coordination compounds.
- v. to explain the various bonding theories (Valence Bond Theory, Crystal Field Theory, Ligand Field Theory and Molecular Orbital Theory) and modifications resulting into Spectrochemical series (due to trend observed in crystal field splitting) and Nephelauxetic series (due to trend observed in cloud expansion).
- vi. to explain how complex formation can assist in stabilization of unusual oxidation states
- vii. to provide students with details of reaction kinetics and mechanisms, thermodynamics and stability constants as well as chelate formation and effect.

OBJECTIVES OF THIS COURSE

At the end of this course, the students should be able to:

- Identify coordination compounds, explain the methods used in preparing them and state areas of their applications.
- Name, classify and identify the possible number of isomers of any given coordination compounds.
- Describe the structures and hybridizations of coordination compounds.
- Apply physical techniques in characterization of coordination compounds.
- Explain the nature of bonding in coordination compounds through the various bonding theories.
- Apply the knowledge of coordination chemistry in stabilization of unusual oxidation states.
- Describe various types of reaction mechanism, kinetics and thermodynamics possible in coordination chemistry.

COURSE REQUIREMENTS

The course content of CHM 423 (Coordination Chemistry) is presented in four (4) modules subdivided into various units. A list of textbooks is provided at the end of each module for further reading. Each unit ends with worked examples and assignments to enable students have better understanding and perform excellently in this Course. Having provided this much information on this Course, it is expected that students taking it study the Course Material in details, organise and attend tutorial classes.

COURSE MATERIALS

The following are to be made available for students:

- i. Course Guide.

- ii. Study Units with worked examples and assignments in four (4) Modules and list of textbooks at the end of each Module.

STUDY UNITS

This Course consists the following Study Units grouped into four Modules

Module 1

Unit 1: Introduction to Coordination Chemistry

Unit 2: Nomenclature and Coordination number of complexes

Unit 3: Isomerism in complexes

Unit 4: Preparation and reactions of complexes

Module 2

Unit 1: Theories of structure and bonding

Module 3

Unit 2: Physical Methods of Structural Investigation

Module 4

Unit 1: Thermodynamic Stability and Reaction Kinetic of complexes

Textbooks suggested for further reading are listed below. Some of these textbooks can be found online and in the libraries. In addition, related information is also available on the internet but students should identify and study information relevant to the Course.

1. Housecroft, C. E. and Sharpe, A. G. *Inorganic Chemistry* (2nd ed.) *Pearson Education Limited*, 2005.
2. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry* (3rd ed.) *Interscience Publishers, a division of John Wiley and Sons*, 1972.

3. Cox, P. A. *Inorganic Chemistry* (2nd ed.) BIOS *Scientific Publishers Taylor and Francis Group*, 2004.
4. Miessler, G. L. and Tarr, D. A. *Inorganic Chemistry* (3rd ed.) *Pearson Education Int*, 2010.
5. Geoffrey, A. L. *Introduction to Coordination Chemistry* *John Wiley and Sons, Ltd.*, 2010

ASSESSMENT

Assessment in this Course is divided into Tutor-Marked Assignment (TMA) and End of Course Examination.

The TMAs shall constitute the continuous assessment component of the course and it shall constitute 30% of the total course score.

The End of Course Examination shall constitute 70% of the total course score.

COURSE OVERVIEW

In all, this Course is presented in four (4) modules.

Module 1 contains introduction to coordination chemistry, IUPAC system of naming complexes, Alfred Werner's contribution to coordination chemistry, coordination number and isomerism in complexes. This module explains the fundamentals of coordination chemistry.

Module 2 explains the bonding schemes (Valence Bond Theory, Crystal Field Theory, Adjusted Crystal Field theory and Molecular Orbital theory) used to describe the nature of bonding in metal complexes and the limitation(s) of each scheme leading to its modification to account for certain properties of metal complexes.

Module 3 describes the electronic and vibrational properties of bonds in metal complexes through which the structural elucidation of complexes can be made with the aid of electronic and vibrational spectroscopic methods. It also explains the magnetic nature of complexes, which also provides information on the structure of metal complexes.

Module 4 provides information on the kinetics (rate of reaction of metal complexes), thermodynamic and stability constant (i.e. equilibrium). It also provides information on the unique stability associated with Chelate formation.

STRATEGIES FOR STUDYING CHM 423

To obtain an excellent grade in this course, students must study each unit of the course in details and carefully practice the worked examples at the end of each unit. Students should also take advantage of group discussion and tutorials to solve the assignment at the end of each unit.

SUMMARY

CHM 423 (Coordination Chemistry) explains the concept of formation of metal complexes, their nomenclature, characterization and applications. The course includes review of Crystal Field Theory, Crystal Field Stabilisation Energies: origin and effects on structures and thermodynamic properties. Also included in the course are introduction to Absorption (Electronic states of partly filled quantum levels, l , m_l and s quantum numbers, Selection rules for electronic transitions, Splitting of the free ion energy levels in Octahedral and Tetrahedral complexes, Orgel and Tanabe-Sugano diagrams) and Vibrational Spectroscopy and Magnetism (Magnetic Susceptibilities transition metal complexes, effect of orbital contributions arising from ground and excited states, deviation from the spin-only approximation).

CHM 423 COURSE MATERIAL

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MODULE 1

UNIT 1: INTRODUCTION TO COORDINATION CHEMISTRY

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1.0 INTRODUCTION

Coordination chemistry is the foundation of modern inorganic and bioinorganic chemistry, both of which have contributed immensely to the development of the chemical industry and medicine. The knowledge of coordination chemistry has provided insight into the mode of actions (kinetics and mechanisms) of biological molecules in living systems. Important biological molecules such as vitamin B₁₂, chlorophyll, haemoglobin and myoglobin are coordination compounds of cobalt, magnesium and iron. The comprehensive understanding of the mode of actions of these complex molecules has been made possible through the knowledge of coordination chemistry. Coordination chemistry has also contributed to the growth of textile industry where dyeing involves the use of coordination compounds. The tremendous growth in the petrochemical industry would not have been made possible without catalyst design which requires the knowledge of coordination chemistry. From this

background, the knowledge of coordination chemistry is inevitable to chemists if not all scientists.

2.0 OBJECTIVES

At the end of this unit students should be able to:

- Define and recognise coordination compounds or complexes
- Explain Werner's contributions and Distinguish between primary and secondary valencies in complexes
- Differentiate between electrolyte and non-electrolyte complexes
- Recognise different types of ligands
- State the difference between homoleptic and heteroleptic complexes
- State areas of application of coordination compounds

3.0 MAIN CONTENT

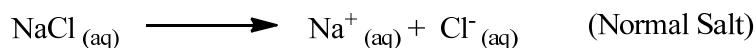
3.1 DEFINITION AND RECOGNITION OF COORDINATION COMPOUNDS (COMPLEXES)

Coordination compounds are formed by the reaction between Lewis acids and Lewis bases. By Definition, Lewis acids are electron pair acceptors while Lewis bases are electron pair donors. Thus a Lewis acid must have empty suitable orbitals to accommodate the donated electron pairs. The presence of empty suitable orbitals in transition metals (Cu, Co, Fe etc) and some compounds (BF₃, BeCl₂ with empty p-orbital) and ions (H⁺) of main block elements makes them to act as Lewis acids. However, the chemistry of coordination compounds is restricted to compounds in which the Lewis acid is a transition metal or d-block elements.

A molecule can function as a Lewis base provided it has heteroatom(s) with lone pair(s) on them. Examples of such molecules are H₂O, NH₃, CO etc, anions such as halides (F⁻, Cl⁻, Br⁻), cyanide (CN⁻) are also Lewis bases. The chemical interaction between a Lewis acid and a Lewis base leads to coordinate bond formation hence the product of the interaction is called coordination compound.

By definition, coordination compound is compound formed when a central metal atom or ion is surrounded (coordinated) to a number of anions or molecules in such a way that the number of the coordinated anions or molecules exceeds the normal covalency of the central

atom or ion. The compound is also referred to as complex because on ionization, it exists as an independent species without dissociation, unlike normal or double salt which dissociates on ionization. Complexes are enclosed in square brackets to distinguish them from other types of salts



Coordination Compounds (Complexes)

Complex	Central Atom/Ion	Anion/molecule	Number coordinated	Valence of the metal
$[\text{Ni}(\text{CO})_4]$	Ni	CO	4	0
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe^{3+}	CN^-	6	+3
$[\text{Ag}(\text{NH}_3)_2]^+$	Ag^+	NH_3	2	+1
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	Co^{3+}	NH_3 and Cl^-	6	+3
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Cu^{2+}	H_2O	6	+2

3.2 WERNER'S CONTRIBUTIONS TO COORDINATION CHEMISTRY

Alfred Werner (1866-1919) became the first Swiss Chemist to receive the Nobel Prize in Chemistry due to his contribution to coordination chemistry. He prepared, characterised and studied both physical and chemical properties of some coordination compounds by simple experimental techniques such as precipitation. From his findings, he made the following conclusions:

- i. Central metal atom or ion in a complex possesses two kinds of valencies named Primary and secondary valencies

- ii. The primary valency is ionisable and can be satisfied by anions only. It can be considered as the oxidation state of the central metal.
- iii. The secondary valency is not ionisable and can be satisfied by both molecules and anions. It gives rise to the coordination number.
- iv. The spatial arrangement of the anions and molecules satisfying the secondary valency determines the shape of the complex.

The complex species is enclosed in square bracket while the anions satisfying only the primary valency lie outside the coordination sphere (square bracket). Note that anions in the coordination sphere satisfied both primary and secondary valencies but the molecules only satisfy secondary valency.

From Werner's postulates geometries have been assigned to complexes based on the number of the secondary valencies

Complex, Primary and secondary valencies, possible shape

Complex	Primary Valency	Secondary valency	Possible Shape
$[\text{Ni}(\text{CO})_4]$	0	4	Tetrahedral or square planar
$\text{K}_4[\text{Fe}(\text{CN})_6]$	+2	6	Octahedral
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	+1	2	Linear
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	+3	6	Octahedral
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	+2	6	Octahedral

3.2.1 ELECTROLYTE AND NON-ELECTROLYTE COMPLEXES

By Precipitation of Chloride ions (Cl^-) using silver nitrate (AgNO_3) solution on complexes of cobalt with similar chemical composition (CoNH_3Cl_3), Werner was able to

distinguish to different kind of complexes which he classified as non-electrolytes and electrolytes

From his experiment, a complex containing chloride(s) which gave precipitate on reacting with AgNO_3 solution was said to be an electrolyte while non-electrolyte gave no precipitate. The precipitated chloride satisfied only primary valency i.e. it was outside the coordination sphere while un-precipitated chloride satisfied both primary and secondary valencies i.e. it was in the coordination sphere.

With improvement in technology, complexes containing other forms of anions can now be classified as electrolyte or non-electrolyte by measuring their electrical conductivity. It is worthy to note that for complexes with net negative charge ($[\text{Fe}(\text{CN})_6]^{4-}$), cations can balance out the charge resulting to electrolyte complexes ($\text{K}_4[\text{Fe}(\text{CN})_6]$). Therefore a complex is said to be an electrolyte if it has counter ion (cation or anion) outside the coordination sphere while a complex with zero net charge is called non-electrolytes because no counter ion will be present.

Electrolyte and Non-Electrolyte Complexes

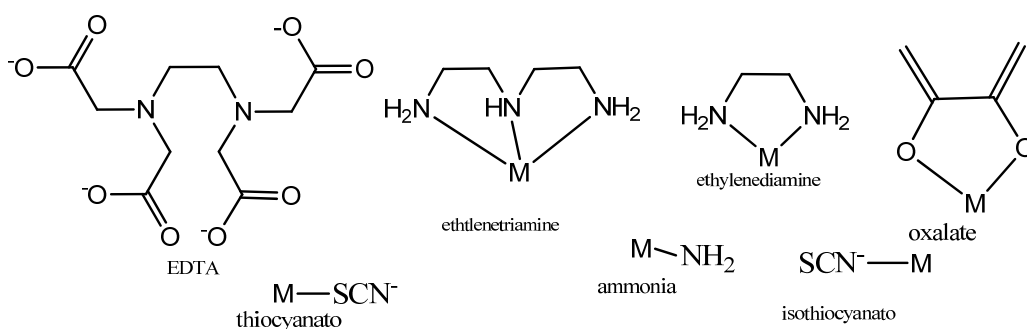
Complex	Colour	Mole of Cl^- precipitated	Class	Electrolyte Ratio
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Yellow	3	Electrolyte	1:3
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Purple	2	Electrolyte	1:2
Trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	Green	1	Electrolyte	1:1
Cis- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	violet	1	Electrolyte	1:1
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$		0	Non-Electrolyte	-

3.2 LIGANDS

Ligands are Lewis bases which coordinate to central metal atom or ion in a complex. They may be molecules with heteroatom (e.g. H_2O , NH_3 , PPH_3 etc) having lone pair(s), anions (e.g.

CN⁻, F⁻, Cl⁻, SCN⁻), unsaturated hydrocarbons (H₂C=CH₂, C₄H₄), aromatics (C₆H₆) or macromolecules like proteins, vitamins, porphyrin etc.

Ligands can be grouped into different classes based on the number of donor atoms (sites) they possess. A ligand with one donor site is called monodentate (e.g. H₂O, NH₃, CN⁻, Cl⁻). Bidentate ligands are those with two binding sites e.g. ethylenediamine (H₂NCH₂CH₂NH₂), oxalate (C₂O₄)²⁻ etc. These ligands are capable of forming ring structure (Chelate) with central metal. Tridentate ligands possess three donor atoms e.g. diethylenetriamine (H₂NCH₂CH₂NHCH₂CH₂NH₂). They have capacity to form two ring structures around the central metal. Ligands with four donor sites are said to be quadridentate e.g. triethylenetetraamine (H₂NCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂), they are capable of forming complexes with four ring structures. Polydentate ligands have many donor sites e.g. EDTA (ethylenediaminetetraacetate). Another category of ligands are called ambidentate ligands because they have two heteroatoms and any can be used to coordinate to metal depending on the reaction conditions e.g. SCN⁻ (it can either coordinate through S or N), NO₂⁻ (it can coordinate through O or N)



Structures of Ligands

3.3 APPLICATION AND IMPORTANCE OF COORDINATION COMPOUNDS

i. Inorganic Analysis

Coordination compounds are employed in quantitative and qualitative analyses of metals. The presence of metal can be detected by using aqueous ammonia to form complex of the metal if present. An example is the deep blue colour given by aqueous solution of Cu²⁺ on addition of ammonia solution. Estimation of the quantity of a metal e.g. Cu²⁺, Zn²⁺, Ni²⁺ etc can be

carried out using EDTA solution in the presence of a suitable indicator. This can be used to quantify the hardness of a given water sample caused Ca^{2+} and Mg^{2+} .

ii. Purification of Metals

Metals such as Gold and Nickel can be purified by complexation reaction. Gold in a given sample can be complexed with CN^- to give $[\text{Au}(\text{CN})_2]^-$. By reacting the complex with Zn, the Gold can be recovered in a pure state. Also, Nickel purification involves formation of $[\text{Ni}(\text{CO})_4]$ from a given impure sample. The complex can be easily decomposed to obtain pure Nickel.

Pure titanium metal is made by chlorination of the oxide TiO_2 to form the tetrahedral complex TiCl_4 . This is then reduced in a redox reaction with magnesium metal to yield free titanium metal as a powder. To provide a continuous loop of reagents, the MgCl_2 also formed in this reduction step is electrolyzed to produce chlorine and magnesium metal. With the chlorine and magnesium re-used fully, this is a good example of an industrial process with little environmental pollution.

iii. Industry

In the petrochemical industry, Nickel, Platinum and Rhodium complexes are used as catalyst in hydrogenation reaction, Cobalt and rhodium complexes are used in hydroformylation (conversion of alkene to aldehyde) reaction. EDTA is used in production of cream, food etc as preservative to trap any metal that may cause discoloration of the products. Brilliant and intense colours of many complexes make them of great value as dyes and pigments. Examples are copper phthalocyanine and Prussian blue.

iv. Medicine

In medicine, metal poison, such as Lead poison, can be treated by the use of ligands like EDTA as sequestering agent to form harmless complex with the toxic metal. Major breakthrough have been reported in the use of Cis-Platin, $[\text{PtCl}_2(\text{NH}_3)_2]$ and other related drugs in cancer treatments. Technetium complexes are used in imaging of internal organ in living organisms. Auranofin (gold complex) is used in treatment of arthritis. Budotitane and titanocene dichloride (anticancer drugs) are titanium complexes.

v. Important Biological Complexes

Photosynthesis is made possible in green plant due to the presence of Magnesium complex chlorophyll used to trap the required light energy. Iron complex called Haemoglobin helps in transportation of Oxygen with the body while Myoglobin another Iron complex helps to store Oxygen.

These are some of the areas where complexes play important role in our lives.

4.0 Conclusion

The chemistry of coordination compounds is an important aspect of modern inorganic chemistry. It helps in transformation of many industries and explains the ways in which biological molecules function in living systems. Many of these transformations are made possible due to the contributions of Alfred Werner and other notable Scientists to coordination chemistry.

5.0 Summary

Werner's contribution provided information on the unique characteristics of coordination compounds. From his findings, it was concluded that complexes possessed two kinds of valencies called primary and secondary valencies. The primary valency is only satisfied by anions but both molecules and anions can satisfy the secondary valency which influences the geometry of the complex unlike primary valency.

The anions and molecules are called ligands which can be monodentate, bidentate, tridentate, quadridentate or polydentate depending on the number of available donor sites. The multidentate have capacity to form multiple ring around the central metal.

6.0 Tutor-Marked Assignment (TMA)

Question

1. Complete the Tables below

Complex	Central Atom/Ion	Anion/molecule	Number coordinated	Valence of the metal
$[\text{Ni}(\text{CO})_4]$	Ni	CO	4	0
$\text{K}_3[\text{Fe}(\text{SCN})_6]$				
$\text{H}_2[\text{Pt}(\text{Cl})_6]$				
$\text{K}_2[\text{Ni}(\text{CN})_4]$				
$[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_2$				

Complex	Primary Valency	Secondary Valency	Possible Shape
$[\text{Ni}(\text{CO})_4]$	0	4	Tetrahedral or square planar
$\text{K}_3[\text{Fe}(\text{SCN})_6]$			
$\text{H}_2[\text{Pt}(\text{Cl})_6]$			
$\text{K}_2[\text{Ni}(\text{CN})_4]$			
$[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_2$			

2. Based on the number of mole of chlorides precipitated with AgNO_3 solution in the complexes below, assign secondary valencies to the metals and write the composition of each complex in square bracket as shown in the given example.

Example: $\text{CoCl}_3 \cdot 6\text{NH}_3$ mole of Cl^- precipitated 3

Solution: The observation implies 3 Cl^- ions are outside the coordination sphere. Therefore the secondary valency is 6 provided by the 6 molecules of NH_3 and the composition is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Formula	Mole of Cl^- Precipitated	Secondary Valency	Complex Composition
$\text{PdCl}_2 \cdot 4\text{NH}_3$	2		
$\text{TiCl}_2 \cdot 6\text{H}_2\text{O}$	2		
$\text{PtCl}_4 \cdot 2\text{HCl}$	0		
$\text{CoCl}_3 \cdot 5\text{NH}_3$	2		
$\text{PtCl}_2 \cdot 2\text{NH}_3$	0		

3. List and draw the structures of five (5) examples of each of the following types of ligands
 - i. Monodentate ligands
 - ii. Bidentate ligands
 - iii. Tridentate ligands
 - iv. Polydentate ligands
 - v. Ambidentate ligands

4. Write the Chemical formula of five complexes used in cancer treatment

7.0 REFERENCES/FURTHER READINGS

1. Housecroft, C. E. and Sharpe, A. G. Inorganic Chemistry (2nd ed.) *Pearson Education Limited*, 2005.
2. Cotton, F. A. and Wilkinson, G. Advanced Inorganic Chemistry (3rd ed.) *Interscience Publishers, a division of John Wiley and Sons*, 1972.

3. Cox, P. A. Inorganic Chemistry (2nd ed.) BIOS *Scientific Publishers Taylor and Francis Group*, 2004.
4. Miessler, G. L. and Tarr, D. A. Inorganic Chemistry (3rd ed.) *Pearson Education Int*, 2010.
5. Geoffrey, A. L. Introduction to Coordination Chemistry *John Wiley and Sons, Ltd.*, 2010

UNIT 2: NOMENCLATURE AND COORDINATION NUMBER OF COMPLEXES

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1.0 INTRODUCTION

Nomenclature in coordination chemistry has undergone several modifications. While some of the old and trivial names are still in use for some complexes, International Union of Pure and Applied Chemistry (IUPAC) provides the modern and most acceptable system of naming complexes. The IUPAC naming system put into consideration the nature of the complex whether cationic or anionic, the number and nature of the ligands as well as the bonding mode (bridging and non-bridging mode) adopted by the ligand. It is worthy to note that isomeric complexes can also be identified from their nomenclature. The IUPAC naming system has many features that make it unique and widely acceptable.

2.0 OBJECTIVES

At the end of this unit students should be able to:

- Name metal complexes
- Identify coordination number of metal complexes
- State possible geometry associated with a given coordination number

3.0 MAIN CONTENT

3.1 IUPAC SYSTEM OF NAMING METAL COMPLEXES

Many coordination compounds have very complex structures due to the nature of their ligands. This may give rise to their name being long and complicated. With IUPAC system of naming, the complication in naming is not removed but the naming process is organised in a way that it can be easily comprehended by anybody who understand the rules behind it.

Rules for Naming Complexes

The following rules must be observed in naming complexes:

Rule 1: For negative complex the positive counter ion (cation) is named first if present, followed by the complex. This is the common way of naming simple salts as well e.g. NaCl Sodium Chloride. For positive complex, the complex is named first before naming the negative counter ion (anion)

Examples:

Complex	Name
$K_2[Ni(CN)_4]$	Potassium tetracyanonickelate(II)
$[Co(NH_3)_6]Cl_3$	Hexamminecobalt(III) chloride

Rule 2: In the coordination sphere, the ligands are named before the metal in alphabetical order of the ligands' names, however the metal ion is written first in formula. The coordination sphere is enclosed in square brackets in the formula.

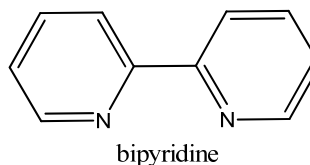
Examples:

Complex	Name
$[Cu(NH_3)_4(H_2O)_2]SO_4$	Tetraamminediaquacopper(II) sulphate
$[Co(NH_3)_5Cl]Cl_2$	Pentaamminechlorocobalt(III) chloride

Rule 3: The number of ligands in a complex is indicated by one or both of the prefixes listed below. If the name of the ligand contains the first prefix or is complicated, it is enclosed in parenthesis and the second set of prefix is used. Examples below will show how these prefixes are used.

Number	First prefix	Second prefix
2	Di	Bis
3	Tri	Tris
4	Tetra	Tetrakis
5	Penta	Pentakis
6	Hexa	Hexakis
7	Hepta	Heptakis
8	Octa	Octakis
9	Nona	Nonakis
10	Deca	Decakis

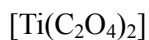
Complex	Name
$[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]\text{Cl}$	Dichlorobis(ethylenediamine)cobalt(III) chloride
$[\text{Fe}(\text{NH}_4\text{C}_5\text{-C}_5\text{H}_4\text{N})_3]\text{Cl}_2$	tris(bipyridine)iron(III) chloride



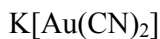
Rule 4: Anionic ligands e.g. Br^- , Cl^- , F^- , SO_4^{2-} etc are named with a suffix “o” while neutral ligands retained their usual name except H_2O called aqua, NH_3 called ammine. Note also that the name of the metal in an anionic complex ends with a suffix “ate”

Ligand	Name	Metal	Name in anionic complex
Br^- (Bromide)	Bromo	Copper	Cuprate
SO_4^{2-} (Sulphate)	Sulphato	Iron	Ferrate
$\text{C}_2\text{O}_4^{2-}$ (Oxalate)	Oxalato	Nickel	Nickelate
CN^- (Cyanide)	Cyano	Platinum	Platinate
$-\text{SCN}^-$ (Thiocyanate)	Thiocyanato-S	Titanium	Titanate
$^-\text{SCN}-$ (Isothiocyanate)	Thiocyanato-N	Gold	Aurate

Complex	Name
$\text{K}_4[\text{Fe}(\text{SCN})_6]$	Potassium hexathiocyanatoferrate(II)
$[\text{Ni}(\text{C}_2\text{O}_4)_2]^{2-}$	bis(oxalato)nickelate(II)

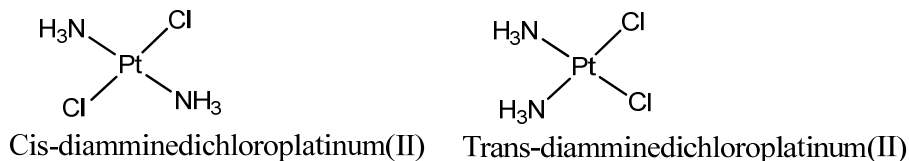


bis(oxalato)titanium(IV)



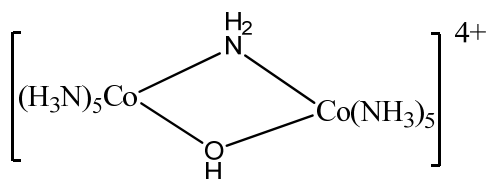
Potassium dicyanoaurate(I)

Rule 5: For complexes with geometric isomers, these isomers are indicated using prefix “cis” and “trans”. For example $[\text{PtCl}_2(\text{NH}_3)_2]$

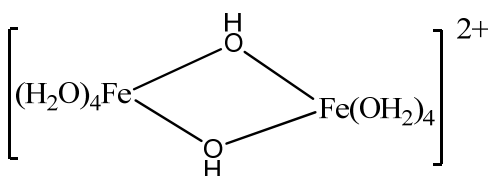


Rule 6: A bridging ligand (a ligand joining two or more metal centers) is indicated with a prefix “ μ ” and a subscript to indicate the number of the metal centers bridged by the ligand.

Examples



μ_2 -amido- μ_2 -hydroxobis(pentaammine cobalt (III)) cation



bis(tetraaqua- μ_2 -hydroxo iron (II)) cation

3.2 COORDINATION NUMBER OF METAL COMPLEXES

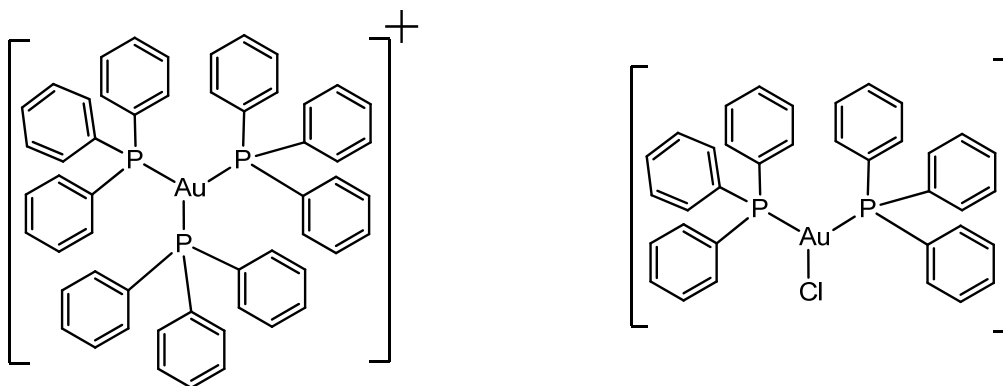
The coordination number of a metal ion in a complex is the number of ligand donor atoms to which the metal is directly bonded. It is determined by counting the number of the donor atoms or site directly attached to the metal. Coordination number varies from 1 to 8, though the two extremes are rare. The structure of a ligand strongly depends on the coordination number as it determines the number of spatial orientation possible in any given complex. The various coordination numbers will be considered and the possible structures discussed.

Coordination Number 1: complexes having coordination number one are rare and little is known of their chemistry.

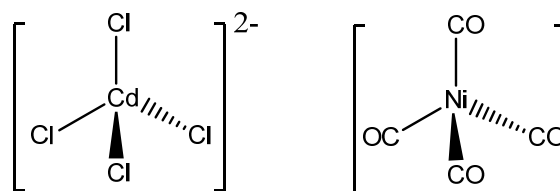
Coordination Number 2: The complex with coordination number 2 well established are silver complexes e.g. $[\text{Ag}(\text{NH}_3)_2]^+$ where the electronic configuration of Ag^+ is d^{10} . The hybridization of Ag^+ is sp with bond angle 180° and the possible shape is linear structure. Other examples are $[\text{Hg}(\text{CN})_2]$, $[\text{Au}(\text{CN})_2]$ etc.

$[\text{H}_3\text{N} \rightarrow \text{Ag} \leftarrow \text{NH}_3]^+$. The arrows point from the donors to the acceptor.

Coordination Number 3: Complexes with coordination number 3 are few. Metals with d^{10} configuration are commonly found with this coordination number. The hybridization is sp^2 bond angle 120° , which gives rise to trigonal planar structure. $[\text{HgI}_3]$, $[\text{AuCl}(\text{PPh}_3)_2]$, $[\text{Au}(\text{PPh}_3)_3]^+$ etc. Coordination number three is favoured by bulky ligand that can induce steric hindrance and prevent further coordination.



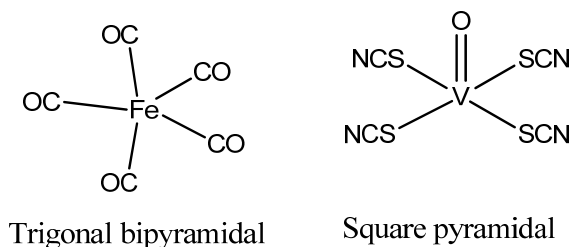
Coordination Number 4: This is a common coordination system which can give rise to two different geometries i.e. Tetrahedral and square planar, depending on the orbitals of the central metal that received the donor pairs. Divalent ions such as Zn^{2+} , Cd^{2+} , Hg^{2+} and Cu^+ with d^{10} electronic configuration and zero crystal field stabilization energy will give rise to tetrahedral complexes with sp^3 hybridization with bond angle 109° examples $[\text{CdCl}_4]^{2-}$, $[\text{Zn}(\text{OH})_4]^{2-}$ and $[\text{Hg}(\text{Br})_4]^{2-}$. Similarly, few metals with d^0 and d^5 are known to form tetrahedral complexes MnO_4^- , MnCl_4^{2-} , TiCl_4 . Metals with other d -configurations have very limited number of tetrahedral complexes e.g. $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ with d^8 configuration.



Square Planar Complexes are common with metals d^8 electronic configuration. Examples are $[\text{PtCl}_2(\text{NH}_3)_2]$, $[\text{Ni}(\text{CN})_4]^{2-}$ and PdCl_4^{2-} . The hybridization in these complexes is dsp^2 with bond angle of 90° .



Coordination number 5: two possible structures with coordination number five are square based pyramidal and trigonal bipyramidal with the metal having sp^3d hybridization. In square planar, dx^2-y^2 orbital in the metal will receive one of the donated pairs while in trigonal bipyramidal, dz^2 orbital of the metal will receive one of the donated pairs. The energy difference between the two configurations is small hence they are interconvertible. Examples are $[\text{Fe}(\text{CO})_5]$ and $[\text{Cu}(\text{bipy})_2\text{I}]^+$, $[\text{VO}(\text{acac})_2]$ and $[\text{VO}(\text{SCN})_4]^{2-}$.



Coordination Number 6: This is the most common coordination number with two possible geometries i.e. octahedral and trigonal prismatic. Octahedral is the most common with metal center having sp^3d^2 or d^2sp^3 hybridization with bond angle 90° . Examples $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.



Higher coordination numbers are possible but not common e.g. coordination seven $[\text{ZrF}_7]^{3-}$ and $[\text{HfF}_7]^{3-}$, coordination number eight $[\text{ZrF}_8]^{4-}$ and $[\text{Mo}(\text{CN})_8]^{4-}$.

4.0 CONCLUSION

Nomenclature in coordination chemistry may be complicated but the rules stated by IUPAC provide a way of having a well organized naming system that is widely embraced. Another

important aspect of coordination chemistry apart from nomenclature is the coordination number which influences the possible geometries complexes can adopt. From coordination number, the shape, bond angle and hybridization of a complex can be predicted.

5.0 SUMMARY

- Coordination compounds can be named with IUPAC system of naming.
- Coordination number can be used to predict the shape, bond angle and hybridization of complex.
- Coordination numbers 1, 2, 3, 7, 8, 9 and 10 are not common like coordination numbers 4, 5 and 6.

6.0 Tutor-Marked Assignment (TMA)

Questions

1. Write the formulas for the following coordination compounds and predict possible shape(s), hybridization(s) and bond angle(s) of each:
 - (i) Tetraammineaquacobalt(III)chloride
 - (ii) Potassiumtetracyanonickelate(II)
 - (iii) Tris(ethylenediamine)chromium(III)chloride
 - (iv) Amminebromochloronitrito-N-platinate(II)
 - (v) Dichlorobis(ethylenediamine)platinum(IV)nitrate
 - (vi) Iron(III) hexacyanoferrate(II)
2. Write the IUPAC names of the following coordination compounds and predict possible shape(s), hybridization(s) and bond angle(s) of each:.
 - (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
 - (ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 - (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 - (iv) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
 - (v) $\text{K}_2[\text{PdCl}_4]$
 - (vi) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$

7.0 REFERENCES/FURTHER READINGS

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UNIT 3: ISOMERISM IN COMPLEXES

Unit 3 Table of Contents

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Isomerism
 - 3.1.1 Structural isomerism
 - 3.1.2 Stereoisomerism
- 5.0 Conclusion
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- 6.0 Tutor-Marked Assignment (TMA)
- 7.0 References/Further Readings

1.0 INTRODUCTION

Just as an infinite number of ways exist to arrange large number of different coloured shoes, there exists different ways on the molecular scale in which a given number of ligands can be arranged in three dimensional array round a central metal. This is the basic concept of isomerism in coordination chemistry. Different coordination numbers, shapes and points of attachment of ligands provide an almost infinite number of three-dimensional structurally related complexes generally called isomers. Isomerism does not exist in complexes with identical monodentate and common donor atom ligands. However, wherever more than one type of ligand is bound, and even where either one type of ligand with a set of more donor atoms than required, or a number of identical chelating ligands bind, the possibility of isomerism needs to be considered. It is important to note that the number of isomers increases with increase in coordination. The concept of isomerism is well developed in complexes with coordination numbers four and six while no established cases of isomerism is associated with coordination numbers one, two and three. The concept of isomerism is very important in drug design as different isomers have certain differences in reactivity, especially optical isomers. An anticancer drug, Budotitane (Titanium complex), lost its market value when it was discovered to possess optical isomers. This because only one isomer may be effective in the

treatment and the other isomer may cause damaging effect. This underscores the need to understand concept of isomerism.

2.0 OBJECTIVES

At the end of this unit students should be able to:

- The concept of isomerism in coordination chemistry
- Differentiate between structural isomerism and stereoisomerism
- Identify different structural isomers of a given complex
- Differentiate between geometric and optical stereoisomerism

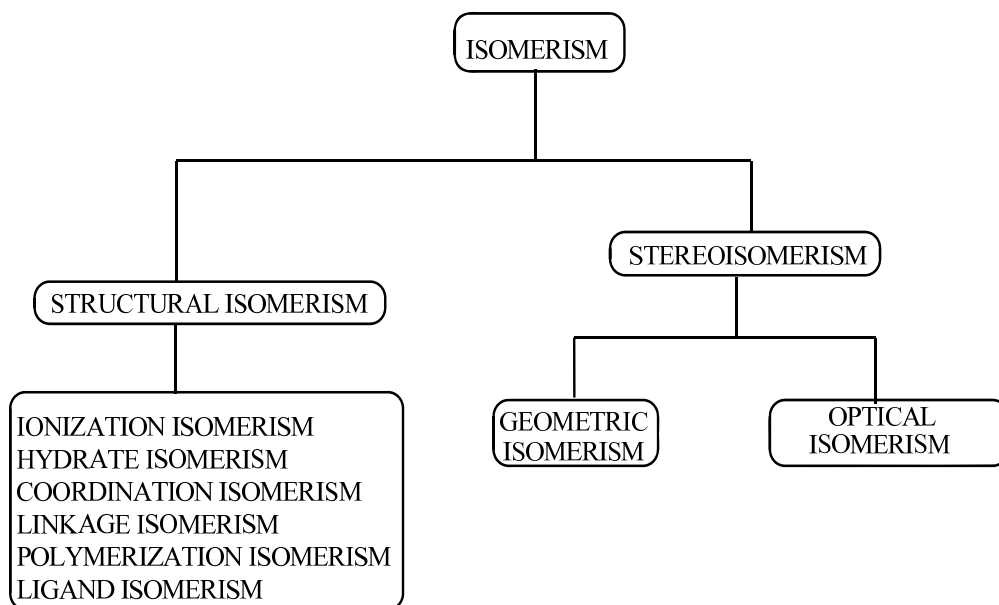
3.0 MAIN CONTENT

3.1 ISOMERISM

Isomerism is a phenomenon used to describe complexes with the same molecular weight and molecular formula but different structural and/or spatial arrangement of donor atoms around the central metal in the coordination sphere. These complexes are called isomers.

In coordination chemistry, Isomers are of different kinds, they include hydrate or solvent isomers, ionization isomers, and coordination isomers having the same overall formula but with different donor atoms of the same or different ligands attached to the central metal atom or ion. The nomenclature of different kinds of isomerisms is an indication of whether solvent, anions, or other coordination compounds imposes the isomerism in the structure. The terms linkage (ambidentate) isomerism is used when ambidentate ligands impose structural differences in complexes due to use of different donor atoms on a ligand. Stereoisomers have the same ligands with the same donor atoms, but differ in the geometric (spatial) arrangement of the ligands. Some stereoisomers are optically active hence they are classified as optical isomers.

Isomerism in coordination chemistry is divided into structural isomerism and stereoisomerism. Structural isomers differ in the way ligands or donor atoms of ligands are arranged round a central metal. Stereoisomers differ in the spatial arrangement of ligands round the central metal. The figure below shows different forms of isomerisms.



3.1.1 STRUCTURAL ISOMERISM

Also known as constitutional isomers, structural isomers have the same empirical formula but differ in the arrangement of their constituent atoms. This results in difference in physical properties such as colour. Many different kinds of structural isomerism occur in coordination chemistry and some of them shall be discussed

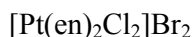
i. IONIZATION ISOMERISM

Ionization isomers give different ions in aqueous solution. This is because different anions coordinated to the metal in the coordination sphere. The isomeric pairs differ in that there is an exchange of two anionic groups within and outside the coordination sphere.

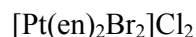
Examples; $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (violet) and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (red)

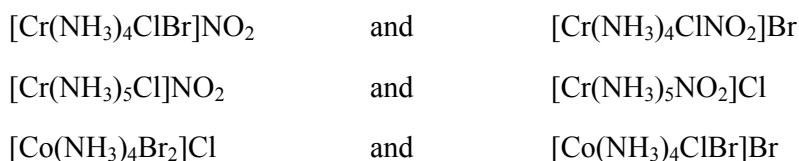
Note that in $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ the sulphate is the counter ion and can be detected by treating the solution of the complex with BaCl_2 to precipitate the sulphate in the form of BaSO_4 (qualitative test for sulphate). The bromide ion is coordinated and will not precipitate with silver nitrate because it is not free.

In $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$, the test for bromide will be positive since Br^- is not coordinated to the metal while the test for sulphate will be negative since the sulphate is in the coordination sphere and not free.



and



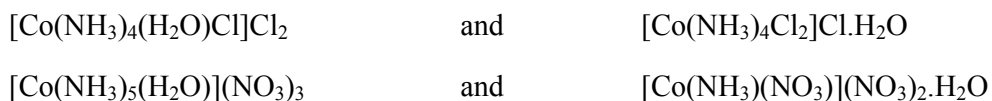


ii. HYDRATE ISOMERISM

As many complexes are prepared in aqueous solutions where water is abundant, complexes can precipitate or crystallise with water of crystallisation outside the coordination sphere or with coordinated water (ligand) inside the coordination sphere. There are many isomers which differ in the position of water molecules in their formula. For example, there are three known hydrate isomers of $\text{CrCl}_3(\text{H}_2\text{O})_6$: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet), $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (pale green) and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green).

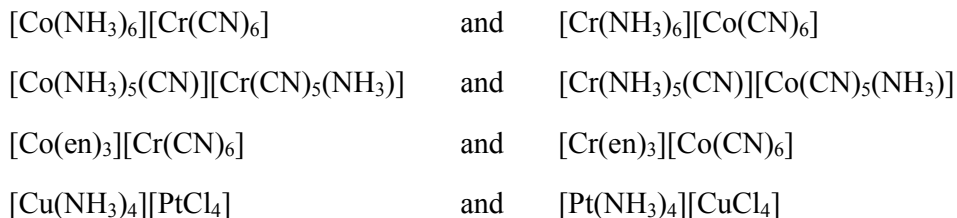
The isomers can be distinguished by the mole of silver chloride precipitated by using silver nitrate on molar solution of the isomers. In $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, 3 mole of silver chloride will be precipitated indicating that none of the Cl^- ion is in the coordination sphere, 2 mole will be precipitated in $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and 1 mole in $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ indicating the number of Cl^- not coordinated to the metal ion. The water of crystallisation outside the coordination sphere can be detected on dehydration of the complexes.

Other examples are:



iii. COORDINATION ISOMERISM

These isomers contain pairs of ionic complexes that exchange ligands with each other. Many isomeric pairs are possible by redistribution of ligands between two metal centres. Examples are:



Note that the cationic complex is written first.

iv. LINKAGE ISOMERISM

This type of isomerism is observed in complexes containing ambidentate ligands which can coordinate through at least two different binding sites. Example of such ligand is nitrite (NO_2^-) which can coordinate through nitrogen or oxygen.



The yellow complex, $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$, is unstable and it is converted into $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ both in solution and the solid state either by heating or by exposure to ultraviolet light. The two isomer can be distinguished through Infrared spectroscopy, for the O-bonded ligand, characteristic absorption bands at 1065 and 1470 cm^{-1} are observed, while for the N-bonded ligand, the corresponding vibrational wavenumbers are 1310 and 1430 cm^{-1} . Other examples are $[\text{Co}(\text{CN})_5(\text{SCN})]^{3-}$ and $[\text{Co}(\text{CN})(\text{NCS})]^{3-}$, where the sulphur and nitrogen of the thiocyanate ligand imposes the observed linkage isomerism.

v. POLYMERIZATION ISOMERISM

Polymerization isomers are isomers with the same simplest unit called monomer. The combination of two or more monomer units results in polymeric complex isomer. An example is the unit $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ which on combination can give; $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$. Also the unit $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ on combination will produce $[\text{Co}(\text{NH}_3)_6][\text{CoCl}_6]$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2][\text{Co}(\text{NH}_3)_2\text{Cl}_4]$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}][\text{Co}(\text{NH}_3)\text{Cl}_5]$.

VI. LIGAND ISOMERISM

This is a form of isomerism due to the isomeric nature of the ligands. Typical examples are $[\text{Pt}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ and $[\text{Pt}(\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2)_2]^{2+}$

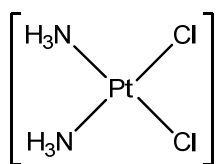
The ligand propane-1, 3-diamine and its isomer methylethylenediamine impose the isomerism.

3.1.2 STEREOISOMERISM

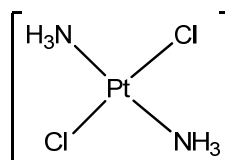
Stereoisomerism occurs in complexes due to difference in spatial arrangement of ligands round the central metal. Stereoisomerism is divided into geometric and optical isomerism.

GEOMETRIC ISOMERISM

The most common type of geometrical isomerism involves *cis* and *trans* isomers in square planar and octahedral complexes. In square planar complex $[\text{Pt}(\text{NH}_3)\text{Cl}_2]$, the *cis*- and *trans*-isomers are shown below. Note that in the *trans*- form, identical ligands are separated by bond angle of 180° while in *cis*- the bond angle between identical ligands is 90° .

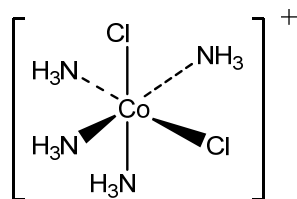


cis-Platin
(Orange-yellow)

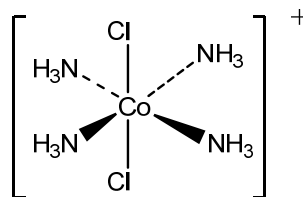


trans-Platin
(Pale-yellow)

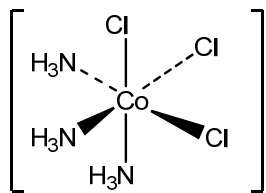
In Octahedral complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, *cis*- and *trans*- isomers occur while in $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, *facial* and *meridional* isomers occur. These are shown below.



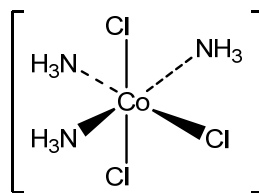
cis-tetraamminedichlorocobalt (III)



trans-tetraamminedichlorocobalt (III)



fac-triamminetrichlorocobalt (III)

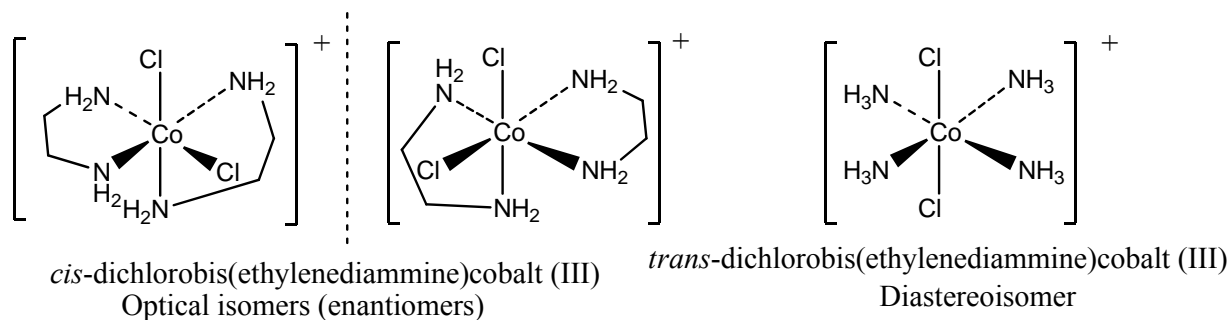


mer-triamminetrichlorocobalt (III)

OPTICAL ISOMERISM

Optical isomers exist in complexes that are not superimposable on their mirror images. These isomers have ability to rotate the plane of polarised light in opposite direction. A mixture of optical isomers of the same quantity will not rotate the plane of polarized light because the effect of one isomer is cancelled out by the other. Such a mixture is called racemic mixture. Optical isomerism is possible in tetrahedral and octahedral complexes (*cis*-isomers) where centre of symmetry is absent but not in square planar complexes. Optical isomers are called

enantiomers. A solution of enantiomer that rotates the plane of polarized light in clockwise direction is designated as positive (+) or dextrorotatory (*d*) enantiomer while the isomer that rotates the plane of polarized light in anticlockwise direction is designated as negative (-) or levorotatory (*l*) enantiomer. Example is dichlorobis(ethylenediamine)cobalt (III). The optical isomers have identical chemical and physical properties but differ in their ability to rotate the plane of polarized light unlike diastereoisomer that differ in both chemical and physical properties and lacks ability to rotate the plane of polarized light.



4.0 CONCLUSION

Isomerism in coordination chemistry provides information on why complexes with the same chemical formula differ in physical and chemical properties, and why some complexes with the same formula, physical and chemical properties differ in their ability to rotate plane polarized light.

5.0 SUMMARY

- Isomerism are grouped into structural (constitutional) and stereoisomerism
- Structural isomerisms include: Ionization, Coordination, Linkage, Hydrate, Polymerization and Ligand isomerisms
- Stereoisomerism is grouped into optical isomerism and geometric isomerism
- Geometric isomerim is possible in square planar and octahedral complexes
- Optical isomerism is possible in tetrahedral and octahedral (*cis*-isomer) with no centre of symmetry complexes

6.0 TUTOR-MARKED ASSIGNMENT (TMA)

Questions

1. Only one compound having the formula $[\text{Zn}(\text{py})_2\text{Cl}_2]$ (where 'py' is pyridine) is known, but two different compounds (isomers) are known with composition $[\text{Pt}(\text{py})_2\text{Cl}_2]$. Explain these observations and describe the structures of each of complexes.
2.
 - (a) Write the formulae of polymerization isomers of $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$
 - (b) Draw the structure of *cis*-bis(oxalato)dichlorochromium(III) ion
 - (c) Write the formula for a coordination isomer of $[\text{Zn}(\text{NH}_3)_4][\text{Pd}(\text{NO}_2)_4]$
 - (d) Draw the structure of diamminedithiocyanatoplatinum(II)
 - (e) Draw the structure of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$
3. What chemical tests would you use to distinguish between;
 - (a) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
 - (b) $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ and $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2\cdot \text{H}_2\text{O}$
 - (c) What is the relationship between these pairs of compounds?
 - (d) What isomers are possible for $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$?
4.
 - (a) Give formulae for compounds that are coordination isomers of the salt $[\text{Co}(\text{bpy})_3][\text{Fe}(\text{CN})_6]$.
 - (b) What other types of isomerism could be exhibited by any of the complex ions noted down in your answer to part (a)?

7.0 REFERENCES/FURTHER READINGS

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UNIT 4: PREPARATION AND REACTIONS OF COMPLEXES

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- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.2 Preparation and reactions of complexes
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment (TMA)
- 7.0 References/Further Readings

1.0 INTRODUCTION

Many methods are used in preparation of coordination complexes and in the transformation of one coordination complex into another. The preparation and reactions of complexes have generated great research outputs in synthetic inorganic chemistry. Complexes preparation may involve; substitution reaction (replacing one or more ligands with others in a complex), direct reaction (involving only ligand and metal salt without solvent provided the ligand is a liquid or gas), decomposition reaction (where a complex is transformed to another by heating at specific temperature) and redox reaction (where change in oxidation state of the metal may lead to formation of a new complexes). Apart from the various methods stated, a change in reaction conditions such as pH, temperature, solvent polarity can lead to formation of new complex. It is therefore important to study the various ways which complexes can be synthesized.

2.0 OBJECTIVES

At the end of this unit students should be able to:

- Explain methods of preparing metal complexes

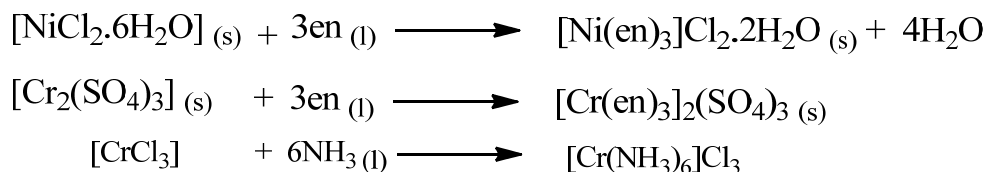
3.0 MAIN CONTENT

3.1 PREPARATION AND REACTIONS OF COMPLEXES

For over two hundred years, coordination complexes have been produced by a variety of techniques. Among the first few complexes synthesized, Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, known for decades, and Werner's cobalt complexes serve as template for synthesis of numerous complexes known today. Synthetic techniques used to prepare coordination complexes range from simply mixing of reactants to variation of reaction's conditions and use of non-aqueous solvents. The methods used in preparation of complexes are numerous and new methods keep emerging due to advancement in technology. Some of these methods will be described in this Course

i. DIRECT REACTION

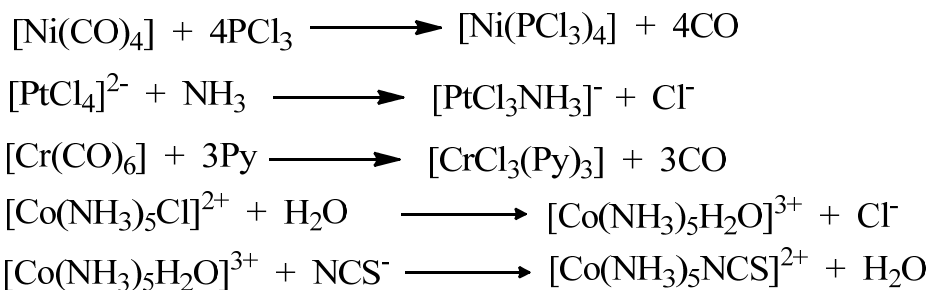
This involves combination reaction of metal salt and ligands in liquid or gaseous state. This reaction can also be carried out in suitable solvent if both reactants are solids. Examples are



The product of the second reaction involving chromium salt is a solid mass which may be difficult to handle but with use of inert solvent like toluene, the product can be easily filtered and dry in purer state. In the third reaction liquid ammonia is used which can be allowed to evaporate to give the product.

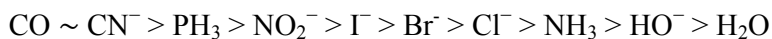
ii. SUBSTITUTION REACTION

The replacement of one ligand by another is the most common type of reaction of coordination complexes, and the number of reactions of this type is great. Some are carried out in aqueous solutions, some in non-aqueous media, and others can be carried out in the gas phase. Numerous examples of these reactions are common and often carried out in qualitative test of cations using aqueous alkali solution or ammonia.

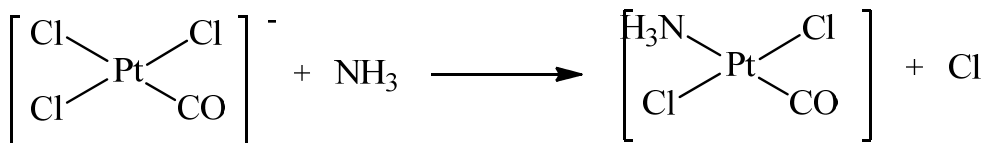
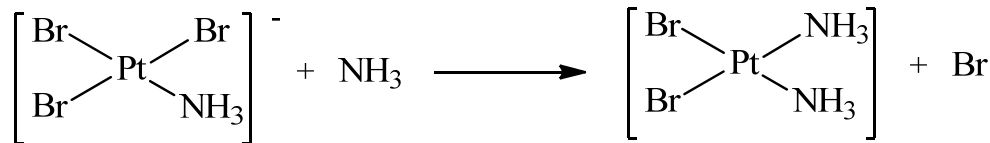
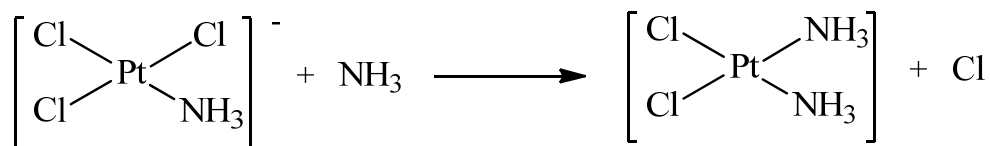


SUBSTITUTION IN SQUARE PLANAR COMPLEXES OF PLATINUM

One observation from a large collection of experimental results is that ligands not undergoing substitution themselves can influence substitution at sites directly opposite them (*trans*) and, to a lesser extent, at adjacent sites (*cis*). Examples lie with Pt(II) square planar complexes, where some ligands show strong *trans* effect, causing ligands directly opposite them to be more readily substituted than those in *cis* position. Ligands opposite a chloro ligand in a square planar platinum complex, are substituted more readily than those opposite an ammine ligand. Experimental studies have produced an order of *trans* effects for various ligands that coordinate to Pt(II).

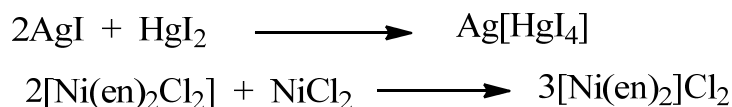


The importance of the order is that it can be used to predict the products of reactions involving Pt square planar complexes and products of other related complexes. In a reaction where a ligand with stronger *trans* effect than Cl⁻ is present, the chloro *trans* to this ligand will be substituted instead of chloro ligand that is in *cis* position to this ligand. The reason is because ligands with stronger *trans* effect form bonds that are stronger with shorter bond length hence making the ligand opposite them to be weak with longer bond length. This makes such *trans* ligand more susceptible to substitution. The following examples illustrate the influence of the *trans* effect. Note that NH₃ has less *trans* effect there the products of the first 2 reactions are *cis* as expected but CO has stronger *trans* effect, the product of the last reaction established this.



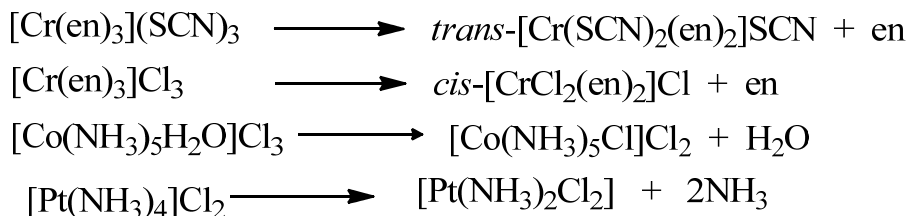
iii. REACTION OF METAL SALTS

Two different metal salts, with suitable anion that can act as ligand, combine together to form complex in such a way that the anion will behave as ligand. Another related reaction is one involving a complex and metal salt to produce a new complex.



iv. PARTIAL DECOMPOSITION REACTIONS

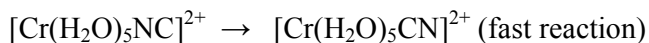
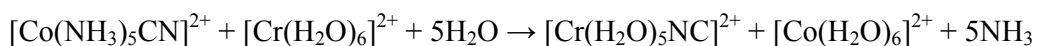
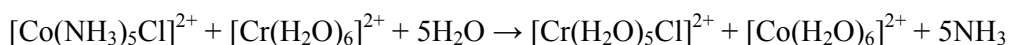
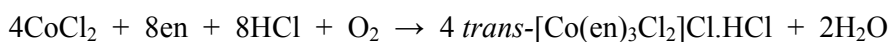
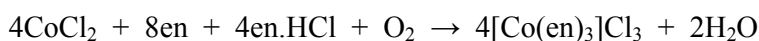
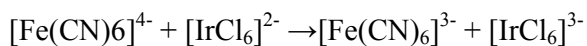
These are reactions in which stable complexes are heated to drive out volatile ligands in order to form new complexes. The coordination number may change and in some cases remain constant. The reactions occur in solid state.



v. REDUCTION AND OXIDATION REACTION

Many coordination complexes can be prepared when a compound of the metal is either reduced or oxidized in the presence of a ligand. The redox reaction can also occur between

two complexes where transfer of electron(s) can lead to new complexes. This method is used to prepare complexes of metal ion in unstable oxidation state. For example Co(III) solution cannot be used to prepare its complexes because it is very unstable due to its strong oxidizing ability. Complexes of the ion are prepared by oxidation of solution of Co(II) in the presence of ligand. The complexation of the Co(III) helps to prevent reduction of this very strong metal ion. Complexes of Cr(III) are also prepared in similar manner.



4.0 CONCLUSION

Preparation of complexes involves many reactions that include; simple mixing of metal salts with ligands, substitution of one ligand with another inside a complex, oxidation and reduction of complexes to effect change in oxidation state and partial decomposition of complexes. Some of these reactions are rapid and may occur with few second.

5.0 SUMMARY

Metal complexes can be prepared by different reaction procedures depending on the desired end product. Reactions such as; direct combination, substitution, decomposition, reduction and oxidation have been used to prepare many complexes.

6.0 TUTOR-MARKED ASSIGNMENT (TMA)

Questions

1. Discuss the following reactions in the in preparation of metal complexes
 - i. Direct reaction
 - ii. Substitution reaction

- iii. Redox reaction
2. Predict the production of the following reactions
- $[\text{PtCl}_3\text{NH}_3]^- + \text{NH}_3 \rightarrow$
 - $[\text{PtCl}_3\text{NO}_2]^{2-} + \text{NH}_3 \rightarrow$
 - $[\text{PtCl}(\text{NH}_3)_3]^- + \text{CN}^- \rightarrow$
 - $[\text{PtCl}_3\text{NH}_3]^- + \text{CO} \rightarrow$
 - $[\text{PtCl}_3\text{NH}_3]^- + \text{PH}_3 \rightarrow$

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MODULE 2

UNIT 1: THEORIES OF STRUCTURE AND BONDING

Unit 1 Table of Contents

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Valence bond theory
 - 3.2 Crystal field theory
 - 3.3 Ligand field theory and Molecular orbital theory
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment (TMA)
- 7.0 References/Further Readings

1.0 INTRODUCTION

Bonding in coordination chemistry has been described by many theories. In order to explain various properties exhibited by complexes, these theories were modified. The theory of Effective Atomic Number (EAN) rule was first used but found to be inadequate as behaviour of many complexes could not be explained by these method. The EAN rule states that stable compound should have electronic configuration of its nearest noble gas. There are many exceptions to this rule because it limits the coordination number possible for each metal. Octahedral complexes of many compounds show exception to this theory. However, the theory is sufficient enough to explain the bonding in metal complexes with metal in zero oxidation state. Examples are $[\text{Ni}(\text{CO})_4]$ and $[\text{Cr}(\text{CO})_6]$ where the central metal has zero oxidation number and accommodates ligands sufficient enough to have the electronic configuration of their nearest noble gas. The theory cannot explain the reason for variation in coordination number, hence the need for another theory. Valence bond theory (VBT) is introduced to explain the reason for the variation in coordination number based on the number of hybridized orbitals of the metal used in bonding. It cannot explain fully the concept of colour and magnetic properties of complexes. Crystal Field Theory (CFT) is used to provide explanation for the spectra and magnetic properties of complexes. Although, CFT

is very useful, it cannot explain some degree of covalence in some complexes. To be able to explain reason for some degree of covalence in some complexes, the CFT is modified to Adjusted crystal Field theory (ACFT) also called Ligand Field theory (LFT). Finally, Molecular Orbital theory (MOT) is introduced to fully explain the various properties of complexes. To have indebt understanding of bonding in complexes these theories must be fully studied.

2.0 OBJECTIVE

At the end of this unit students should be able to:

- State the theories used to describe bonding in metal complexes
- Explain Valence Bond Theory (VBT)
- Explain Crystal Field theory (CFT)
- Explain Ligand Field Theory (LFT)
- Explain Molecular Orbital Theory (MOT)

3.0 MAIN CONTENT

3.1 VALENCE BOND THEORY

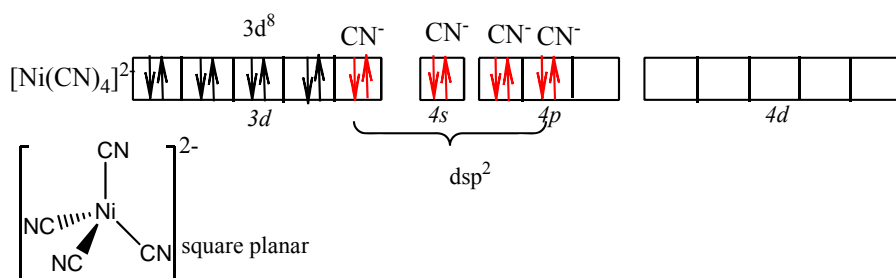
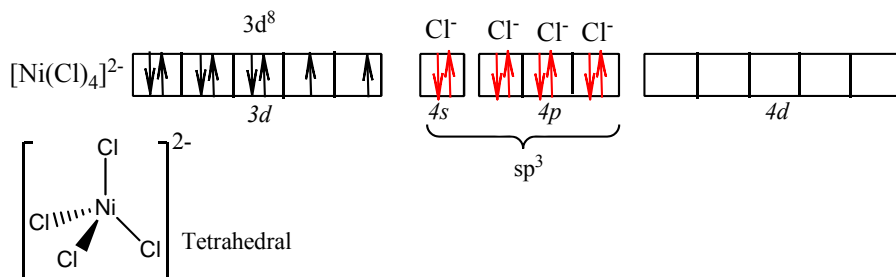
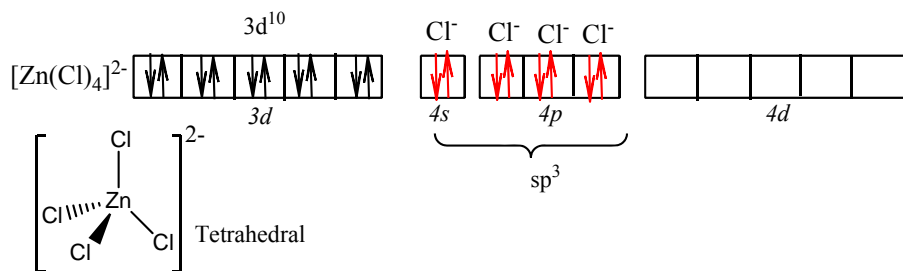
Valence Bond Theory (VBT) describes bonding in coordination complexes by considering the hybridization of the orbitals involved in the bonding and stereochemical consequences of the hybridization. This theory was first extended to explain bonding in coordination complexes by Pauling in 1930. With the theory, He was able to account for the stereochemistry and magnetical behaviour of many complexes through the inner and outer orbital bonding concept. The electronic configurations of the transition metals allow them to make use of either $3d$ or $4d$ orbitals in coordination with ligands. Pauling described complexes formed by the use of $3d$ orbitals as inner complexes and those formed by the use of $4d$ orbitals as outer complexes. The inner orbital complexes have less number of unpaired electrons compare to the outer orbital complexes, hence the inner orbital complexes are called low spin complexes and the outer orbital complexes are called high spin complexes. With this concept Pauling was able to account for the magnetic behaviour of some complexes. The nature of coordinating ligands determines the spin adopted by complexes. According to VBT, coordination complexes are formed by:

- i. Dissociation of the salt to make the cation (M^+) available for coordination.

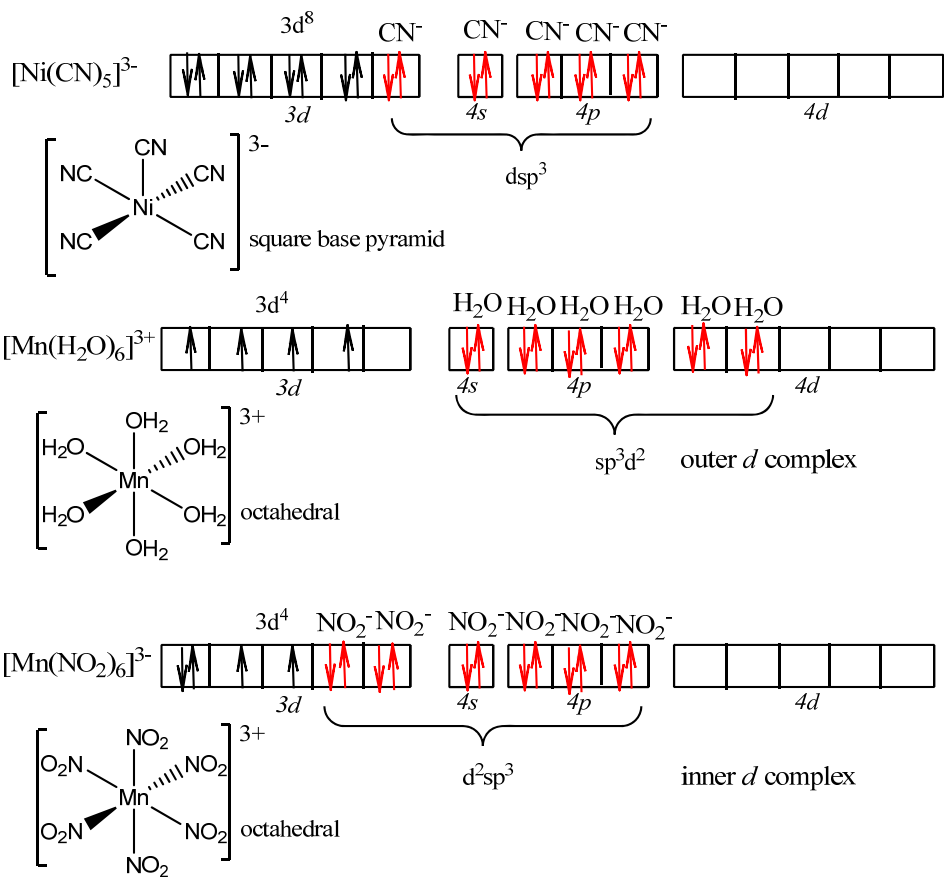
- ii. Hybridization of atomic orbitals of the cation required to accommodate the electron pairs to be donated
- iii. Rearrangement of electrons in the cation atomic orbitals, where necessary to ensure that the hybridized orbitals are free to accommodate the donated electron pairs.
- iv. Bond formation between the cation and the ligands by overlapping of atomic orbitals of ligands containing the lone pair and the hybridized orbitals of the cation.
- v. Spatial orientation of the ligands to minimize repulsion between them leading to stereochemistry (shape) of the complex

Stereochemistry in complexes depends on the type and number (coordination number) of atomic orbitals of the central metal atom or ion hybridized. Below is a Table showing possible structures for different coordination number and hybridization.

CN	Atomic Orbital	Hybrid type	Structure	Example
2	s, p _x	Sp	Linear	[Ag(CN) ₂]
3	s, p _x , p _y	sp ²	Trigonal planar	[HgI ₃] ⁻
4	s, p _x , p _y , p _z	Sp ³	Tetrahedral	[ZnCl ₄] ²⁻
4	s, p _x , p _y , d _{x²-y²}	dsp ²	Square planar	[Ni(CN) ₄] ²⁻
5	s, p _x , p _y , p _z , d _{z²}	sp ³ d	Trigonal bipyramidal	[Cu(Cl) ₅] ³⁻
5	s, p _x , p _y , p _z , d _{x²-y²}	sp ³ d	Square pyramidal	[Cu(CN) ₅] ³⁻
6	s, p _x , p _y , p _z , d _{x²-y²} , d _{z²}	sp ³ d ²	Octahedral	[Cu(H ₂ O)] ²⁺
6	d _{x²-y²} , d _{z²} , s, p _x , p _y , p _z	d ² sp ³	Octahedral	[Ni(CN)] ⁴⁻



The coloured arrows indicate the spins of the electrons of the donated pairs while the dark arrows represent the spins of the metal. Generally, tetrahedral complexes are high spin complexes while square planar complexes are low spin complexes. The number of unpaired electrons determines the magnitude of the magnetic properties of the complexes. Complexes without unpaired electron are diamagnetic while those with unpaired electrons are paramagnetic in nature. In $[Ni(CN)_4]^{2-}$, the two unpaired electron in the Ni^{2+} d orbitals are forced to pair up due to approach of strong CN^- ligand unlike Cl^- which has less repulsion effect on the unpaired electrons in $[Ni(Cl)_4]^{2-}$ complex.



Note that two electrons in Mn^{2+} are forced to pair up in $[Mn(NO_2)_6]^{3-}$ due to approach of the strong ligand (NO_2^-) while in the hexaqua complex of Mn^{3+} , these electrons remained unpaired.

Valence bond theory limitations:

- It cannot explain relative stability of complexes
- It cannot explain colours and spectra of complexes

3.2 CRYSTAL FIELD THEORY (CFT)

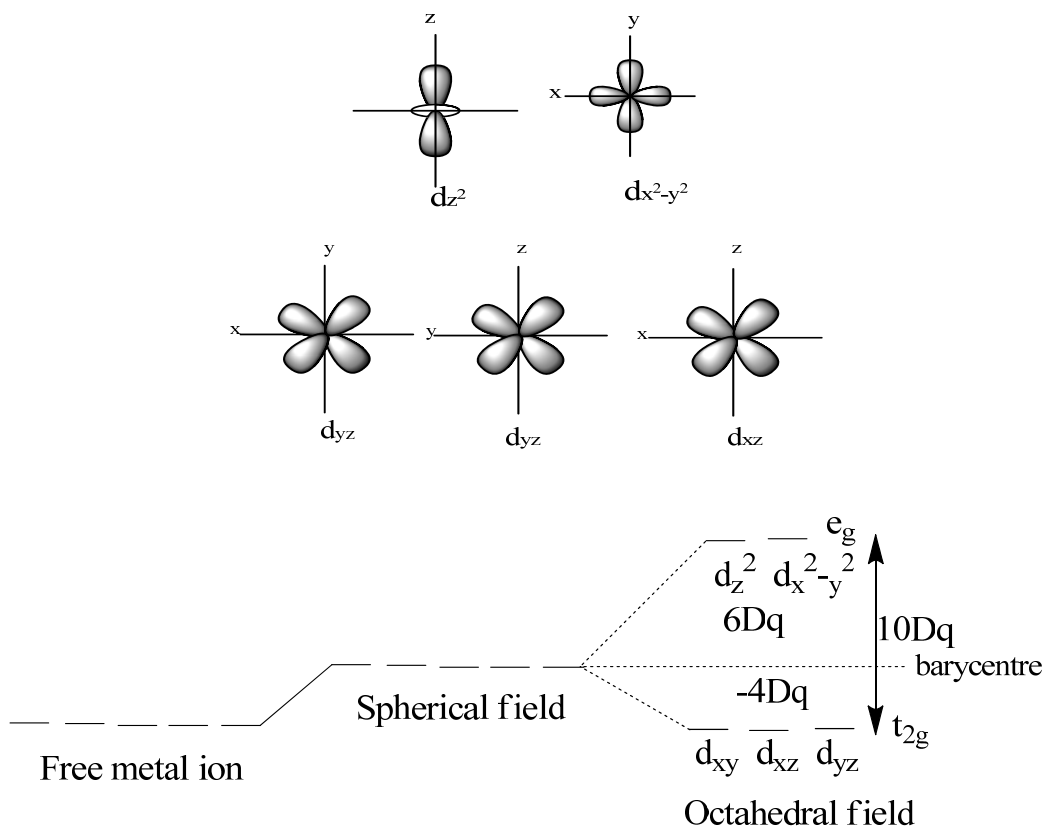
There are several characteristics of coordination complexes that are not satisfactorily explained by VBT description of the bonding. For example, the magnetic moment of $[CoF_6]^{3-}$ shows that there are four unpaired electrons in the complex, whereas that of $[Co(NH_3)_6]^{3+}$ shows that this complex has zero unpaired electrons, although in the two complexes Co^{3+} is a d^6 ion. In VBT, the bonding types in these complexes are shown to involve sp^3d^2 and d^2sp^3 hybrid orbitals respectively, but that does not provide an explanation as to why the two cases exist. Another aspect that is inadequately explained by VBT approach is the number and type

of absorption bands observed in the spectra of complexes. One of the most successful approaches to explaining these characteristics is known as crystal field theory.

When a metal ion is surrounded by anions in a crystal, there is an electrostatic force (field) produced by the anions that changes the energies of the d orbitals of the metal centre. The field produced is known as a crystal field. Crystal field theory was introduced in 1929 by Hans Bethe to explain the spectral characteristics of metal complexes. This is a purely electrostatic model which assumes electrostatic interaction between positively charged metal centre and negatively charged anions or polar molecules. Unlike VBT, CFT predicts properties of complexes based on repulsion between electrons of the metal and those of the ligands in a complex. The positive charge on the metal is assumed to be the source of attraction for the ligands however; the ligands are also repelled by the d -orbital electrons of the metal. The repulsion on the d -orbital electrons is not uniform leading to splitting of the d -orbitals. The splitting of the orbitals results in loss of degeneracy among the 5 d -orbitals. The pattern of splitting is dependent on the coordination number and stereochemistry of the complex. CFT approach considers the metal as positive point charge and the ligands as negative point charges. The ligands move towards the centre of the metal in the direction of the coordinates related to the shape to be adopted by the metal.

OCTAHEDRAL FIELD

Before the resultant effect of the field around a metal centre generated by the ligands can be illustrated, it is important to have an understanding of the shapes and orientations of the d orbitals of the metal. The set of 5 d -orbitals are shown below. In free gaseous metal ion, the 5 orbitals are degenerate (of equal energy). The 5 orbitals remain degenerate in a spherical electrostatic field with a higher energy since all will be equally raised by the same amount. An octahedral complex can be considered as a metal ion approached by six ligands along the x , y and z axes. When six ligands surround the metal ion, the degeneracy of the d orbitals is lost because three of the orbitals; d_{xy} , d_{yz} and d_{xz} orbitals, are directed *between* the axes while the others, $d_{x^2-y^2}$ and d_z^2 , are directed *along* the axes pointing at the ligands. Therefore, there is greater repulsion between the electrons in orbitals on the ligands and the $d_{x^2-y^2}$ and the d_z^2 orbitals than there is toward the d_{xy} , d_{yz} and d_{xz} orbitals. Because of the electrostatic field produced by the ligands, all of the d orbitals are raised in energy, but two of them are raised more than the other three.



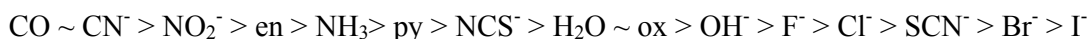
The two orbitals of higher energy are designated as the e_g orbitals, and the three orbitals of lower energy make up the t_{2g} orbitals. The “g” subscript implies being symmetrical with respect to a centre that is present in a structure that has octahedral symmetry. The “t” refers to a triply degenerate set of orbitals, whereas “e” refers to a set that is doubly degenerate. The energy separating the two groups of orbitals is called the crystal splitting, Δ_0 . Splitting of the energies of the d orbitals occurs in such a way that the overall energy remains unchanged and the “center of energy” (barycentre) is maintained. The e_g orbitals are raised 1.5 times as much as the t_{2g} orbitals are lowered from the center of energy. Although the splitting of the d orbitals in an octahedral field is represented as Δ_0 , it is also sometimes represented as $10 Dq$, where Dq is an energy unit for a particular complex. The two orbitals of the e_g , are raised by $3/5\Delta_0$ or $6Dq$ while the t_{2g} orbitals are lowered by $2/5\Delta_0$ or $4dq$ relative to barycentre. The crystal splitting (Δ_0) determines the energy required for an electron to be promoted from the lower energy level or orbital to the higher energy level. Δ_0 depends on the nature of the Ligand the stronger higher the electrostatic force generated by the approach of the ligand the greater Δ_0 . For electron to be promoted to a higher energy level, it must absorb light energy with wavelength equivalent to Δ_0 .

The effect of crystal field splitting is easily observed by studying the absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ since Ti^{3+} ion has $3d^1$ outer electronic configuration. In the octahedral field generated by the six H_2O , the 3d orbitals split in energy. The only transition possible is promotion of the electron from an orbital in the t_{2g} set to one in the e_g set. This transition shows a single absorption band, the maximum of which corresponds directly to the energy represented as Δ_o . As expected, the spectrum shows a single, broad band that is centred at $20,300 \text{ cm}^{-1}$. This energy (243 kJmol^{-1}) is large enough to cause other effects when a metal ion is surrounded by six ligands. However, only for a single electron system is the interpretation of the spectrum simple. With multiple electrons in the d-orbitals, the electrons interact by spin-orbit coupling leading to complication in the interpretation of the spectra.

SPECTROCHEMICAL SERIES

LIGAND SERIES

If several complexes of the same metal ion and the same coordination number are prepared using different ligands, the positions of the absorption bands will be shifted to higher or lower wave numbers depending on the nature of the ligand. In this manner, it is possible to arrange ligands according to their ligand field splitting capacity. The series of ligands arranged this way is called as the spectrochemical series of the ligands.



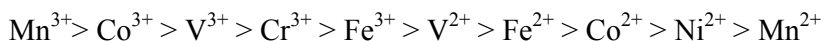
Strong field

Weak field

Differences between the splitting produced by adjacent members in the series are small, and the order is approximate in some cases ($[\text{Fe}(\text{H}_2\text{O})_6]^{3+} = 14,000 \text{ cm}^{-1}$ and in $[\text{Fe}(\text{ox})_3]^{3-} = 14,140 \text{ cm}^{-1}$), especially when different metal ions or metal ions in different rows of the periodic table are considered. For example, the order of the halide ions is changed if the metal ion is from the second transition series. The spectrochemical series is a very useful guide because reversals between rather widely separated members such as NO_2^- and NH_3 do not take place. Ligands that force electron pairing are known as strong field ligands, and these ligands can be expected to give low-spin octahedral complexes with first-row metal ions. Weak field ligands are known to give high-spin octahedral complexes with first-row metal ions.

METAL ION SERIES

It is possible to range metal ions in terms of the splitting of the d orbitals produced by a given ligand and stereochemistry. The arrangement which is independent of the nature of the ligand is called spectrochemical series of the metal ions. From the series, it can be observed that the higher the oxidation state the greater the splitting. For first-row metal ions the arrangement is

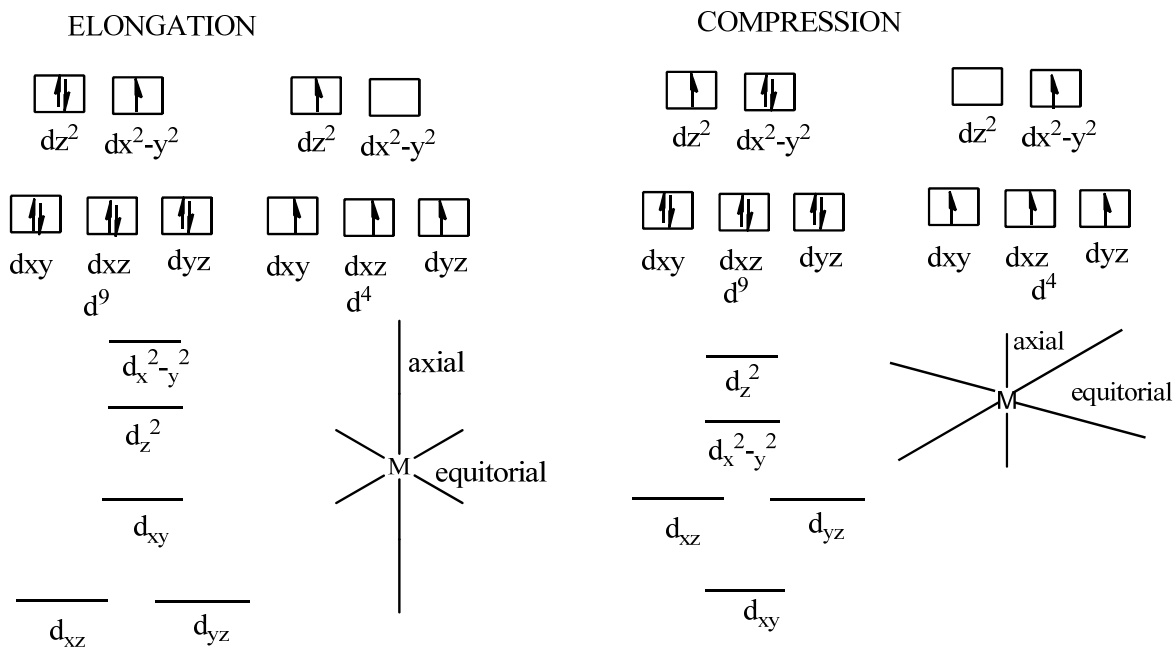


Δ_o for Octahedral Complexes of First-Row Transition Metal Ions (cm^{-1})				
METAL ION	LIGANDS			
	F^-	H_2O	NH_3	CN^-
Co^{3+}	-	20, 800	22, 900	33, 000
V^{3+}	16, 100	18, 500	-	26, 600
Cr^{3+}	15, 100	17, 900	21, 600	26, 600
Fe^{3+}	14, 000	14, 000	-	-

JAHN TELLER DISTORTIONS

Jahn Teller theory states that any non linear molecular system in a degenerate electronic state will be unstable and will undergo some sort of geometrical distortion to lower its symmetry and remove the degeneracy. Distortion is inevitable if there is unsymmetrical occupation of degenerate orbitals. Metal ions with d^9 (Cu^{2+}) and d^4 (Cr^{2+}) high spin in octahedral field are known to have distorted octahedral shapes due to unequal number of electrons occupying the e_g orbitals. With nine electrons, the two orbitals of e_g cannot contain the same number of electrons, there will be two electrons in one orbital and one electron in the other. The orbital with two electrons will have greater repulsion for ligands on its axis compare to the orbital with one electron. Therefore, all the ligand-metal bond length will not be equal hence distortion occurs in the complex. If the orbital with the greater number of electron is d_z^2 , the ligands along the z-axis will not be as close to the metal centre as others. The ligands in d_z^2 direction will have longer ligand-metal bond length. This will result in elongation distortion. If the $d_x^2 - y^2$ contains greater number of electron compare to d_z^2 in an octahedral field, the ligands along the x and y plane will experience greater repulsion leading to increase in length of the ligands along the equatorial region.

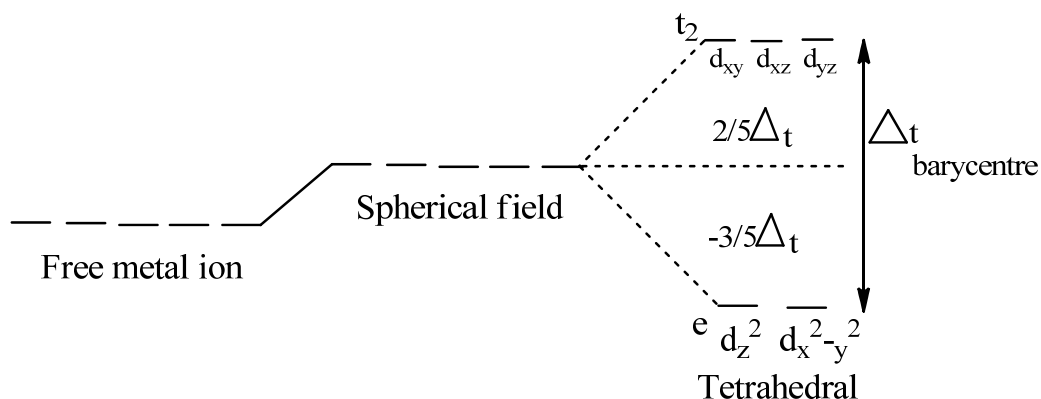
The d^9 configuration is not the only one for which distortion leads to a lower energy. The d^4 high-spin configuration will have one electron in every of the four lowest-lying orbitals with an energy that is lower as a result of splitting the $d_{x^2-y^2}$ and d_z^2 orbitals. The Cr^{2+} ion has d^4 configuration, distortion is expected to occur for complexes of this ion, and this is indeed the case. Similarly, a distortion would be predicted for a d^1 or d^2 ion, for which the electrons would be located in the two orbitals of lowest energy. However, the magnitude of splitting in t_{2g} is much smaller than that of e_g because the orbitals involved are directed between the axes, not at the ligands. These are nonbonding orbitals, so the effect of moving the ligands on the z axis farther from the metal ion is much smaller. The result is that any distortion involving metals with these configurations is very small. This type of distortion is called compression. Distortion is also possible in tetrahedral complexes but not as pronounced as in octahedral complexes.



TETRAHEDRAL FIELD

It is important to note that not all complexes are octahedral or even have six ligands bonded to the metal ion. Therefore there is need to study behaviour of other possible crystal fields. Many complexes are known to have tetrahedral symmetry hence, the need to determine the effect of a tetrahedral field on the d orbitals. In a tetrahedral field, none of the metal's d orbitals point exactly in the direction of the ligands rather they are in between the ligands in

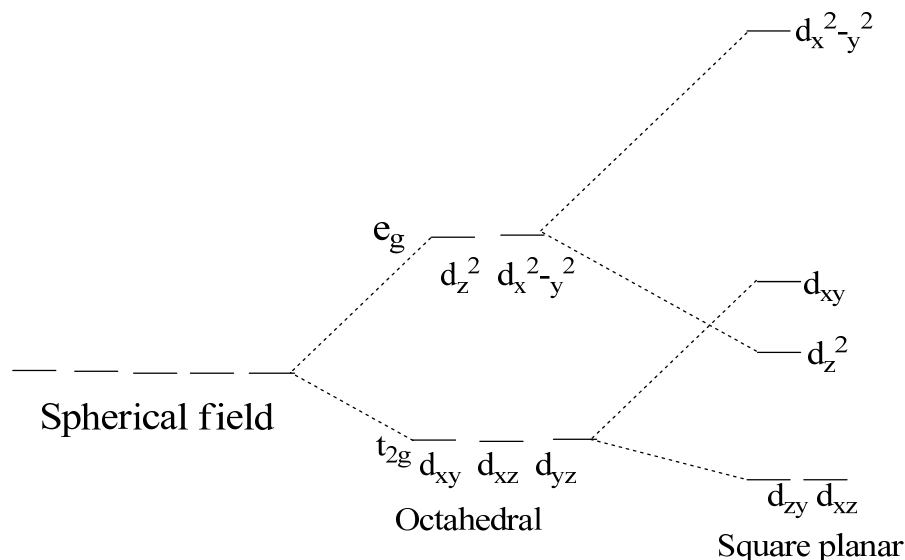
the crystal field. However, the triply degenerate orbitals (d_{xy} , d_{yz} and d_{xz}) are closer to the ligands' path on approaching the metal centre than the doubly degenerate orbitals ($d_{x^2-y^2}$ and d_z^2). The result is that the d_{xy} , d_{yz} and d_{xz} orbitals are higher in energy than are the $d_{x^2-y^2}$ and d_z^2 orbitals because of the difference in how close they are to the ligands. In a simple language, the splitting pattern produced by a tetrahedral field is an inversion of an octahedral field's splitting pattern. The magnitude of the splitting in a tetrahedral field is designated as Δ_t . There are differences between the splitting in octahedral and tetrahedral fields. The two sets of orbitals are inverted in energy and the splitting in the tetrahedral field is much smaller than that produced by an octahedral field. Reasons; there are only four ligands producing the field rather than the six ligands in the octahedral complex, none of the d orbitals point directly at the ligands in the tetrahedral field and in an octahedral complex, two of the orbitals point directly toward the ligands and three point between them. This results in a maximum energy splitting of the d orbitals in an octahedral field. In fact, it can be shown that if identical ligands are present in the complexes and the metal-to-ligand distances are related, $\Delta_t = (4/9) \Delta_o$. This difference in energy value explain the reason why tetrahedral complexes are rare or simply put do not exist because the splitting of the d orbitals is not large enough to force electron pairing. Also, because there are only four ligands surrounding the metal ion in a tetrahedral field, the energy of all of the d orbitals is raised less than they are in an octahedral complex. No symmetry symbol is required to describe the bond in tetrahedral field because there is no centre of symmetry in a tetrahedral structure.



SQUARE PLANAR COMPLEX

A square planar arrangement of ligands can be obtained from octahedral model by removal of the two ligands point directly along the z axis. This will result in decrease in repulsion experienced along the z-axis and orbitals with z component will experience decrease in

energy and greater stability. The energy of d_z^2 , d_{xz} and d_{yz} will be reduced while those of $d_x^2-y^2$ and d_{xy} will increase. The orbital arrangement in square planar complex is shown below. Metal ions with d^8 (Ni^{2+} , Pt^{2+} and Pd^{2+}) configuration are known to form square planar complexes which are diamagnetic in nature resulting from relatively large difference in energy of d_{xy} and $d_x^2-y^2$ forcing the electrons to pair in orbital of lower energy level.



FACTORS AFFECTING CRYSTAL FIELD SPLITTING

- i. The nature of the ligands- the smaller the size of the anions the greater the splitting. This can be observed with the halides $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. Similarly, ligands with ability to form π -bond cause greater splitting. $\text{Co} > \text{CN}^- > \text{phen} > \text{NO}_2^-$.
- ii. The higher the oxidation state or the primary valence of the metal the greater the splitting. Generally, M^{3+} ions cause greater splitting than M^{2+} ions.
- iii. The type of d-orbital involved in the bonding scheme, the splitting pattern in 5d is the greatest because it spread more into space than others. The observed trend is $3d < 4d < 5d$ e.g. $[\text{Co}(\text{H}_2\text{O})_6]^{3+} = 20,800 \text{ cm}^{-1}$ and $[\text{Rh}(\text{H}_2\text{O})_6]^{3+} = 27,200 \text{ cm}^{-1}$

LIMITATION OF CRYSTAL FIELD THEORY (CFT)

Although crystal field theory provides insight to spectra and magnetic properties of complexes through the concept of strong and weak field ligands, it cannot account for the position of these ligands on the spectrochemical series and it cannot also explain the reason why some degree of covalency is observed in a number of complexes.

3.3 LIGAND FIELD THEORY AND MOLECULAR ORBITAL THEORY

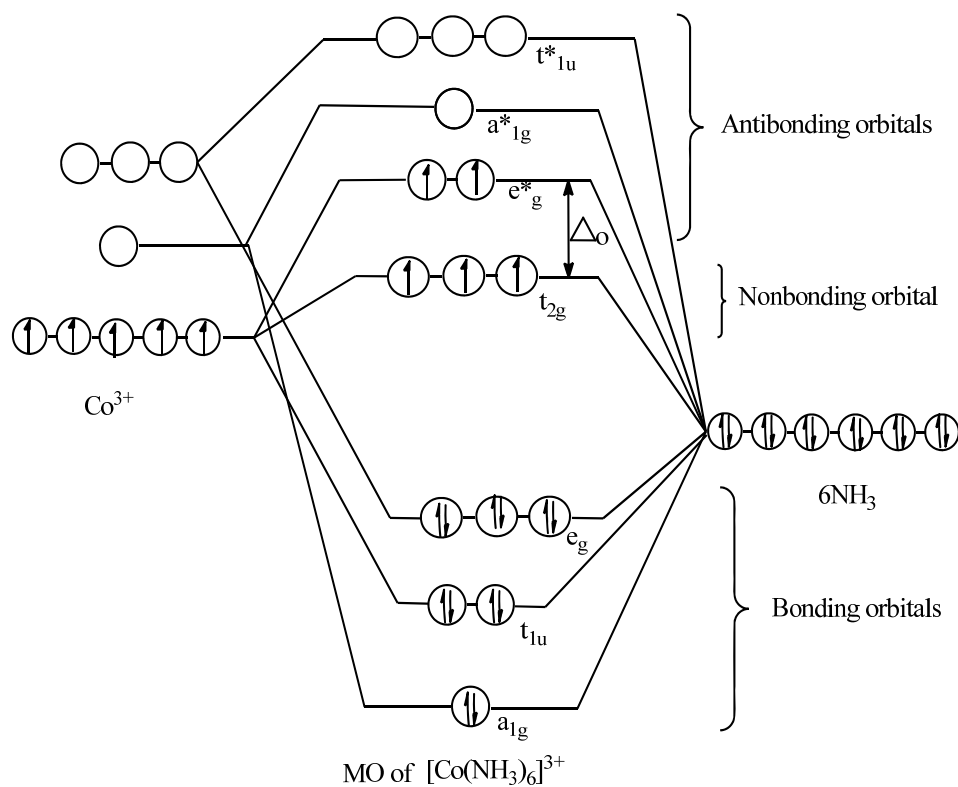
The crystal field theory is modified to take into account the existence of some degree of covalence in transition complexes based on the evidence from electron spin resonance spectra which shows that certain percentage of the electrons is diffused into the ligand orbital. Consequently, the bond existing in complexes is not purely electrostatic. The modification of CFT results into Adjusted Crystal Field Theory also called Ligand Field theory (LFT). If the degree of diffusion or overlap is in excess, the LFT will not hold rather a pure covalent treatment will be suitable hence the use of Molecular Orbital theory (MOT). The LFT can be considered as a mid-point between electrostatic and covalent description of bonding in metal complexes. The LFT is purely a parameter based model involving the uses of experimentally derived data or parameters like Crystal field stabilization energy, Racah parameters which are derived from electronic spectra of complexes.

Molecular Orbital Theory is the result of overlap of bonding atomic orbital of the ligands and the hybridized orbital of the metal leading to formation of both bonding and antibonding molecular orbitals. In a molecular bonding scheme, the numbers of bonding and antibonding orbitals are equal but the antibonding orbitals canceled out the resultant effect of the bonding orbitals.

Molecular Orbital Theory in an octahedral complex can be illustrated with complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ in which metal–ligand σ -bonding is dominant. In the construction of an molecular orbital energy level diagram for such a complex, many approximations are made and the outcome is considered to be qualitatively accurate. Despite this, the results provide useful explanation on metal–ligand bonding.

Cr^{3+} is a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p. in octahedral symmetry the s orbital has a_{1g} symmetry, the p orbitals are degenerate with t_{1u} symmetry, and the d orbitals split into two sets with e_g (d_z^2 and $d_x^2 - y^2$) and t_{2g} (d_{xy} , d_{yz} and d_{xz}) symmetries. Each ligand, NH_3 , provides one orbital. Six orbitals from the ligands are assigned a_{1g} , t_{1u} and e_g symmetries. The nine valence orbitals of the metal are grouped into bonding and non-bonding orbitals the bonding orbitals are; 4s, $3p_x$, $3p_y$, $3p_z$, $d_x^2 - y^2$ and d_z^2 which are in the direction of the approaching hence suitable for overlapping. The t_{2g} set (d_{xy} , d_{xz} , d_{yz}) which are not exactly in the direction of the approaching ligands are considered non-bonding. The diagram below shows the Molecular orbital arrangement for the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$. The six ligand orbitals and six orbitals of the metal are grouped into six bonding molecular orbitals and six antibonding molecular orbitals, while t_{2g} orbitals are left as nonbonding

molecular orbitals. Electrons from the ligands are filled into the bonding orbitals while the d electrons are filled into nonbonding t_{2g} orbitals and Lowest unoccupied Molecular Orbital (LUMO) which are the antibonding orbitals representing the e_g set of the metal d orbitals.

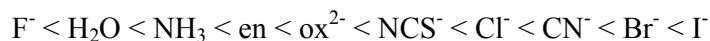


THE NEPHELAUXETIC EFFECT

A metal ion surrounded by ligands in a complex will experience changes in the total electron environment of the metal ion when compared to the environment in the uncomplexed metal ion due to the coordinated ligands. One consequence is that the energy required to pair up electrons will be altered. Although the energy necessary to pair up electrons in a free metal ion can be easily estimated from the appropriate spectroscopic data, this is not applicable to a metal ion that is contained in a complex. When ligands bind to a metal ion, the orbitals on the metal ion are spread out over a larger region of space and extend to the orbitals of the ligand. In molecular orbital terminology, the d-orbital electrons of the metal ion become more delocalized in the complex than they are in the free ion. This expansion of the electron cloud is called the nephelauxetic effect. As a result of the nephelauxetic effect, the energy required to pair up electrons in the metal ion is somewhat smaller than it is for the free ion. When

ligands such as CN^- , CO and NO_2^- are present, the nephelauxetic effect is quite large owing to the ability of the ligands to π bond to the metal as a result of back donation.

For complexes with a common metal ion, it is found that the nephelauxetic effect of ligands varies according to a series independent of metal ion:



A nephelauxetic series for metal ions independent of ligands is:



4.0 CONCLUSION

The bonding theories in coordination chemistry provide insight to properties of transition metal complexes. Valence Bond Theory explains the shape and predicts magnetic properties of complexes based on hybridised orbitals of the metals but fails to explain the colour and spectra properties of metal complexes. Crystal Field Theory is a very important model that explains the spectra properties of complexes based on electrostatic treatment of the bonding mode in complexes. Ligand Field and Molecular Orbital theory provide information on how some degree of covalence exists within complexes contrary to the pure electrostatic treatment of CFT.

5.0 SUMMARY

From bonding theories in coordination chemistry the following deductions can be made:

- The shape of complex is determined by coordination number, hybridization and type of atomic orbitals of the metal hybridised.
- With concept of inner and outer orbital complexes, magnetic properties of low and high spin complexes can be predicted
- Electrostatic treatment of bonding in complexes provides information on colour and spectra of complexes.
- The Ligand Field and Molecular Orbital theories help to explain the concept of covalence observed in some complexes
- With the same metal and stereochemistry, ligands can be arranged based on their ability to cause crystal field splitting, which gives rise to spectrochemical series of the ligand. Similarly, a spectrochemical series is observed with metal ions when the same ligand and stereochemistry are employed.

- On complexation the pairing energy of the metal ion is less than that in free metal ion. This is due to the influence of the ligand resulting into the Nephelauxetic effect.

6.0 TUTOR-MARKED ASSIGNMENT (TMA)

1. The complexes $[\text{NiCl}_2(\text{PPh}_3)_2]$ and $[\text{PdCl}_2(\text{PPh}_3)_2]$ are paramagnetic and diamagnetic respectively. What is the implication of these magnetic properties about their structures?
2. The anion $[\text{Ni}(\text{SPh}_4)]^{2-}$ is tetrahedral. Explain why it is paramagnetic.
3. For each of the following complexes, give the hybrid orbital type and the number of unpaired electrons: $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{PdCl}_4]^{2-}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{NO}_2)_6]^{3-}$
4. Which of the following complexes would undergo Jahn-Teller distortion?
(a) $[\text{Fe}(\text{Cl}_6)^{3-}]$, (b) $[\text{MnCl}_6]^{3-}$, (c) $[\text{CuCl}_6]^{4-}$, (d) $[\text{CrCl}_6]^{3-}$, (e) $[\text{VCl}_6]^{4-}$
5. Draw the molecular orbital diagram of $[\text{CoF}_6]^{3-}$ and $[\text{MnCl}_6]^{3-}$
6. State five factors which influence crystal field splitting in coordination compounds

7.0 REFERENCES/FURTHER READINGS

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MODULE 3

UNIT 1: PHYSICAL METHODS OF STRUCTURAL INVESTIGATION

Unit 1: Table of Contents

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2.0 Objectives

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1.0 INTRODUCTION

In simple language, physical methods of structural investigation are processes of acquiring information about a newly synthesized complex. Much of what we know today about properties of complexes comes from physical methods of structural investigation. Working at the atomic and molecular level, physical methods of structural investigation involves the application of an array of physical methods which can provide information on the complex under investigation. Since there are many methods, it is important to know the method most suitable for acquiring the information desired. Once a new complex is synthesized and purified, the first investigation is to know elements that constitute the complex which relates to the chemical composition. The next investigation should be on the shape of the complex, which is a far more complex involving defining what components are involved and how they are assembled together.

Synthesis and purification of complexes may be difficult; the processes involved in structural investigation are more complex and multi-tasking. Defining molecular structure in both

solution and the solid state requires a wide range of physical methods for characterization. Quite a number of physical methods have been employed to study properties of metal complexes in order to provide information on molecular structure and reactivity. Characterization in metal complexes includes isolating a complex in the solid state. This process is difficult and may be complicated if there exist differences in the nature of the complex in solution and the solid state. Physical methods employed in characterization of complexes include; electronic absorption spectroscopy, vibrational spectroscopy, magnetic measurement, conductivity, elemental analysis, thermal analysis, x-ray crystallography, mass spectroscopy, nuclear magnetic resonance, electron spin resonance and others. The list is actually endless as different methods are used for different purposes of investigating properties of complexes. It is therefore important to acquire knowledge on some of these investigative methods.

2.0 OBJECTIVES

At the end of this unit students should be able to:

- State various methods used in structural investigation of complexes
- Explain the principle and use of electronic spectroscopy in structural investigation of complexes
- Explain the principle and use of vibrational spectroscopy in structural investigation of complexes
- Explain the principle and use of magnetic measurement in structural investigation of complexes

3.0 MAIN CONTENT

3.1 METHOD USED IN STRUCTURAL INVESTIGATION OF COMPLEXES

Comprehensive structural investigation of complexes involves many analyses providing different kinds of information on nature and structure of complexes. It is therefore important to know what information can be acquired from each analysis carried out on complexes.

Elemental analysis of a pure complex will provide information on the percentage composition of the various elements (C, H, N and S) that constitute the complex. This will help to predict a suitable formula for the complex. Thermal analysis may be carried out to determine change in mass with temperature. This helps to know the number of waters of crystallization present in complex and also helps to determine the heat stability of the complex.

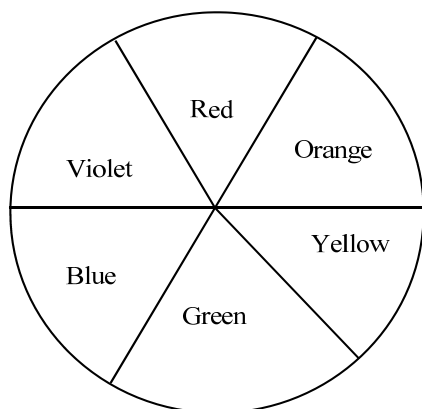
Conductivity measurement helps to distinguish between ionic and neutral complexes. Magnetic properties of complexes are obtained through magnetic measurement. Electronic (UV-VIS) spectroscopy provides information on the geometry of complexes and vibrational spectroscopy helps to determine the possible binding site(s) of ligand to complex. The molecular mass of a complex can be obtained with mass spectroscopy. If a suitable crystal of a complex is available, x-ray crystallography can be used to establish the structure of the complex. Other forms of analyses are also carried out to obtain more information on other properties of complexes.

It is not enough to know the various techniques used in structural investigation of complexes, it is very important to get acquainted to the principles behind some of these analyses to facilitate interpretation and understanding of results obtained from them. This course shall focus on electronic spectroscopy, vibrational spectroscopy and magnetic measurement.

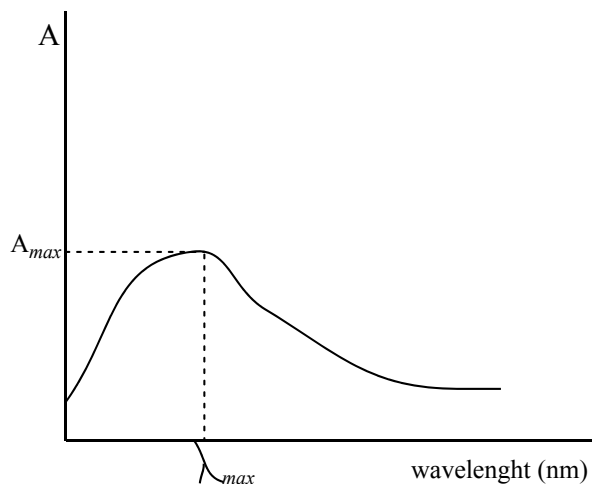
3.2 ELECTRONIC SPECTROSCOPY

One of the notable characteristics of the transition metal ions and their complexes is their colourful appearances. This is attributed to the partial filling of the d-orbitals, which makes them capable of absorbing light energy in the visible region leading to electronic transitions between different energy levels within split d-orbitals. In an electronic transition, an electron is excited from an occupied to an empty orbital. The energy of such transitions normally corresponds to light in the near IR, visible or UV region of the electromagnetic spectrum. In *d*-block complexes various types of electronic transitions are possible depending on the nature of their constituents. Some of these transitions occur within the ligand (intra-ligand transition), within the split d-orbitals (ligand field or d-d transition) and/or between the metal d-orbitals and ligand orbitals (charge transfer transition).

To provide explanation on the colours of complexes, it is necessary to have understanding of complementary colours. When light of a particular colour is absorbed by a complex, the complementary colour to the absorbed colour is observed. For example, when white light (containing a broad spectrum of all visible wavelengths) is allowed to pass through a substance that has capacity to absorb blue light, the substance will appear in orange since the complementary colour of blue is orange. A simple way to remember complementary colour is shown below using colour wheel.



When light intensity I_0 is allowed to pass through a standard solution of a complex in a UV/Visible spectrophotometer, electron(s) in the complex will absorb part of the light and be promoted to a higher energy level while the unabsorbed light with intensity I will be transmitted through the solution. A graph of $\log [I_0/I]$ (Absorbance) can be made against wavelength in nm. This plot is known as the electronic absorption spectrum from which the various absorptions of the compound can be determined. The intensity of the absorption (molar absorptivity (ϵ)) can also be determined using Beer-Lambert Law, mathematically expressed as; $\epsilon = A/lc$, A = absorbance, l = path length (cm) through the solution and c = concentration in mol/ dm³. The unit of ϵ is $\frac{L}{mol\ cm}$. It is possible to calculate wave number (ν) in cm⁻¹ equivalent to the wave length (λ) using the expression: $\nu = 1/\lambda$. With high ϵ , complexes are intensely coloured and appear very bright.



An example of Electronic Absorption Spectrum

TRANSITIONS IN COMPLEXES

Transitions in complexes can be grouped into three categories; intraligand transitions, ligand field transitions and charge transfer transitions.

INTRALIGAND TRANSITIONS

These are transitions that depend on the nature of the chromophores (group of atoms capable of absorbing light energy) present in the ligands. These chromophores include organic functional groups such as alkenes, aromatic hydrocarbons, heterocyclic compounds, amines, alcohols and ethers.

$n \rightarrow \sigma^*$ transition: - In saturated molecules that containing heteroatoms with nonbonding lone pairs of electrons, the transition of the lowest energy will be $n \rightarrow \sigma^*$. This is possible because both the bonding and nonbonding orbitals are filled with electron and the highest occupied molecular orbital (HOMO) is the nonbonding orbital n while the lowest unoccupied molecular orbital (LUMO) is antibonding σ^* . Examples of ligands with this transition are; amines, alcohols, ammonia, water and ethers.

$n \rightarrow \pi^*$ transition: - this is possible in ligands with both nonbonding and π bonding molecular orbitals. In such a ligand, the HOMO will be n , LUMO will be π^* and transition with the lowest energy will be $n \rightarrow \pi^*$. Examples of such ligands are aldehydes (R-CHO), ketones (R-CO-R), esters (RCOOR), amides (RCONH₂) and carboxylic acids (RCOOH).

$\pi \rightarrow \pi^*$ transition: - ligands containing double double bonds or triple bonds without any heteroatom will have transition of lowest possible energy to be $\pi \rightarrow \pi^*$. Examples are olefins, conjugated dienes and aromatic hydrocarbons.

Unsaturated heterocyclic compounds (such as 1, 10-phenanthroline, 2, 2'-bipyridine and pyridine, multiple transitions) have different transitions including; $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$. The ligand transitions are often in the ultra violet range of the spectrum but with extended conjugations, some transitions in the visible regions will be inevitable.

CHARGE TRANSFER TRANSITIONS

Electron can be excited from a metal orbital to ligand orbital in a transition complex. This is made possible when, the metal has electron in t_{2g} orbitals (which are nonbonding orbitals) and

the ligand has suitable empty orbitals (π^*). The transition of electron in this process will lead to decrease in electron density around the metal centre (oxidation). This transition is called Metal to Ligand Charge Transfer (MLCT) transition commonly found in complexes with metal ion in low oxidation state, which can be easily oxidised. Examples are complexes of Ti^{3+} and Cu^+ . Generally, Charge Transfer (CT) transitions are more intense and may likely mask $d-d$ transitions though they occur at higher wave number usually above $40,000\text{cm}^{-1}$ with molar absorptivity above $10,000\text{ L mol}^{-1}\text{ cm}^{-1}$. This is because the CT transitions are spin-allowed and Laporte-allowed. However, $d-d$ transitions are only spin-allowed.

What can be tagged the reverse of MLCT is Ligand to Metal Charge Transfer (LMCT) where electron density is transferred to the metal, which is therefore reduced in the excited state. The higher the oxidation state of the metal concerned, the easier such reduction will be, and so the lower the LMCT energy. LMCT transitions in the visible region of the spectrum give intense colour, as is found with permanganate (MnO_4^-) a d^0 complex, in which no $d-d$ transition is expected. Other examples are: TiF_6^{2-} , CrO_4^{2-} and TcO_4^- .

In a complex with two metal ions in different oxidation state, there may be transfer of electron from orbital of metal in lower oxidation state to that in higher oxidation state. This transition is called Metal to Metal Charge Transfer and it can be observed in $\text{KFe}[\text{Fe}(\text{SCN})_6]$ and $[[\text{Au}^{\text{III}}\text{Cl}_4][\text{Au}^{\text{I}}\text{Cl}_2]]^{2-}$.

3.3 LIGAND FIELD SPECTRA ($d-d$ TRANSITION)

Ligand field spectra results from the transition within metal d -orbitals which have been split due to the ligand field on coordination. They are also called $d-d$ transitions because they occur within d -orbitals. For proper understanding of $d-d$ transitions, knowledge of interactions between electrons in the d -orbitals is highly essential. An electron in a given atom has a set of four quantum numbers; the principal (n), the subsidiary (l), the magnetic (m) and the spin quantum numbers. Interaction can occur between spin angular momentum and orbital angular momentum of the single electron. However, if two or more unpaired electrons are present with an atom, three different interactions are possible between the angular momenta; spin-spin, orbit-orbit and spin-orbit interactions. The angular momenta are vector quantities that interact (couple) in accord with quantum-mechanical rules. In spin-spin coupling schemes, the spin angular momenta of the electrons couple to give an overall resultant spin (S). Similarly, the orbital angular momenta of the electrons couple to give an

overall resultant orbital angular momentum (L). The resulting vector quantities (S and L) couple to give the total angular momentum vector (J) for the atom.

Coupling occurs by this scheme, which is known as L - S or Russell-Saunders coupling. The coupling scheme can be expressed as;

$S = \sum s_i = s_1 + s_2, s_1 + s_2 - 1, \dots, s_1 - s_2$, where S represents vector sum of the resultant spin angular momenta and s_i represents the spin of the individual electron.

$L = \sum l_i = l_1 + l_2, l_1 + l_2 - 1, \dots, l_1 - l_2$, where L represents vector sum of the resultant orbital angular momenta and l_i represents the orbital angular momentum of the individual electron.

$J = L + S = L + S, L + S - 1, \dots, L - S$, where J represents vector sum of the resultant orbital and spin angular momenta.

Under Russell-Saunders coupling, the spin-spin coupling is assumed to be greater than orbit-orbit coupling which is also greater spin-orbit coupling for the first row transition metals.

Examples: for d^1 electronic configuration, $s = +1/2$ and $l = 2$, since only one electron is involved only spin-orbit coupling is applicable. $J = 2 + 1/2, 2 - 1/2$. $J = 5/2$ and $3/2$.

Note that spin of electron is either $-1/2$ or $+1/2$ and atomic orbitals designated as s, p, d , and f have values 0, 1, 2, 3 and 4 respectively.

In a manner similar to that by which the atomic orbitals are designated as s, p, d , or f , the letters S, P, D , and F correspond to the values of 0, 1, 2, and 3, respectively, for the resultant angular momentum vector (L). After the values of the vectors L, S , and J have been determined, the overall angular momentum is described by a symbol known as a term symbol or spectroscopic state. This symbol is constructed as $(2S + 1)L_J$ where the quantity $(2S + 1)$ is known as the multiplicity. For one unpaired electron system $s = +1/2, (2(1/2) + 1) = 2$, and a multiplicity of 2 implies doublet state. Therefore for one unpaired electron system the following are obtained $S = 1/2, L = 2$ and $J = 5/2$ and $3/2$, which give the term symbols $^2D_{5/2}$ and $^2D_{3/2}$.

The spectroscopic terms for d^1 and d^9 are the same as both contain the same number of unpaired electron. Other related d-configurations with the same term symbols can be determined using the expression $d^n = d^{10-n}$.

For d^2 and d^8 configurations, the term symbols can be similarly determined. These are two electron systems $\uparrow \uparrow _ _ _$ with $s_1 = +1/2, s_2 = +1/2, l_1 = 2$ and $l_2 = 2$

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, s_1 - s_2 = 1 \text{ and } 0 \quad L = l_1 + l_2, l_1 + l_2 - 1, \dots, l_1 - l_2 = 4, 3, 2, 1 \text{ and } 0$$

$$J = L + S = L + S, L + S - 1, \dots, L - S, \text{ with } L = 4 \text{ and } S = 1 \quad J = 5, 4, 3 \text{ multiplicity is } 2(1) + 1 = 3$$

Term symbols are ${}^3G_5, {}^3G_4$ and 3G_3 . Other symbols are derived in similar manner;

With $L = 3$ and $S = 1, J = 4, 3, 2$ Term symbols are ${}^3F_4, {}^3F_3$ and 3F_2

With $L = 2$ and $S = 1, J = 3, 2, 1$ Term symbols are ${}^3D_3, {}^3D_2$ and 3D_1

With $L = 1$ and $S = 1, J = 2, 1, 0$ Term symbols are ${}^3P_2, {}^3P_1$ and 3P_0

With $L = 4$ and $S = 0, J = 4$ Term symbols are 1G_4 Note $2(0) + 1 = 1$ singlet state

With $L = 3$ and $S = 0, J = 3$ Term symbols are 1F_3

With $L = 2$ and $S = 0, J = 2$ Term symbols are 1D_2

With $L = 1$ and $S = 0, J = 1$ Term symbols are 1P_1

With $L = 0$ and $S = 0, J = 0$ Term symbols are 1S_0

NOTE: $L; 0, 1, 2, 3, 4, 5$ and 6 have symbols S, P, D, F, G, H and I

Not all the derived terms are allowed by Pauling exclusion principle, which states that no two electrons must have the same values for the four quantum numbers in a given atom, and Hund's rule which states that degenerate states must be singly filled before pairing.

To determine the allowed term symbols, the microstates of the electronic configuration must be generated and then arranged to obtain the derived term symbols. This is a very complex but interesting process that must be carefully studied in order to have indebt knowledge of electronic transition. The microstate for d^1 and d^9 is shown below;

$$S = 1/2, M_S = S, S - 1, \dots, 0, \dots, -S, M_S = +1/2, -1/2. M_S \text{ is possible spin microstate}$$

$$L = 2, M_L = L, L - 1, \dots, 0, \dots, -L, M_L = 2, 1, 0, -1, -2 \quad M_L \text{ is possible orbital microstate.}$$

From the various spin and orbital microstates possible, a table of all the combined microstates

can be generated. The microstates are the possible orientations of the electron that are allowed by the Pauling's and Hund's rules. A microstate is represented with the orbital in which the electron is located with superscript representing the spin of the electron. The total number (N) of microstates for a given d-configuration can be calculated from the expression;

$$N = \frac{(2(2l+1))!}{x!(2(2l+1)-x)!}$$

where l is electronic orbital angular momentum and x is number of unpaired electrons.

For d^1 configuration, $l = 2$, $x = 1$ and $N = \frac{(2(2(2)+1))!}{1!(2(2(2)+1)-1)!} = 10$

	Ms	
	$-\frac{1}{2}$	$\frac{1}{2}$
-2	-2^-	-2^+
-1	-1^-	-1^+
0	0^-	0^+
1	1^-	1^+
2	2^-	2^+

-2 ⁻	—	—	—	—	↓
	2	1	0	-1	-2
-1 ⁻	—	—	—	↓	—
	2	1	0	-1	-2
0 ⁻	—	—	↓	—	—
	2	1	0	-1	-2
1 ⁻	—	↓	—	—	—
	2	1	0	-1	-2
2 ⁻	↓	—	—	—	—
	2	1	0	-1	-2
	down spin (-)				
-2 ⁺	—	—	—	—	↑
	2	1	0	-1	-2
-1 ⁺	—	—	—	↑	—
	2	1	0	-1	-2
0 ⁺	—	—	↑	—	—
	2	1	0	-1	-2
1 ⁺	—	↑	—	—	—
	2	1	0	-1	-2
2 ⁺	↑	—	—	—	—
	2	1	0	-1	-2
	up spin (+)				

$$\frac{{}^3F_2, {}^3F_3, {}^3F_4, {}^3P_0, {}^3P_1, {}^3P_2, {}^1G_4, {}^1D_2, {}^1S_0}{\text{Most stable} \qquad \qquad \qquad \text{least stable}}$$

From the microstates, only 2D term is possible as shown by the coloured microstates. For d^2 and d^8 the highest $L = 4$, $M_L = 4, 3, 2, 1, 0, -1, -2, -3, -4$. The highest $S = 1$, $M_S = 1, 0, -1$

$$N = \frac{(2(2(2)+1))!}{2!(2(2(2)+1)-2)!} = 45$$

note that $l = 2$ and $x = 2$ for d^2 or d^8 .

USEFUL GUIDE FOR MICROSTATES' REPRESENTATION

- I. Ensure that the sum of angular momentum value equals M_L for each row.
- II. Ensure that the sum of spin angular momentum value equals M_S for each column.
- III. Ensure the arrow corresponds to the spin of the microstate; + (\uparrow) and - (\downarrow).
- IV. Ensure Pauling's exclusion principle is obeyed; two electrons in the same orbital must have opposite spins. Such state has no replicate because both electrons are in the same orbital e. g. $+1^+ +1^-$ ($\uparrow\downarrow$) but not $+1^+ +1^+$ ($\uparrow\uparrow$)

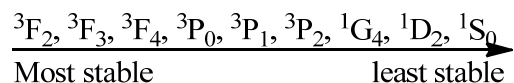
		M _S								
		-1		0				+1		
M _L	-4			↑ ↓ -2 ⁺ -2 ⁻						
	-3	↓ ↓ -1 ⁻ -2 ⁻		↑ ↓ -1 ⁺ -2 ⁻	↓ ↑ -1 ⁻ -2 ⁺			↑ ↑ -1 ⁺ -2 ⁺		
	-2	↓ ↓ 0 ⁻ -2 ⁻		↑ ↓ -2 ⁺ 0 ⁻	↓ ↑ -2 ⁻ 0 ⁺	↑ ↓ -1 ⁺ -1 ⁻		↑ ↑ -2 ⁺ 0 ⁺		
	-1	↓ ↓ 0 ⁻ -1 ⁻	↓ ↓ -2 ⁻ +1 ⁻	↑ ↓ -1 ⁺ 0 ⁻	↓ ↑ -1 ⁻ 0 ⁺	↑ ↓ +1 ⁺ -2 ⁻	↓ ↑ +1 ⁻ -2 ⁺	↑ ↑ -1 ⁺ 0 ⁺	↑ ↑ +1 ⁺ -2 ⁺	
	0	↓ ↓ +1 ⁻ -1 ⁻	↓ ↓ +2 ⁻ -2 ⁻	↑ ↓ +2 ⁺ -2 ⁻	↓ ↑ +2 ⁻ -2 ⁺	↑ ↓ +1 ⁺ -1 ⁻	↓ ↑ +1 ⁻ -1 ⁺	↑ ↓ 0 ⁺ 0 ⁻	↑ ↑ +2 ⁺ -2 ⁺	↑ ↑ -1 ⁺ +1 ⁺
	1	↓ ↓ 0 ⁻ +1 ⁻	↓ ↓ +2 ⁻ -1 ⁻	↑ ↓ +1 ⁺ 0 ⁻	↓ ↑ +1 ⁻ 0 ⁺	↑ ↓ -1 ⁺ +2 ⁻	↓ ↑ -1 ⁻ +2 ⁺		↑ ↑ +1 ⁺ 0 ⁺	↑ ↑ -1 ⁺ +2 ⁺
	2	↓ ↓ 0 ⁻ +2 ⁻		↑ ↓ +2 ⁺ 0 ⁻	↓ ↑ +2 ⁻ 0 ⁺	↑ ↓ +1 ⁺ +1 ⁻			↑ ↑ +2 ⁺ 0 ⁺	
	3	↓ ↓ +1 ⁻ +2 ⁻		↑ ↓ +1 ⁺ +2 ⁻	↓ ↑ +1 ⁻ +2 ⁺				↑ ↑ +1 ⁺ +2 ⁺	
	4			↑ ↓ +2 ⁺ +2 ⁻						

The terms allowed are determined from the table by the numbers of column(s) and row(s); one column represents singlet spin state, two represents doublet spin state, three represents triplet spin state and four quartet spin state. The number of rows represents $M_L = \pm L$ (atomic orbital angular momentum):

NO OF COLUMNS	NO. OF ROWS	TERM SYMBOL
3	± 3	³ F
3	± 1	³ P
1	± 4	¹ G
1	± 2	¹ D
1	0	¹ S

After determination of the allowed term symbols in a free ion, it is necessary to arrange them in order of stability. The state or term with the lowest energy (ground term) is determined by considering the following steps according to Hund's rule.

1. The state with the highest spin multiplicity is considered most stable.
2. If there are two or more states with the same multiplicity, the state with the highest L value is considered most stable.
3. If there are two or more states with the same spin multiplicity and L value, the state with the lowest J (spin-orbit coupling constant) will be most stable for d-configuration (d^1 - d^4), while the state with the highest J will be most stable for d-configuration (d^6 - d^9). An example using d^2 configuration is:



The difference in energy between adjacent levels of J is $(J' + 1) \lambda$, where J' is the lower adjacent J value and λ is the spin-orbit coupling constant e.g. energy difference between 3F_2 and 3F_3 is $(2+1) \lambda = 3 \lambda$. Under the influence of an external magnetic field, the various J states split into $(2J + 1)$ energy levels corresponding to the values the magnetic quantum number M_J can assume i.e. from $J, J-1, \dots, -J$. The splitting is called Zeeman Effect. The separation between the levels is given as $\rho\beta H$ where ρ = Lande's splitting factor, β = Bohr magneton and H = applied magnetic field.

$$\rho = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Example; to calculate ρ for 3F_2 , $S = 1$, $L = 3$, $J = 2$

$$\rho = \frac{3}{2} + \frac{1(1+1) - 3(3+1)}{2 \cdot 2(2+1)} = 0.5$$

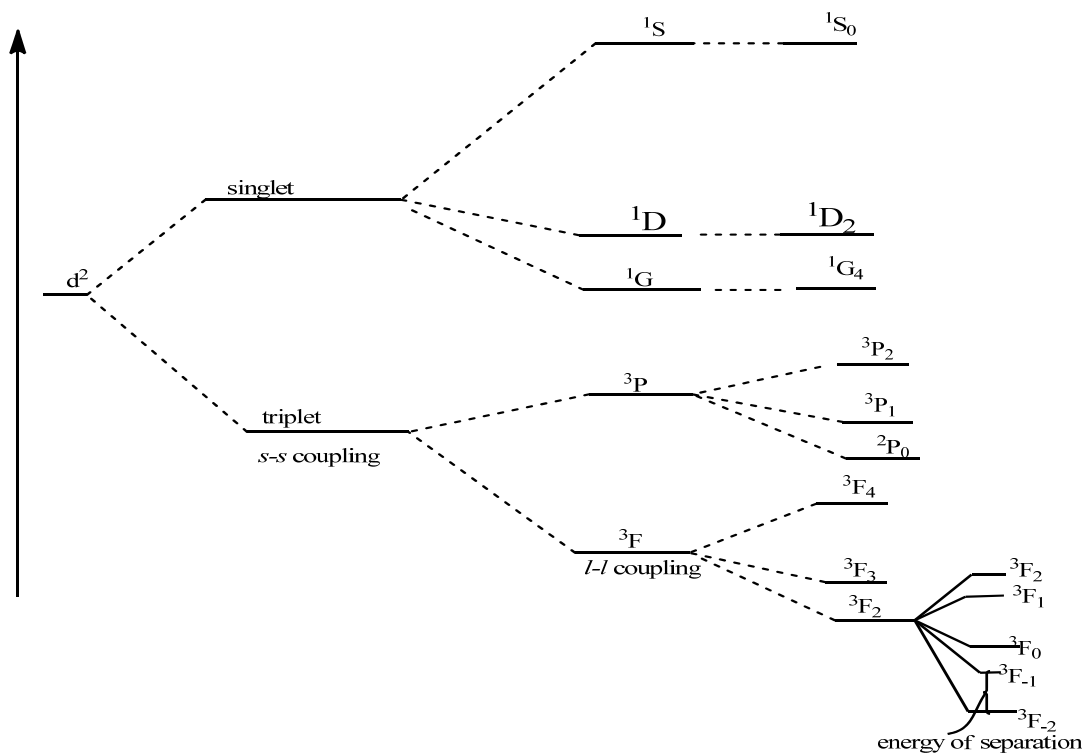


Table below shows the allowed free ion terms for various d^n configuration

d^n, d^{10-n}	No. Unpaired electron	Allowed free ion terms
d^1, d^9	1	2D
d^2, d^8	2	$^3F, ^3P, ^1G, ^1D, ^1S$
d^3, d^7	3	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$
d^4, d^6	4	$^5D, ^3H, ^3G, ^3F(2), ^3D, ^3P(2), ^1I, ^1G(2), ^1D(2), ^1S(2)$
d^5	5	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S$

SPLITTING OF FREE ION TERMS IN OCTAHEDRAL/TETRAHEDRAL FIELDS

Just as the free ions split under the influence of external magnetic fields, the approach of the ligands also splits the free ion terms. The splitting pattern depends on the geometry of the complex. The spectroscopic states are split into components that have the same multiplicity as the free ion states from which they arise. A single electron in a d orbital (d^1 and d^9) gives rise to a 2D term for the free ion (uncoordinated), but in an octahedral field the electron will reside in a t_{2g} orbital, and the spectroscopic state for the t_{2g}^1 configuration is $^2T_{2g}$. If the electron were excited to an e_g orbital, the spectroscopic state would be 2E_g . Thus, transitions between $^2T_{2g}$ and 2E_g states would not be spin forbidden because both states are doublets.

Note that lowercase letters are used to describe orbitals, whereas capital letters describe spectroscopic states.

Term	Splitting in Octahedral	Splitting in tetrahedral	Total degeneracy
S	A_{1g}	A_1	1
P	T_{1g}	T_1	3
D	$T_{2g} + E_g$	$T_2 + E$	5
F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$	7
G	$A_{1g} + E_g + T_{2g} + T_{1g}$	$A_1 + E + T_2 + T_1$	9
H	$E_g + T_{2g} + 2T_{1g}$	$E + T_2 + 2T_1$	11
I	$A_{1g} + A_{2g} + E_g + 2T_{2g} + T_{1g}$	$A_1 + A_2 + E + 2T_2 + T_1$	13

SELECTION RULE

Spin Rule:- states that transitions between states of the same multiplicity are allowed but transitions between states of different multiplicities are not allowed. Examples; transitions between 2T_g and 2E_g , ${}^3T_{1g}$ and ${}^3T_{2g}$ are allowed but transitions between 2T_g and 1E_g , ${}^4T_{1g}$ and ${}^3T_{2g}$ are not allowed or forbidden.

Laporte Rule:- states that transitions between state with $\Delta L = \pm 1$ are allowed but those with change in L greater or less than ± 1 are forbidden. This rule implies change in parity or symmetry of orbital; $g \rightarrow g$ and $u \rightarrow u$ are allowed but $g \rightarrow u$ and $u \rightarrow g$ are not allowed. $s \rightarrow s$, $p \rightarrow p$, $s \rightarrow d$ and $p \rightarrow f$ are not allowed but $s \rightarrow p$, $p \rightarrow d$ and $d \rightarrow f$ are allowed.

MOLAR ABSORPTIVITY (ϵ_{\max})

The molar absorptivity determines the intensity of a given absorption, a band with high ϵ_{\max} will be intensely coloured while those with low ϵ_{\max} will not. The value of ϵ_{\max} depends on the transition. Transitions which are Spin and Laporte allowed have high ϵ_{\max} .

Transition	ϵ_{\max} ($L \text{ mol}^{-1} \text{ cm}^{-1}$)	Examples
Spin-forbidden (and Laporte forbidden)	< 1	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, d^5
Laporte-forbidden (spin allowed)	20 – 100	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, d^1
Laporte-allowed	~ 500	$[\text{NiCl}_4]^{2-}$, d^8
Symmetry allowed (charge transfer)	1000 – 50000	$[\text{MnO}_4]^-$, d^0

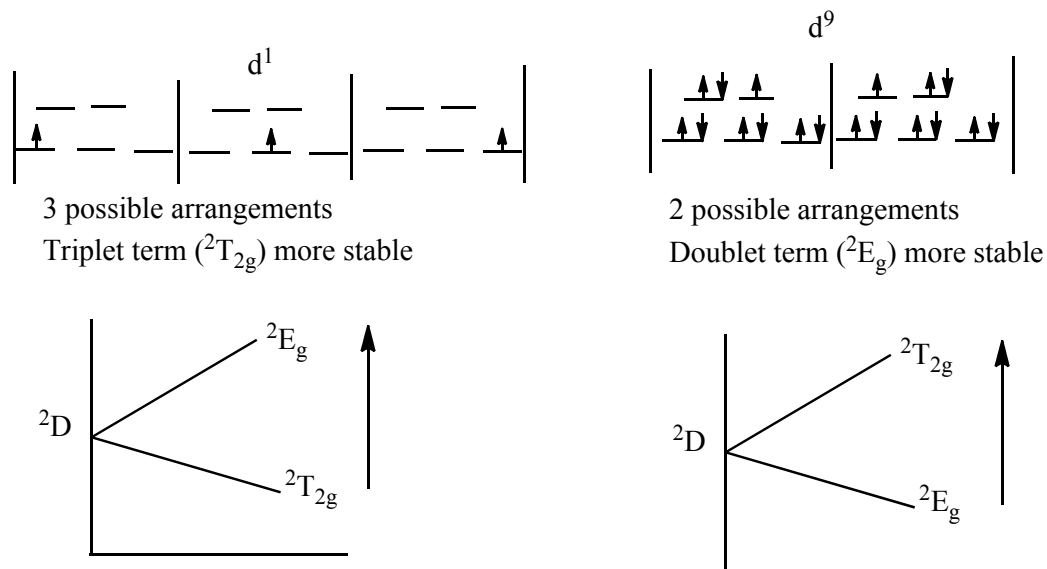
TRANSITIONS IN OCTAHEDRAL FIELD

d^1 and d^9 complexes

d^1 complex example is $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and d^9 complex example is $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, ground term is determined and the split terms arising from the ground term are arranged based on stability (the number of possible arrangements in ground state).

Ground term is 2D for d^1 and d^9

2D splits into 2E_g and ${}^2T_{2g}$ for d^1 and d^9

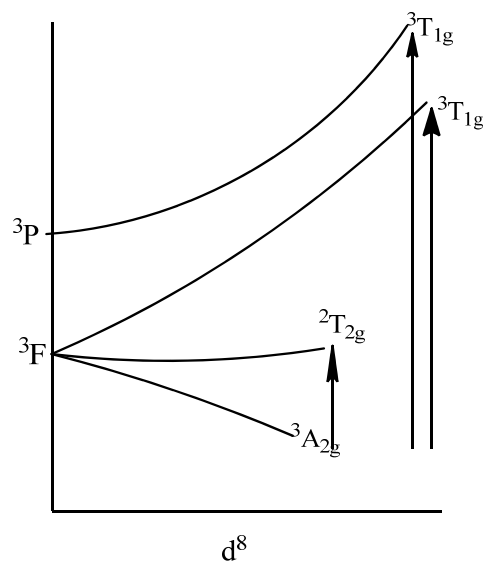
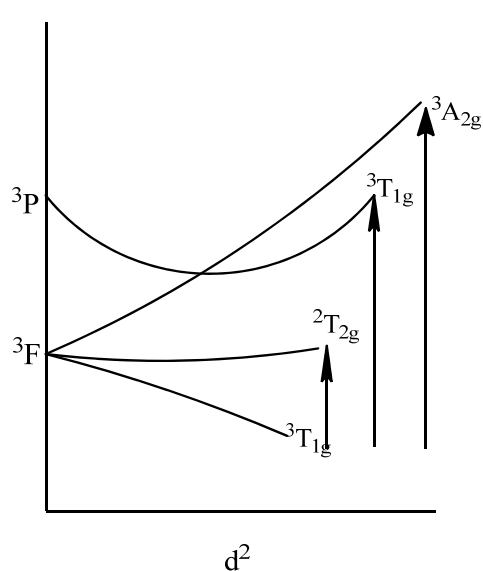
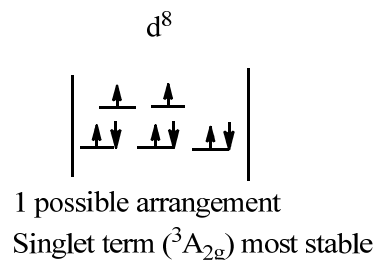
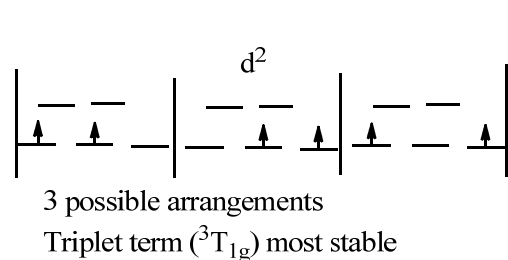


${}^2T_{2g} \rightarrow {}^2E_g = 20,300 \text{ cm}^{-1}$ for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

d^2 and d^8 complexes

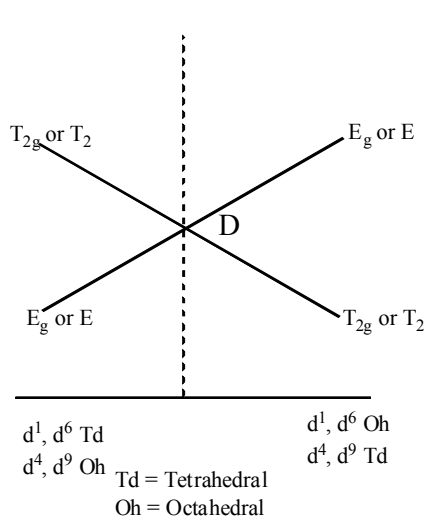
d^2 complex example is $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ and d^8 complex example is $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. Ground term is 3F for d^2 and d^8 with 3P excited state of same multiplicity with ground state.

3F splits into ${}^3A_{2g}$, ${}^3T_{2g}$ and ${}^3T_{1g}$ while 3P gives rise to ${}^3T_{1g}$.

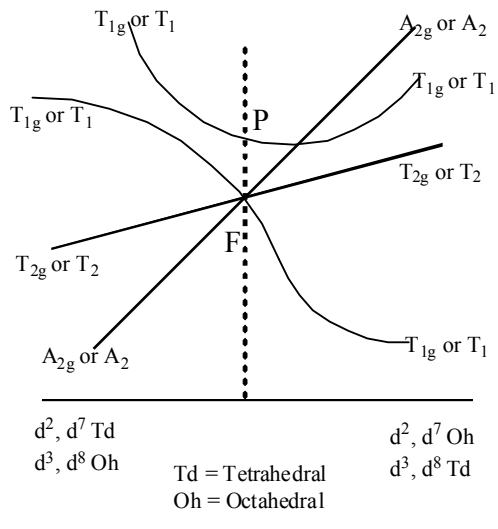


From the splitting pattern in octahedral field, three transitions are possible in d^2 and d^8 complexes. These transitions are observed at specific bands for individual complexes.

In the spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$; ${}^3T_{1g} \rightarrow {}^3T_{2g}$ occurs at $17,800\text{cm}^{-1}$ and ${}^3T_{1g} \rightarrow {}^3T_{1g}(\text{P})$ occurs at $25,700\text{cm}^{-1}$. The third transition ${}^3T_{1g} \rightarrow {}^3A_{2g}$ is weak though of higher energy. In $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the bands are 8500cm^{-1} for ${}^3A_{2g} \rightarrow {}^3T_{2g}$ $13,800\text{cm}^{-1}$ for ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ and $25,300\text{cm}^{-1}$ for ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$. Suitable diagrams in which all the various splitting pattern are well illustrated is established by Orgel.



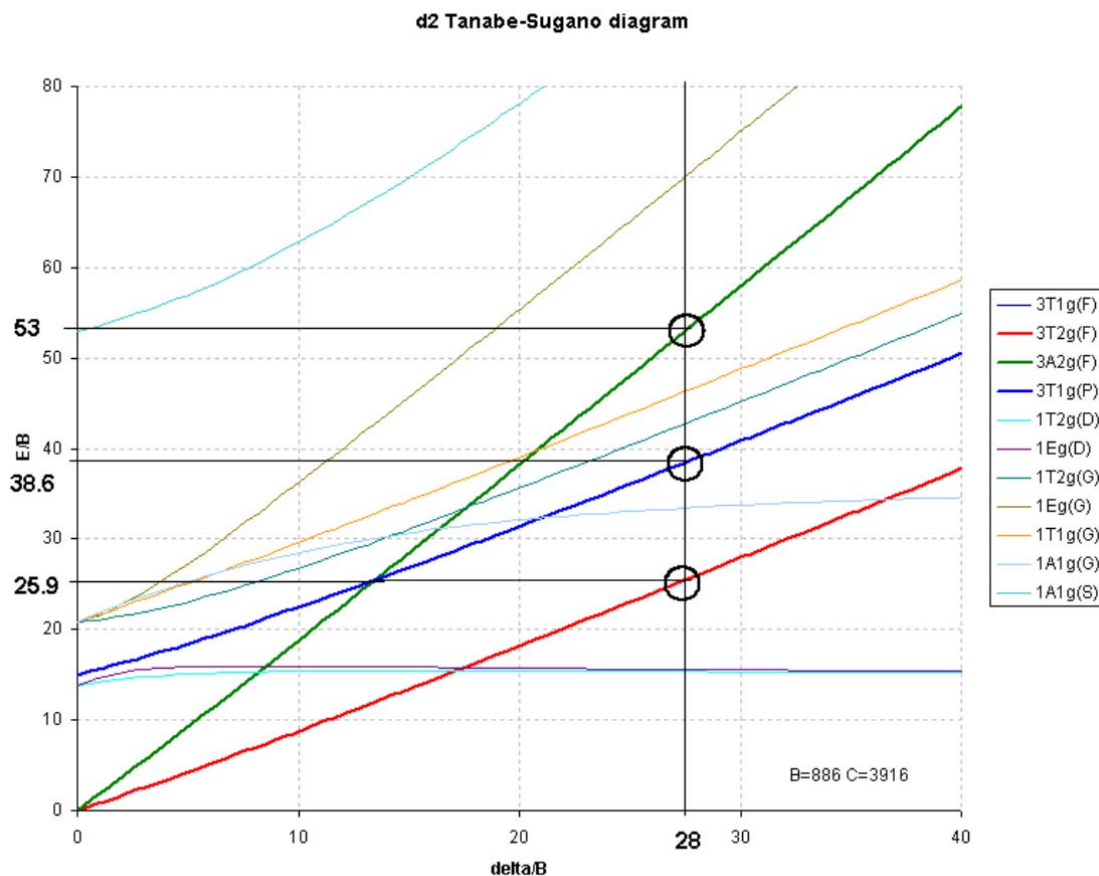
Orgel Diagram for D ground term



Orgel Diagram for F ground term with an excited P term

Tanabe-Sugano Diagrams

Orgel diagrams allows a qualitative description of the spin-allowed electronic transitions expected for states derived from D and F ground terms while Tanabe-Sugano (TS) diagrams give a semi-quantitative approach, including both high and low spin ions. TS diagrams cover both the spin-allowed transitions and the spin-forbidden transitions which are weak and may not likely be observed. TS diagrams are complex in nature but a good understanding of the diagrams is very useful in spectra interpretation. TS diagrams are plots of ratio of energy (E) of transition to Racah parameter B, (E/B), against ratio of Δ_0/B . Different diagrams are available for different d configurations. The TS diagram d^2 is shown in the figure below.



Tanabe-Sugano diagram for the octahedral d^2 case

APPLICATION OF THE TS DIAGRAM

An aqueous solution of the complex $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ shows two absorption bands in the region $17,200 \text{ cm}^{-1}$ and $25,600 \text{ cm}^{-1}$. These bands have been assigned to the first two transition in the complex. With the aid of TS diagram calculate the values of Racah parameter B, octahedral splitting crystal field (Δ_0) and the band for the third transition not observed in the spectrum.

V^{2+} (d^2) has free ion ground term ^3F with an excited ^3P term of the same multiplicity. In Octahedral field, the ^3F will give $^3\text{T}_{1g}$, $^3\text{T}_{2g}$ and $^3\text{A}_{2g}$ while the excited state will give $^3\text{T}_{1g}$. This will give three transitions from the ground term of $^3\text{T}_{1g}$.

$$^3\text{T}_{1g} \rightarrow ^3\text{T}_{2g} \text{ energy of transition } E_1 = 17,200 \text{ cm}^{-1}$$

$$^3\text{T}_{1g} \rightarrow ^3\text{T}_{1g} (\text{P}) \text{ energy of transition } E_2 = 25,600 \text{ cm}^{-1}$$

$$^3\text{T}_{1g} \rightarrow ^3\text{A}_{2g} \text{ energy of transition } E_3 = ?$$

E/B ratio for the given absorptions E_1/B and E_2/B

$$(E_2/B)/(E_1/B) = E_2/E_1 = 25600/17200 = 1.49.$$

Various points on the Δ_0/B axis are tried to locate the corresponding values of E_1/B and E_2/B that will give the ratio 1.49, from which B can be calculated.

When $\Delta_0/B = 28$. The ratio of $(E_2/B)/(E_1/B)$ is 1.49. From the diagram, the following are obtained $E_1/B = 25.9$, $E_2/B = 38.6$ and $E_3/B = 53$

$$E_1/B = 25.9$$

$$17200 \text{ cm}^{-1}/B = 25.9, B = 664 \text{ cm}^{-1}$$

$$E_3/B = 53, E_3 = 53 \times 664 \text{ cm}^{-1} = 35,197 \text{ cm}^{-1}$$

$$\Delta_0/B = 28, \Delta_0 = 28 \times 664 \text{ cm}^{-1} = 18,592 \text{ cm}^{-1}$$

TRANSITIONS IN TETRAHEDRAL FIELD

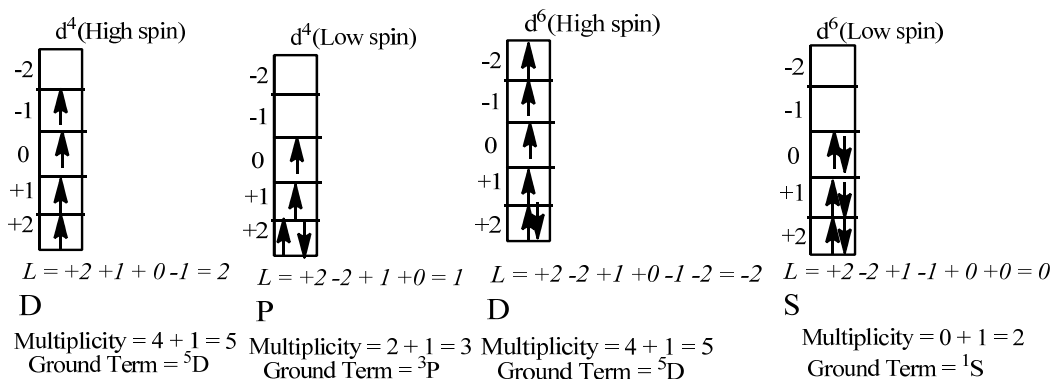
Generally, tetrahedral complexes have more intense absorptions than octahedral complexes.

This is as a result of the absence of a centre of symmetry in tetrahedral complexes which makes transitions between d orbitals more intense than in octahedral complexes. From the Orgel diagrams, the d orbitals for tetrahedral complexes are split in the opposite fashion to octahedral complexes.

Given any d^n configuration the ground term can be easily determined by following these steps

1. Filling the electrons into the five degenerate d-orbitals and calculate the $|L|$ value for the ground term based on the positions of the electrons in the orbitals. The filling must follow Hund's rule and Pauling Exclusion Principle.
2. The multiplicity is obtained as number of unpaired electrons plus one ($n + 1$)

Examples:



3.3 VIBRATIONAL SPECTROSCOPY

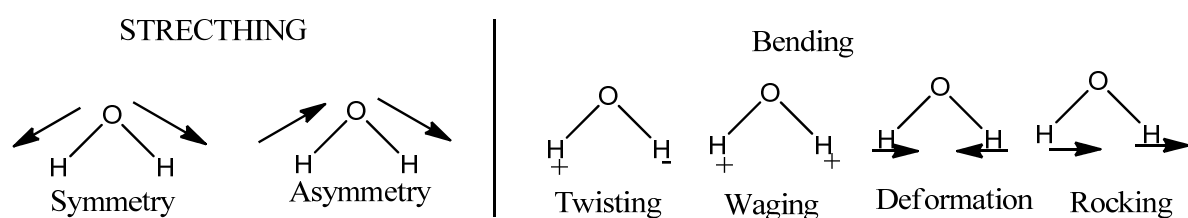
Like the bonds in functional groups of organic compounds, bonds in inorganic compounds produce infrared spectra that can be used in their characterisation. Unlike the bonds in functional groups of organic compounds, the infrared bands for inorganic materials are broader, fewer in number and appear at lower wavenumbers than those observed for organic materials. If an inorganic compound forms covalent bonds within an ion, it can give a characteristic infrared spectrum. The bands in the spectra of ionic or coordination compounds depend on the structures and orientations of the central metal and the ligands. Generally, complexes with organic ligands will have characteristic infrared absorption bands of the functional groups in the ligands. Though as often expected these bands are expected to shift on coordination especially bands that are characteristics of the binding site within the organic ligands. The basic principle of infrared is studied major in organic chemistry but it will be of significance to mention important aspects of this principle as it will provide information on why bonds absorb infrared electromagnetic radiation.

Infrared spectroscopy is an important analytical techniques used to study the nature of bonding in a given chemical compound to determine the various functional groups present. This is made possible as different bonds have different and unique region of infrared absorption. Infrared spectroscopy is one of the best analytical instruments as virtually all forms of samples including inorganic samples can be easily studied on it. Infrared spectroscopy is based on the vibrations of the bonds joining atoms together in a molecule. The product of infrared analysis is the infrared spectrum which is obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy just like in electronic spectroscopy. The peaks in the spectrum are characteristics of the frequencies of absorption of bonds present in the sample analysed. The spectrum is a plot of percentage transmittance against wavenumber expressed in cm^{-1} . With the wavenumber scale, infrared absorptions for all organic compounds (functional groups) occur from 4000 cm^{-1} to 400 cm^{-1} . However, those of ionic compounds like NaCl and KBr have absorption bands at higher wavenumber. In complexes, the bonds between the metal and the binding site in an organic ligand absorb at lower wavenumber.

Only compounds with dipole moment are capable of absorbing infrared energy and are said to be infrared active while molecules without dipole moment are said to be infrared inactive these group of compound are studied using Raman Spectroscopy. Thus molecules like water,

ammonia are active but molecules like O_2 , Cl_2 are inactive to infrared. The dipole moment of an infrared-active molecule changes as the bond expands and contracts. By comparison, an infrared inactive molecule will have its dipole moment remains zero no matter how long the bond vibrates.

The fundamental modes of vibration in compounds are stretching and bending. The stretching can be symmetric or asymmetric while the bending can be wagging, twisting, rocking or deformation. These modes have different regions of infrared absorption. The energy of the stretching mode is usually higher than that of bending mode.



Interpretation of Infrared spectra

After an infrared spectrum has been obtained, it must be interpreted to determine the functional groups present in the sample. Spectrum is not complicated like electronic spectrum in ultra violet/ visible spectroscopy. The various bands in infrared in spectrum have been grouped into what is known as group frequencies. The characteristic group frequencies are far infrared (less than 400cm^{-1}), mid-infrared ($400\text{-}4000\text{cm}^{-1}$) and near infrared ($4000\text{-}13,000\text{cm}^{-1}$) regions.

Far-Infrared Region

The far-infrared region, by definition, has the region between 400 and 100 cm^{-1} . This region is more limited than the mid infrared for spectra–structure characterisation. However, it does provide information regarding the vibrations of molecules of heavy atoms. Intramolecular stretching modes involving heavy atoms can be helpful for characterizing compounds containing halogen atoms, organometallic compounds and inorganic compounds.

Near-Infrared Region

The absorptions in the near-infrared region ($13\ 000\text{--}4000\text{ cm}^{-1}$) are usually overtones or combinations of the fundamental stretching bands which occur in part of the mid infrared region ($3000\text{--}1700\text{ cm}^{-1}$). The bands involved are usually due to C–H, N–H or O–H stretching. The resulting bands in the near infrared are often weak in intensity and the intensity generally decreases by a factor of 10 between adjacent successive overtones. The bands in the near infrared are often overlapped, making them less useful than the mid-infrared region for qualitative analysis.

Mid-Infrared Region

The mid-infrared spectrum ($4000\text{--}400\text{ cm}^{-1}$) is broadly grouped into four regions and the character of a group frequency can be determined by the region in which it is localized. The regions are: the region of absorption for bond between hydrogen and heteroatom (O–H, C–H, N–H) stretching region ($4000\text{--}2500\text{ cm}^{-1}$), the triple-bonds ($\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$) region ($2500\text{--}2000\text{ cm}^{-1}$), the double-bond ($\text{C}=\text{C}$, $\text{C}=\text{N}$, $\text{C}=\text{O}$) region ($2000\text{--}1500\text{ cm}^{-1}$) and the fingerprint (characteristic of the molecule being analysed) region ($1500\text{--}600\text{ cm}^{-1}$). For the fundamental vibrations in the $4000\text{--}2500\text{ cm}^{-1}$ region, O–H stretching gives broad band that occurs in the range $3700\text{--}3600\text{ cm}^{-1}$. N–H stretching is found in the narrow range $3400\text{--}3300\text{ cm}^{-1}$ with sharper absorption than O–H stretching and can be easily differentiated, with NH_2 , resonance occurs and two close sharp bands are seen instead of one. C–H stretching bands occur at the range $3000\text{--}2850\text{ cm}^{-1}$ in most aliphatic compounds. If the C–H bond is next to a double bond or aromatic ring, the C–H stretching band occurs between 3100 and 3000 cm^{-1} . Triple-bond stretching absorptions occur in the $2500\text{--}2000\text{ cm}^{-1}$ region due to high force constants of the bonds. $\text{C}\equiv\text{C}$ bonds absorb between 2300 and 2050 cm^{-1} , while the nitrile group ($\text{C}\equiv\text{N}$) occurs between 2300 and 2200 cm^{-1} . These groups can be easily identified since $\text{C}\equiv\text{C}$ stretching is often very weak, while $\text{C}\equiv\text{N}$ stretching is of medium intensity. These are the most common absorptions in this region, but you may come across some X–H stretching absorptions, where X is a more massive atom such as phosphorus or silicon. These absorptions usually occur near 2400 and 2200 cm^{-1} , respectively.

The major bands in the $2000\text{--}1500\text{ cm}^{-1}$ region are caused by $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching. Carbonyl stretching is a very easy absorption to recognize in this region. It is usually the most intense band in the spectrum. The nature of $\text{C}=\text{O}$ bond can also be confirmed as there are regions for various carbonyl contain organic moieties. It very germane to know that metal carbonyls may absorb above 2000 cm^{-1} $\text{C}=\text{C}$ stretching is much weaker and occurs at around

1650 cm^{-1} , but this band is often not observed for symmetry or dipole moment reasons. C=N stretching also occurs in this region and is found to be sharper and more intense. The bands in the region 1500–650 cm^{-1} are characteristic of the molecule being analysed hence region is called the fingerprint region. It is very important to note that most of the bands may vary from one compound to another and also from one environment to another. This implies that the values are not fixed and in few cases variation may occur up to 100 cm^{-1} .

Table of Infrared bands of functional groups

<u>Absorbance</u>	<u>Wavenumber, cm^{-1}</u>
O-H stretch of carboxylic acid	3300-2800 (strong, broad, centers at ~ 3000)
N-H stretch	3400-3250 (medium intensity, often broad)
sp^2 C-H stretch	3100-3020
sp^3 C-H stretch	2960-2850
aldehyde C-H stretch	2830-2695
aromatic overtones	2000-1600
C=O stretch	See Table 1
aromatic C=C stretch	1600-1585
alkene C=C stretch	1680-1620
C-O stretch	1150-1050
aromatic ring bends	770-730 and 710-690 (for mono-sub'd ring)

Infrared of coordination compounds

Coordination complexes are considered by their structural types and the vibrational wavenumbers of some common functional groups present in them. Monatomic ligands (halides, oxide and hydride) which coordinate with metal produce characteristic infrared bands examples; M-X (X= halides and M= metal) band occurs at 750-100 cm^{-1} , M=O occurs at 1010-850 cm^{-1} and $\text{M}\equiv\text{N}$ at 1020-875 cm^{-1} . Coordination compounds may also contain diatomic ligands, in which a metal atom coordinated to molecules such as CO, NO, O₂, N₂, H₂, OH⁻ or CN⁻. The wavenumbers of such ligands are shifted to lower regions on coordination due to increase in bond length.

The absorption bands in coordination compounds depend on the geometries and the coordination numbers and the donor atoms. Tetrahedral complexes have two infrared active mode of vibration, square planar complexes have three active modes of infrared vibration

while only two are present in octahedral provided the ligands are identical. Few examples are presented below:

Complex	Geometry	Bands (cm ⁻¹)
[PtCl ₄] ²⁻	Square planar	147, 313, 165
[PdCl ₄] ²⁻	Square planar	150, 321, 161
[MnO ₄] ⁻	Tetrahedral	902, 386
[CrO ₄] ⁻	Tetrahedral	890, 378
[PtCl ₆] ²⁻	Octahedral	343, 183
[VCl ₆] ²⁻	Octahedral	646, 300

There are however many complexes with complicated IR spectra. Generally, Metal complexes or chelates are largely covalent in nature and the spectra of such compounds are overwhelmed by the contribution of the ligand and its coordination modes. The ligands may be small species, such as water, ammonia, CO or phosphine or as large as porphyrin.

Infrared spectra can help to identify linkage isomers as there are differences in characteristic absorptions of the isomers. Linkage isomerism occurs when a ligand has the ability to coordinate to a central metal using either of two atoms within the ligand. The nitrite ion exhibits this type of isomerism. When the nitrite ion is attached to a central metal ion via the nitrogen atom, it is known as a *nitro* ligand. When one of the oxygen atoms is the donor, it is known as a *nitrito* ligand. When NO₂⁻ bonds undergo bonding through an oxygen bond, one of the NO bonds is 'nearly' a double bond, while the other is a single bond. In the other coordination, both NO bonds are intermediate between single and double bonds. The infrared band of a bond increases as its strength increases and so it would be expected that the wavenumbers of the NO bonds in NO₂⁻ increase in the order: single-bond NO (in O-bonded) < NO (in N-bonded) < double-bond NO (in O-bonded). It is observed that in complexes when NO₂⁻ is bonded through oxygen, N=O stretching appears in the 1500–1400 cm⁻¹ range while N–O stretching appears at 1100–1000 cm⁻¹. In complexes in which NO₂⁻ is bonded through nitrogen, the infrared bands appear at 1340–1300 cm⁻¹ and 1430–1360 cm⁻¹, which are intermediate values when compared to the oxygen-bonded complex. This indicates that it is possible to use infrared spectroscopy to determine whether a nitrite is coordinated and whether it is coordinated through a nitrogen or oxygen atom.

3.4 MAGNETIC MEASUREMENT

Movement of electrical charge generates magnetic field in any material. Magnetism is therefore a characteristic property of all materials that contain electrically charged particles that are in continuous motion and for most purposes can be considered to be entirely of electronic origin. In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes whereas the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties. Many transition metal compounds are paramagnetic due to the presence of unpaired electrons. Magnetic moment of each such electron is associated with its spin angular momentum and orbital angular momentum.

PRINCIPLE OF MAGNETISM

According to Lenz's Law, which states that when a substance is placed within a magnetic field, H , the field within the substance, B , differs from H by the induced field, which is proportional to the intensity of magnetisation (I).

It can be mathematically expressed as $B = H + 4\pi I$, where B is the magnetic field within the substance, H is the applied magnetic field and I is the intensity of magnetisation. By dividing through with H , It can also be expressed as;

$$B/H = 1 + 4\pi I/H, \text{ or } P = 1 + 4\pi K$$

where B/H is called the magnetic permeability (P) of the material and K is the magnetic susceptibility per unit volume, (I/H). By definition, K in a vacuum is zero, where $B = H$. Note that $P = B/H = 1$

It is usually more convenient to measure mass than volume and the mass susceptibility, χ_g , is related to the volume susceptibility, K , through the density.

$$\chi_g = K/d \text{ where } d \text{ is the density.}$$

It is necessary to measure this quantity on the basis that can be related to atomic properties, it therefore converted to molar susceptibility by multiplying the mass susceptibility with relative molar mass (RMM) of the atom.

$$\chi_m = \chi_g \cdot \text{RMM}$$

All materials are known to have inherent diamagnetism, it is important to include a term that will reflect this diamagnetism of the material being measured to have a corrected molar susceptibility.

$$\chi_{\text{corr}} = \chi_m + \chi_{\text{dia}}$$

Curies Law is obeyed by Normal paramagnetic substances

$$\chi_m = C/T$$

where C is the Curie constant. A plot of 1/X versus T should give a straight line with the slope 1/C passing through the origin (0 K). Some substances give a straight line that intercepts just a little above or below 0K and these are said to obey the Curie-Weiss Law:

$$\chi = C/(T \pm \phi) \text{ where } \phi \text{ is known as the Weiss constant.}$$

The constant C is given by the Langevin expression which relates the susceptibility to the magnetic moment;

$$m = N\mu^2/3kT$$

where N is Avogadro's number, k is the Boltzmann constant and T the absolute temperature.

$$\mu = 2.828 \sqrt{\chi_m \cdot T}$$

Based on quantum mechanics, the magnetic moment is dependent on both spin and orbital angular momentum contributions. The spin-only (s.o.) formula is expressed as

$$\mu_{\text{s.o.}} = \sqrt{4S(S + 1)} \text{ or } \mu_{\text{s.o.}} = \sqrt{n(n + 2)}$$

where S is the resultant spin angular momentum and n is the number of unpaired electrons.

This expression can be modified to include orbital contribution to the magnetic moment.

$$\mu = \sqrt{(4S(S + 1) + L(L + 1))}$$

TYPES OF MAGNETIC BEHAVIOURS

DIAMAGNETISM

Diamagnetism is a phenomenon in some materials in which the susceptibility is negative (χ_m), i.e. the induced magnetism opposed the applied field. It arises from the precession of spinning charges in a magnetic field. The magnetization is in the *opposite* direction to that of the applied field, i.e. the magnetic susceptibility is negative ($\chi_m < 0$). Although *all* substances are diamagnetic, it is a weak form of magnetism and may be masked by other, stronger forms. Diamagnetism results from changes induced in the orbits of electrons in the atoms of a

substance by the applied field, the direction of change (in accordance with Lenz's law) opposing the applied magnetic flux. There is thus a weak negative susceptibility ($\chi_m < 0$)

Diamagnetism is a very weak form of magnetism that is only exhibited in the presence of an external magnetic field. It is the result of changes in the orbital motion of electrons due to the external magnetic field. The induced magnetic moment is very small and in a direction opposite to that of the applied field. When placed between the poles of a strong electromagnet, diamagnetic materials are attracted towards regions where the magnetic field is weak. Diamagnetism is found in all materials; however, because it is so weak it can only be observed in materials that do not exhibit other forms of magnetism. Also, diamagnetism is found in elements with paired electrons. Complexes without unpaired electrons are diamagnetic in nature; this is a characteristic of d^0 and d^{10} complexes with other d configuration with no unpaired electrons.

PARAMAGNETISM

In paramagnetism, the atoms or molecules of the substance have net orbital or spin magnetic moments that are capable of being aligned in the direction of the applied field. They possess positive magnetic susceptibility (χ_m). Paramagnetism occurs in all substances with unpaired electrons; e.g. free atoms, free radicals, and complexes of transition metals containing ions with partially filled d orbitals. It also occurs in metals as a result of the magnetic moments associated with the spins of the conducting electrons.

Paramagnetism is the tendency of the atomic magnetic dipoles, due to quantum-mechanical spin angular momentum, in a material that is otherwise non-magnetic to align with an external magnetic field. This alignment of the atomic dipoles with the magnetic field tends to strengthen it, and is described by magnetic permeability greater than unity or equivalently a positive magnetic susceptibility above zero.

In pure paramagnetism, the external magnetic field acts on each atomic dipole independently and there are no interactions between individual atomic dipoles. Such paramagnetic behaviour can also be observed in ferromagnetic materials that are above their Curie temperature. Paramagnetic materials attract and repel like normal magnets when subject to a magnetic field. Under relatively low magnetic field saturation when the majority of the atomic dipoles are not aligned with the field, paramagnetic materials exhibit magnetization according to Curie's law;

$$\chi_m = C/T$$

The law shows that paramagnetic material becomes less magnetic as temperature is increased. Paramagnetic materials in magnetic fields will act like magnets but when the field is removed, thermal motion will quickly disrupt the magnetic alignment. In general paramagnetic effects are small (magnetic susceptibility of the order of $\chi_m \sim 10^{-3}$ to 10^{-5}).

Ferromagnetic materials above the Curie temperature become paramagnetic.

FERROMAGNETISM

When the centres of paramagnetic species are very close, a magnetically ordered material in which there is a bulk magnetic moment with large magnetization is obtained. The electron spins of the atoms in the microscopic regions, domains, are aligned. In the presence of an external magnetic field the domains oriented favourably with respect to the field at the expense of the others and the magnetization of the domains tends to align with the field. This phenomenon is called Ferromagnetism. Above the Curie temperature, the thermal motion is sufficient to offset the aligning force and the material becomes paramagnetic. Certain elements (iron, nickel and cobalt), and alloys with other elements (titanium, aluminium) exhibit relative magnetic permeabilities up to 10^4 (ferromagnetic materials). Below a certain temperature, called the Curie point (or Curie temperature) an increasing magnetic field applied to a ferromagnetic substance will cause increasing magnetization to a high value called the saturation magnetization. This is because a ferromagnetic substance consists of small magnetized regions called domains. The total magnetic moment of a sample of the substance is the vector sum of the magnetic moments of the component domains. Ferromagnetic materials obey the Curie-Weiss Law:

$$\chi = C/(T+\phi)$$

ANTIFERROMAGNETISM

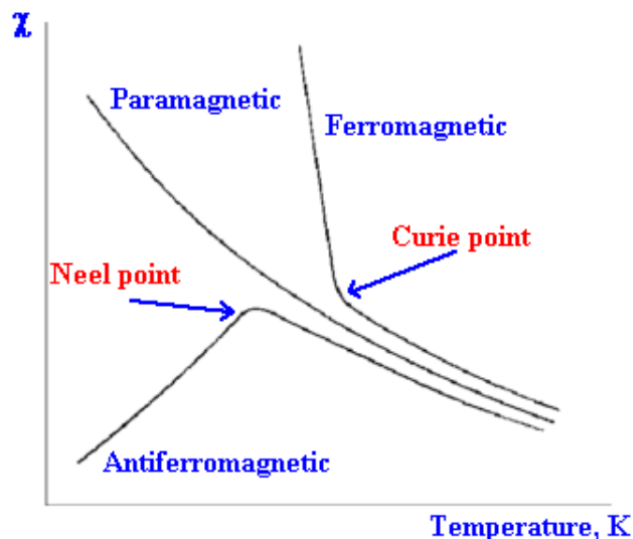
This is a phenomenon in some magnetically ordered materials in which there is an anti-parallel alignment of spins in two or more close centres of paramagnetic structures so that there is overall cancellation of bulk spontaneous magnetization. In antiferromagnetic materials, the condition is such that the spins aligned in a manner in which they cancelled out the overall magnetization. **Antiferromagnetism** results in the spins of magnetic electrons align in a regular pattern with neighbouring spins pointing in opposite directions. This is the opposite of ferromagnetism. Generally, antiferromagnetic materials exhibit antiferromagnetism at a low temperature, and become disordered above a certain

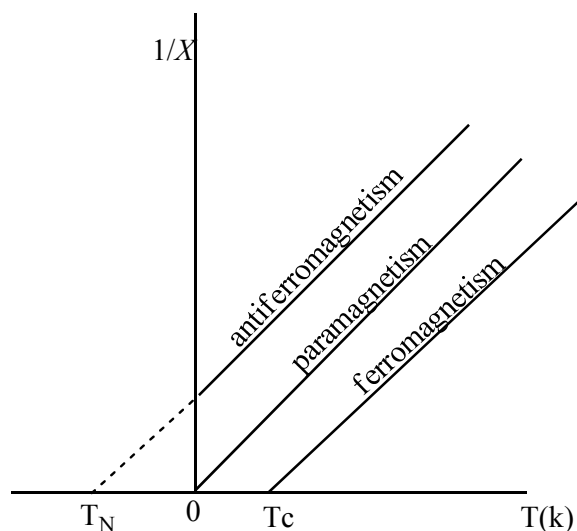
temperature; the transition temperature is called the Néel temperature. Above the Néel temperature, the material is typically paramagnetic. The antiferromagnetic behaviour at low temperature usually results in diamagnetic properties, but can sometimes display ferromagnetic (where some spins are not cancelled out) behaviour, which in many physically observable properties are more similar to ferromagnetic interactions.

The magnetic susceptibility, χ_m of an antiferromagnetic material will appear to go through a maximum as the temperature is lowered; in contrast, that of a paramagnet will continually increase with decreasing temperature. Antiferromagnetic materials have a negative coupling between adjacent moments and low frustration. Antiferromagnetic materials are relatively uncommon. There are also numerous examples among high nuclearity metal clusters.

$$\chi = C/(T - \phi)$$

Ferrimagnetism is a property exhibited by materials whose atoms or ions tend to assume an ordered but nonparallel arrangement in zero applied field below a certain characteristic temperature known as the Néel temperature. In the usual case, within a magnetic domain, a substantial net magnetization results from the antiparallel alignment of neighboring non-equivalent sublattices. The macroscopic behavior is similar to ferromagnetism. Above the Néel temperature, these substances become paramagnetic.





T_c : ferromagnetic Curie temperature (below T_c , sample is ferromagnetic)

T_N : Néel Temperature (below T_N , sample is antiferromagnetic)

ORBITAL CONTRIBUTION TO MAGNETIC MOMENT IN PARAMAGNETIC COMPLEXES

T Ground Term

An orbital angular momentum contribution is expected when the ground term is triply degenerate i.e. a T state such T_1 or T_2 in both tetrahedral and octahedral fields. Octahedral complexes where the triply degenerate (d_{xy} , d_{yz} and d_{xz}) orbitals are not equally (such as d^1 , d^2 , d^4 and d^5 low spins) will have orbital contribution to magnetic moment. This implies that the experimental magnetic moment μ_{eff} will be greater than the $\mu_{\text{s.o.}}$. These complexes will also show temperature dependence in magnetic moment as well.

In order for an electron to contribute to the orbital angular momentum the orbital in which it resides must be able to transform into an exactly identical and degenerate orbital by a simple rotation (it is the rotation of the electrons which induces the orbital contribution). For example, in an octahedral complex the degenerate t_{2g} set of orbitals (d_{xz}, d_{yx}, d_{yz}) can be interconverted by a 90° rotation. However the orbitals in the e_g subset ($d_z^2, d_x^2-y^2$) cannot be interconverted by rotation about any axis as the orbital shapes are different; therefore an electron in the e_g set does not contribute to the orbital angular momentum and is said to be quenched. In the free ion case the electrons can be transformed between any of the orbitals as they are all degenerate, but there will still be partial orbital quenching as the orbitals are not identical. Electrons in the t_{2g} set do not always contribute to the orbital angular momentum. For example in the d^3, t_{2g}^3 case, an electron in the d_{xz} orbital cannot by rotation be placed in the

d_{yz} orbital as the orbital already has an electron of the same spin. This process is also called quenching.

Tetrahedral complexes can be treated in a similar way with the exception that we fill the e orbitals first, and the electrons in these do not contribute to the orbital angular momentum. Tetrahedral complexes of d^3 , d^4 , d^8 and d^9 are going to experience orbital contribution to magnetic moment.

Configurations corresponding to the T_2 term (from D) or a T_1 term (from an F term) have direct contribution to orbital angular momentum. The magnetic moments of complexes with T terms are often found to show considerable temperature dependence. This is as a result of spin-orbit coupling that produces levels whose energy differences are frequently of the order kT , so as a result, temperature will have a direct effect on the population of the levels arising in the magnetic field.

A₂ or E Ground Term

The configurations corresponding to the A_1 (free ion S term), E (free ion D term), or A_2 (from F term) do not have a direct contribute to the orbital angular momentum. For the A_2 and E terms there is always a higher T term of the same multiplicity as the ground term which can affect the magnetic moment (usually by a only small amount).

$$\mu_{\text{eff}} = \mu_{\text{s.o}} (1 - \alpha\lambda/\Delta)$$

where α is a constant (2 for an E term, 4 for an A_2 term) λ is the spin-orbit coupling constant which although generally not available does give important information since the sign of the value varies depending on the orbital occupancy. For d^1 to d^4 the value is positive hence μ_{eff} is less than $\mu_{\text{s.o}}$ while for d^6 to d^9 the value is negative hence μ_{eff} is greater than $\mu_{\text{s.o}}$. Δ is the crystal field splitting factor for complexes.

Table showing Octahedral d^n and possibility of orbital contribution (OC) to magnetic moment

Ion	d^n	Config.	Free ion term	Ground term	O. C.	$\mu_{\text{s.o}}$ (BM)	μ_{obs} (BM)	$\mu_{\text{L+S}}$ (BM)
Ti^{3+}	d^1	t_{2g}^1	2D	$^2T_{2g}$	Yes	1.73	1.6-1.7	3.00
V^{3+}	d^2	t_{2g}^2	3F	$^3T_{1g}$	Yes	2.83	2.7-2.9	4.47
V^{2+}	d^3	t_{2g}^3	4F	$^4A_{2g}$	No	3.88	3.8-3.9	5.20
Cr^{2+}	d^4 HS	$t_{2g}^3 e_g^1$	5D	5E_g	No	4.90	4.7-4.9	5.48
Cr^{2+}	d^4 LS	t_{2g}^4	3F	$^3T_{1g}$	Yes	2.83	3.2-3.3	4.47

Mn ²⁺	d ⁵ HS	t _{2g} ³ e _g ²	⁶ S	⁶ A _{1g}	No	5.92	5.6-6.1	5.92
Mn ²⁺	d ⁵ LS	t _{2g} ⁵	² D	³ T _{2g}	Yes	1.73	1.8-2.1	
Fe ²⁺	d ⁶ HS	t _{2g} ⁴ e _g ²	⁵ D	⁵ T _{2g}	Yes	4.9	5.1-5.7	5.48
Fe ²⁺	d ⁶ LS	t _{2g} ⁶	¹ S	¹ A _{1g}	No	0	0	
Co ²⁺	d ⁷ HS	t _{2g} ⁵ e _g ²	⁴ F	⁴ T _{1g}	Yes	3.88	4.3-5.2	5.20
Co ²⁺	d ⁷ LS	t _{2g} ⁶ e _g ¹	² D	² E _g	No	1.73	1.8	
Ni ²⁺	d ⁸	t _{2g} ⁶ e _g ²	³ F	³ A _{2g}	No	2.82	2.9-3.3	4.47
Cu ²⁺	d ⁹	t _{2g} ⁶ e _g ³	² D	² E _g	No	1.73	1.7-2.2	3.00

Table showing Tetrahedral dⁿ and possibility of orbital contribution (OC) to magnetic moment

Ion	d ⁿ	Config.	Free ion term	Ground term	O. C.	μ _{s.o} (BM)	μ _{obs} (BM)
Cr ⁵⁺	d ¹	e ¹	² D	² E	No	1.73	1.7-1.8
Cr ⁴⁺	d ²	e ²	³ F	³ A ₂	No	2.83	2.8
Fe ⁵⁺	d ³	e ² t ¹	⁴ F	⁴ T _i	No	3.88	3.6-3.7
Mn ²⁺	d ⁵	e ² t ₂ ³	⁶ S	⁶ A ₁	No	5.92	5.9-6.2
Fe ²⁺	D ⁶	e ³ t ₂ ³	⁵ D	⁵ E	No	4.9	5.3-5.5
Co ²⁺	d ⁷	e ⁴ t ₂ ³	⁴ F	² A ₂	No	3.88	4.2-4.8
Ni ²⁺	d ⁸	e ⁴ t ₂ ⁴	³ F	³ T ₁	No	2.83	3.7-4.0

Example:

Account for the magnetic moments of the complex, [NiCl₄]²⁻ recorded at 80, 99 and 300 K.

80K 99K 300K

3.24 3.42 3.89 B.M.

Ni²⁺ (d⁸)

The formula suggests a 4 coordinate complex and it can be assumed that the complex is tetrahedral with a d electron configuration of e⁴ t₂⁴ therefore the spin-only magnetic moment is 2.83 BM.

From the table above, the ground term is 3T_1 therefore orbital contribution is going to influence the magnetic moment which must also be temperature dependent. It is necessary to include the orbital terms in estimating the magnetic moment. $S = 1$ and $L = 3$

$$\mu = \sqrt{4S(S+1) + L(L+1)} = \sqrt{20} = 4.47 \text{ BM}$$

The value obtained is in between the room temperature magnetic moment and the spin only value. The difference between μ_{L+S} and μ_{obs} may be attributed to partial quenching of the orbital contribution to magnetic moment.

Example:

At 300 K, the observed value of μ_{eff} for $[\text{V}(\text{NH}_3)_6]\text{Cl}_2$ is 3.9 BM. Confirm that this corresponds to what is expected for an octahedral d^3 complex.

$$n = 3 \text{ and } S = 3(1/2), \mu_{\text{s.o.}} = \sqrt{4S(S+1)} \text{ or } \mu_{\text{s.o.}} = \sqrt{N(N+2)}$$

$$\mu_{\text{s.o.}} = \sqrt{4S(S+1)} = \sqrt{4(3/2)(3/2+1)} = 3.9 \text{ BM or } \mu_{\text{s.o.}} = \sqrt{3(3+2)} = 3.9 \text{ BM}$$

Example:

Determine the spin state of the complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_2$ given that its μ_{eff} is 4.85 BM at 298K

$$4.85 = \sqrt{n(n+2)}$$

$$4.85^2 = n^2 + 2n$$

$$0 = n^2 + 2n - 23.5225$$

Solve the equation using $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Where $a = 1$, $b = 2$, $c = -23.5225$

$n \approx 4$ Cr^{2+} (d^4) has high spin in the octahedral complex.

Example:

Given that Δ_0 is $10,800 \text{ cm}^{-1}$ and $\lambda = -315$ for the complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$, determine the μ_{eff} and compare the result with $\mu_{\text{s.o.}}$ and μ_{S+L} . Comment on the values.

Ni^{2+} has d^8 configuration and 3F free ion ground term, which will give rise to ${}^3A_{2g}$ in octahedral field. Since there exist a triple degenerate excited term, orbital contribution is expected. Note that $\alpha = 4$ for A_2 term, $\mu_{\text{s.o.}} = 2.83 \text{ BM}$ and $\mu_{S+L} = 4.47 \text{ BM}$

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} (1 - \alpha\lambda/\Delta) = 2.83(1 - 4(-315/10,800)) = 3.16 \text{ BM}$$

The result of the calculation shows that there is orbital contribution to magnetic moment due to excited T term the contribution is however very small as the estimated value is less than

4.47 BM expected with a T ground term but consistent with experimental value of 3.16 BM reported for similar Ni^{2+} complex.

6.0 CONCLUSION

The Magnetic, electronic absorption and vibrational properties of complexes have been discussed and it is expected that students should be able to apply the principles of electronic absorption and vibration to interpret the spectra of octahedral and tetrahedral complexes. With knowledge of infrared spectroscopy, linkage isomers can be easily distinguished. The electronic spectra interpretation helps to determine the energy of transition between split d orbitals in a complex. The magnetic moment can be used to identify the spin state of complexes.

5.0 SUMMARY

- The electronic absorption spectra of complexes have been interpreted using Orgel diagrams and Tanabe-Sugano diagrams.
- The magnetic moments of complexes have been calculated based on spin angular momentum and a combination of spin and orbital angular momenta. The results of room temperature magnetic moment of complexes have been interpreted based on possible orbital contributions as observed in some complexes.
- The four basic forms of magnetisms adopted by complexes (paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism) have been discussed.
- Curie's law and Curie-Weiss laws have been used to describe the forms of magnetism and their temperature dependence as observed in complexes.
- The principle and application of infrared vibrational spectroscopy in structural determination of complexes have been discussed

6.0 Tutor-Marked Assignment (TMA)

1. For the following high spin ions, describe the nature of the possible electronic transitions and give them in the order of increasing energy.
(a) $[\text{Ni}(\text{NH}_3)_6]^{2+}$, (b) $[\text{FeCl}_4]^-$, (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, (d) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, (e) $[\text{FeF}_6]^{4-}$, (f) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
2. Given that Δ_0 is 8,500 cm^{-1} and $\lambda = -315$ for the complex $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, determine the μ_{eff} and compare the result with $\mu_{\text{s.o}}$ and $\mu_{\text{S+L}}$. Comment on the values.

3. Determine the ground term for the following and predict the most likely value of effective magnetic moments of the following complexes. State the possibility of orbital contribution where appropriate.
- (a) $[\text{Ni}(\text{NH}_3)_6]^{2+}$, (b) $[\text{FeCl}_4]^-$, (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, (d) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, (e) $[\text{FeF}_6]^{4+}$, (f) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
4. Differentiate between different forms of magnetism in complexes
5. Interpret the following room temperature (300K) magnetic moments.
- (i) $\text{Fe}(\text{acac})_3$ 5.92BM (ii) $\text{Mn}(\text{acac})_3$ 4.86BM (iii) BaMnF_6 3.80BM
 (iv) Cs_2CoCl_4 4.71BM (v) $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ 1.91BM (vi) $[\text{Cr}(\text{en})_3]\text{I}_3 \cdot \text{H}_2\text{O}$ 3.93BM
 (vii) VCl_4 1.69BM (viii) $\text{K}_4[\text{Mn}(\text{oxalate})_3] \cdot 3\text{H}_2\text{O}$ 3.18BM
 (ix) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ 3.11BM (x) $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ 1.89BM
6. The absorbance of a 0.1 M aqueous solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ was found to be 0.56 when measured in a 1 cm cuvette. A distorted absorption band was centered at 20,300 cm^{-1} . Account for the spectrum and calculate the molar absorbance (ϵ). What would be the absorbance of the same solution in a 2 cm cuvette?
7. The electronic absorption spectrum of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ shows three bands at 8,500, 15,400 and 26,000 cm^{-1} . Account for these bands using an Orgel diagram.

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MODULE 4

UNIT 1: THERMODYNAMIC STABILITY AND REACTION OF COMPLEX

1.0 Introduction

2.0 Objectives

3.0 Main Content

3.1 Thermodynamic stability of complex compound

3.2 The Chelate effect

3.3 Kinetics and mechanism of complexes

3.4 Reaction mechanism in complexes

4.0 Conclusion

5.0 Summary

6.0 Tutor-Marked Assignment (TMA)

7.0 References/Further Readings

1.0 INTRODUCTION

Thermodynamic stability and reaction kinetics of coordination compound is a very important aspect of coordination chemistry and its application cut across all disciplines including; catalyst design in production industries, pharmaceutical studies of drug design, chemical analysis and biochemical studies of drug metabolism. This is because the stability study and reaction mechanism of complexes determine their behaviour in different environments that may include change in temperature or change in pH of reaction medium. It is important to know that there is a line of separation between kinetic and thermodynamic stability of complexes as sometime the two terms are without conveying their real meaning. Thermodynamic stability is a function of the equilibrium constant. Higher the equilibrium constant indicates greater stability of a complex. However, kinetics is a function of the rate constant. The reaction with high rate constant is expected to proceed fast.

2.0 OBJECTIVE

At the end of this unit students should be able to:

- Explain the fundamental difference between reaction thermodynamic and kinetics.
- Write chemical equilibrium expression and determine step-wise stability constant and overall stability constant of complexes.

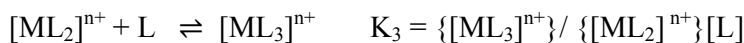
- Estimate and interpret the entropy and free energy of complexes
- Understand reaction mechanism in complexes

3.0 MAIN CONTENT

3.1 THERMODYNAMIC STABILITY OF COMPLEX COMPOUNDS

A metal ion in solution exists in complex form, in combination with ligands (such as solvent molecules or simple ions) or chelating groups. As noted earlier, complexes may be neutral or cationic or anionic, depending on the charges carried by the central metal ion and the coordinated groups. Stability of a complex in solution refers to the degree of association between the two species involved in a state of equilibrium. Qualitatively, the greater the association, the greater is the stability of the compound. The magnitude of the equilibrium stability constant for the association, quantitatively determines the stability.

Thermodynamic stability of a complex is a measure of the extent to which this complex will be formed or be transformed into another complex under stated conditions on reaching equilibrium. If only soluble mononuclear complexes are formed in a solution containing metal ion, M^{n+} , and monodentate neutral ligand, the system at equilibrium can be described by the following expression;



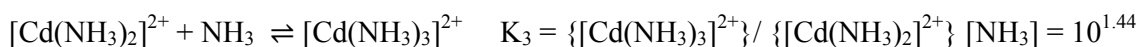
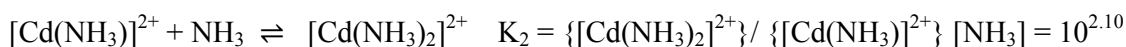
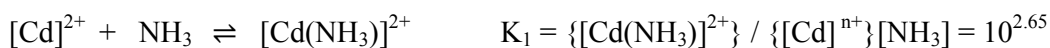
The reaction will proceed till a certain coordination number (N) is attained

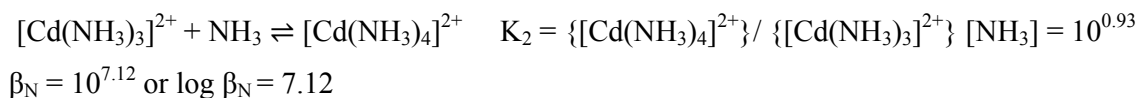


The equilibrium constants $K_1, K_2, K_3, K_4, \dots$ and K_N are called stepwise formation or stability constants. When combined together, the overall formation constant (β_N) is derived

$$\beta_N = K_1 \times K_2 \times K_3 \times K_4 \dots K_N \quad \text{or} \quad \log \beta_N = \log k_1 + \log k_2 + \log k_3 + \log k_4 + \dots \log k_N$$

In most cases the value of stepwise formation constant decreases as the coordination number increases. Example is the reaction between aqueous solution of Cd^{2+} and NH_3





Reasons for the decrease in the K value are statistical factors, increased steric hindrance when the incoming ligand is larger than the leaving ligand and the coulombic force if the ligand is charged. Provided known concentrations of metal ion and ligand react together to give a complex whose composition is known, the stability constant can be determined for such reaction by measuring the concentration of the unreacted ligand, metal ion or the complex formed. This can be achieved by monitoring change in one of the properties of a component in the system or use of pH measurement, ion-exchange, electronic or NMR techniques.

Example: The aqueous substitution reaction of Ni^{2+} with NH_3 is study at 300 K using pH measurement. The stepwise formation constants for the various steps in the reaction are $K_1 = 10^{2.79}$, $K_2 = 10^{2.26}$, $K_3 = 10^{1.69}$, $K_4 = 10^{1.25}$, $K_5 = 10^{0.74}$, $K_6 = 10^{0.03}$ determine the overall formation constant, the free energy (ΔG) at 300 K and entropy (ΔS) given that change in enthalpy (ΔH) is -60.28kJ/mol and gas constant (R) = 8.314J/(K.mol).

$$\beta_6 = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6 = 10^{8.76}$$

$$\Delta G = -RT \ln \beta_6 = -8.314 \times 300 \times \ln 10^{8.76} = -50.31 \text{ kJ/mol}$$

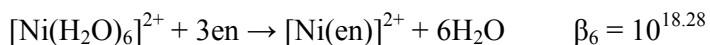
$$\Delta S = (\Delta H - \Delta G)/T = (-60.28 - (-50.31))/300 = 33.23 \text{ J/(K.mol)}$$

3.2 THE CHELATE EFFECT

The term chelate effect is used to describe special stability associated with complexes containing chelate ring when compared to the stability of related complexes with monodentate ligands. The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2, 2'-bipyridine with pyridine or 1,2 diaminoethane (ethylenediamine = en) with ammonia.

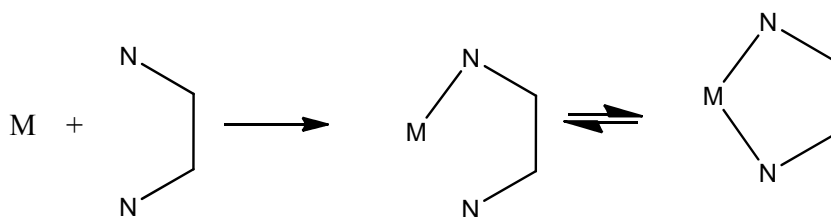
It has been established for many years that keeping the coordination number of the metal ion same, the complex resulting from coordination with the chelating ligand is much more thermodynamically stable as compared to that formed with monodentate ligand. This can be established from the stability constant of the complexes formed adding two monodentate ligands compared with adding one didentate ligands, or adding four monodentates compared to two didentates, or adding six monodentates compared to three didentates. The complex

formation of Ni²⁺ with ammonia or 1, 2-diaminoethane, can be expressed by the following equations:



The overall stability constant value for the Ni²⁺ complex with three chelate rings (en) is about 10¹⁰ greater than that formed with six monodentate ligands (NH₃). Major factors responsible for the special stability of chelate can be attributed to increase in entropy as the reaction leading to the formation of the chelate results in increase in pollution of product species when compared to reactant species. However, with monodentate ligand, the reaction results in no change in population.

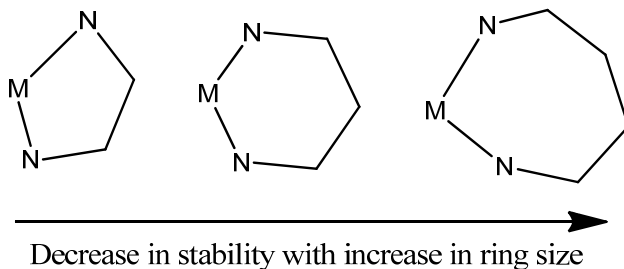
Another factor could be based on the understanding of how the reactions might proceed. To form a complex with 6 monodentate ligands requires 6 separate favourable collisions between the metal ion and the ligand molecules. On the contrary, the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm, the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring. Thus in the process of dissociation, when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again. These conditions favour the formation of the complex with bidentate ligands rather than monodentate ligands.



One ligand that forms very stable complexes is the anion ethylenediaminetetraacetate (EDTA⁴⁻). This ion can bond at six sites, so one EDTA⁴⁻ ion replaces six water molecules when the reaction is carried out in aqueous solution. The result is the formation of complexes that have very high stability constants. This ligand is widely used in analytical chemistry in complexometric titrations to determine concentrations of metal ions. Because it holds metal ions so securely, EDTA⁴⁻ (in the form of Na₄EDTA, Na₂CaEDTA, or Ca₂EDTA) is added to

salad dressings. Traces of metal ions catalyze oxidation reactions that lead to spoilage, but when EDTA^{4-} is added, it binds to the metal ions so effectively that they cannot act as catalysts for the undesirable oxidation reactions. Many metal ions are effectively complexed (or sequestered) by EDTA^{4-} or $\text{H}_2\text{EDTA}^{2-}$, including main-group ions such as Mg^{2+} , Ca^{2+} and Ba^{2+} .

It is not only the formation of chelate rings that influences the stability of complexes, but also ring size is important. Studies have shown that chelate rings having five or six members are generally more stable than those of other sizes. For example, when the series of ligands having the formula $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ (where $n = 2, 3,$ or 4) forms complexes with the same metal ion, the most stable complex is with ethylenediamine ($n = 2$), which results in a 5-membered chelate ring. If $n = 3$, which corresponds to 1, 3-diaminopropane, the complexes formed have 6-membered rings and are less stable than are those of en. The complexes with the ligand having $n = 4$ (1,4-diaminobutane) are even less stable. A similar situation exists for complexes of the anions of dicarboxylic acids, $^-\text{OOC}-(\text{CH}_2)_n-\text{COO}^-$ (where $n = 0, 1, \dots$).



3.3 KINETICS AND MECHANISMS OF COMPLEXES

Kinetics of complex reaction is the speed at which transformations leading to attainment of equilibrium will occur. Most often, complexes undergo reaction in which composition of their coordination sphere change by substitution of one ligand by another. The process by which this substitution occurs in complex reactions is referred to as lability. Complex that undergo lability very fast said to be labile while others that undergo similar reaction at slow rate are called inert. It is important to note that a complex can be inert and yet be thermodynamically unstable. Typical example is $[\text{Co}(\text{NH}_3)_6]^{3+}$ which will persists for days in acid medium but yet unstable thermodynamically. On the other hand, $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$ is labile and yet thermodynamically stable. Complexes of d^3 , low spin d^4 , d^5 and d^6 as well as d^8 square planar are chemically inert. Complexes of d^1 , d^2 high spin d^4 , d^5 and d^6 as well as d^7 , d^9 and d^{10} are labile.

KINETIC STUDY

Kinetic study can be carried out with different forms of techniques depending on the rate of the reaction to be studied. Experimental techniques have been developed to monitor reactions over time scales varying from as low as 10^{-15} s to hours or days. While it is relatively simple to monitor the kinetics of a slow reaction occurring in few minutes or hours, highly specialised techniques are required in order to study fast reactions.

Generally, kinetics study involves techniques essentially consists of mixing the reactants and initiating reaction on a time scale that is negligible relative to that of the reaction, and then monitoring the concentration(s) of one or more reactants and/or products as a function of time. Because rate constants vary with temperature, it is also important to determine and control accurately the temperature at which the reaction occurs. The techniques generally used to study reaction kinetics can be grouped into;

1. Static methods (for reaction with half-life greater than one minute)
2. Flow or rapid mixing techniques ($1 \text{ min.} \geq \text{half-life} \geq 10^{-3} \text{ sec.}$)
3. Relaxation methods (when half-life is less than 10^{-1} sec.)

STATIC METHODS OF KINETIC STUDY

Static methods are used for studying inert reactions which occur over minutes to hours. The reaction is usually initiated simply by mixing the reactants together by hand or with a magnetic stirrer or other mechanical device and the progress of the reaction can be monitored over a time frame by observing a change in physical or chemical properties of one of the reactants or product. pH change, gas evolution, colour change, isotopic exchange can be the change being observed.

FLOW OR RAPID MIXING TECHNIQUES OF KINETIC STUDY

Flow techniques are used to study reactions occurring on timescales of seconds to milliseconds. In the simplest flow method reactants are mixed at one end of a flow tube, and the composition of the reaction mixture is monitored at one or more positions further along the tube. If the flow velocity along the tube is known, then measurements at different positions provide information on concentrations at different times after initiation of reaction. The progress of the reaction can be monitored using physical and chemical changes mentioned static methods.

Continuous flow methods have the disadvantages that relatively large quantities of reactants are needed, and very high flow velocities are required in order to study fast reactions. These problems may be avoided by using a stopped flow technique. In this method, a fixed volume of reactants are rapidly flowed into a reaction chamber and mixed by the action of a syringe

fitted with an end stop. The composition of the reaction mixture is then monitored spectroscopically as a function of time after mixing at a fixed position in the reaction chamber.

RELAXATION METHODS OF KINETIC STUDY

These methods involve generating of a disturbance or perturbation on a state of equilibrium over a short time range. The disturbance may be temperature or pressure jump. The relaxation of the perturbed system is monitored to a new state of equilibrium by spectrophotometric and fast electronic devices. Radiofrequency and ultrasonic waves can also be used to induce the disturbance and the relaxation can be monitored with Nuclear Magnetic Resonance (NMR).

TECHNIQUES USED FOR MONITORING CONCENTRATIONS

For slow reactions, the composition of the reaction mixture can be determined while the reaction is in progress either by withdrawing a small sample or by monitoring the bulk. This is known as a real time analysis. Another option is to use the quenching method, in which reaction is stopped a certain time after initiation so that the composition may be analysed at leisure. Quenching may be achieved in a number of ways such as sudden cooling, adding a large amount of solvent, rapid neutralisation of an acid reagent, removal of a catalyst or addition of a quencher. The key requirement is that the reaction must be slow enough (or the quenching method fast enough) for little reaction to occur during the quenching process itself. Often, the real time and quenching techniques are combined by withdrawing and quenching small samples of the reaction mixture at a series of times during the reaction.

The composition of the reaction mixture may be followed in any one of a variety of different ways by tracking any chemical or physical change that occurs as the reaction proceeds. e.g.

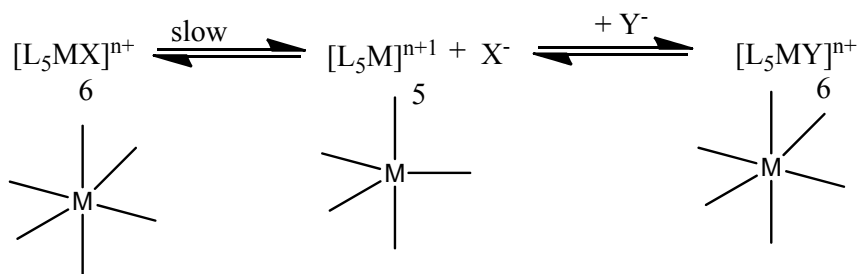
- For reactions in which at least one reactant or product is a gas, the reaction's progress may be followed by monitoring the pressure, or possibly the volume change.
- For reactions involving ions, conductivity or pH measurements may often be employed.
- If the reaction is slow enough, the reaction mixture may be titrated.
- If one of the components is coloured then colourimetry may be appropriate.
- Absorption or emission spectroscopy are common (more on these later)
- For reactions involving chiral compounds, polarimetry (measurement of optical activity) may be useful.

- Other techniques include mass spectrometry, gas chromatography, NMR/ESR, and many more.

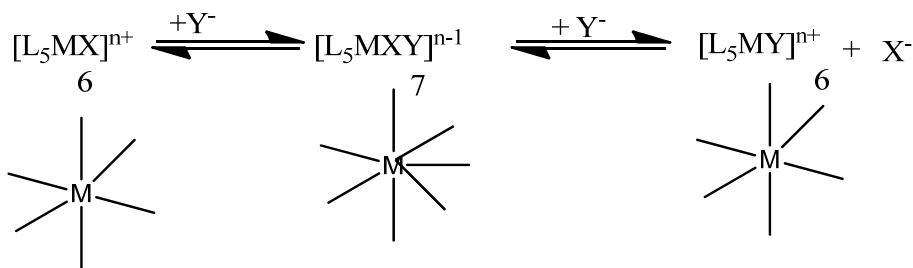
3.4 REACTION MECHANISM IN COMPLEXES

Reaction mechanism is the pathway leading to the formation of the product or attainment of equilibrium in a given reaction. There are two extreme cases in reaction mechanisms of complexes; S_N1 (substitution Nucleophilic unimolecular reaction) and S_N2 (substitution Nucleophilic bimolecular reaction)

In S_N1 mechanism, only one species occurs at the transition state. In such a reaction, the departing ligand will leave before the attachment of the incoming ligand, leading to a reduction in coordination number at the transition state. An illustration is shown below, where X represents the leaving group and Y the entering group.



The first stage is the rate determining step because it is slow. The expression for the rate law can be written as $R = k \{[L_5MX]^{n+}\}$ where k is the rate constant and not equilibrium constant. In S_N2 mechanism, two species appear at the transition state. The incoming ligand gets attached before the departure of the leaving group leading to an increase in coordination number at the transition state. The rate of the reaction is dependent on the concentrations of both the reacting complex and the incoming ligand. The expression for rate law can be presented as $R = k \{[L_5MX]^{n+}\}[Y^-]$



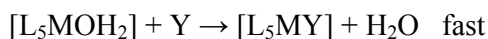
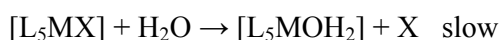
Most often, complex reactions do not really fall into these two (S_N1 and S_N2) extremes because the transition states in most cases are very difficult to identify (or may not be

detected). However, mechanisms of reactions in complexes are between these extremes. When the contribution of the incoming group to the transition state is small the reaction mechanism can be approximated to be S_N1 but if the contribution is significant, the reaction is approximated to S_N2 .

Factors that influence the rate of complex reactions are solvent intervention, ion-pair formation and conjugate-base formation

SOLVENT INTERVENTION

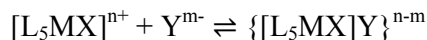
Since most reactions of complexes are studied in aqueous system where water can act as ligand and abundant in extremely high concentration, a possible reaction path is shown below
Where X and Y are neutral ligands



Since the concentration of water is constant, the reaction can be considered as S_N1

ION-PAIR FORMATION

In a reaction involving positively charged complex and negatively charged ligand, the two reactants will be attracted together by their electric charges. The greater the charges, the greater the attractive force between the reactants. This will lead to equilibrium.



$$K = \frac{\{[L_5MX]Y\}^{n-m}}{\{[L_5MX]^{n+}\}[Y^{m-}]}$$

$$\{[L_5MX]Y\}^{n-m} = K \{[L_5MX]^{n+}\}[Y^{m-}]$$

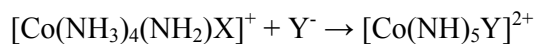
If the reaction proceeds with speed by formation of the ion pair, the rate of the reaction can be expressed as $R = k K \{[L_5MX]^{n+}\}[Y^{m-}] = k'' \{[L_5MX]^{n+}\}[Y^{m-}]$, where k'' as both kinetic and thermodynamic contributions. This reaction can be considered as S_N2 after further investigation on the transition state composition.

CONJUGATE-BASE FORMATION

There are two possibilities with a pH dependent reaction, these possibilities are explained below;

- The rate law may include $[OH^-]$ such that the hydroxyl group attacks the metal complex leading to S_N2 reaction
- The $[OH^-]$ may be involved in deprotonation in such a way that it reacts fast to remove a proton from a protonated ligand in the reacting metal complex forming a conjugate base (CB) which then reacts slowly to substitute for the leaving group.





In the presence of a protonic hydrogen (ionisable), this proposed reaction pathway is favourable and the rate law follow $\text{S}_{\text{N}}1$ (CB), this implies that the reaction is dependent on the concentration of the reacting complex in the presence of OH^- .

In the absence of a protonic hydrogen or if the removal of proton in the above reaction is slow, the $\text{S}_{\text{N}}2$ is most suitable reaction mechanism.

$$R = \{[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}\}[\text{OH}^-]$$

4.0 CONCLUSION

In conclusion, the thermodynamic stability studies of complexes provide insight to the special stability of chelate complexes and their applications. Stability of chelate is attributed to increase in entropy. Also, Kinetics of reactions shows the nature of reactions in complexes with different mechanisms that are similar to, but not exactly, $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$.

5.0 SUMMARY

- Thermodynamic Equilibrium of complexes has been studied and the stability constants estimated.
- The ring formation and ring sizes effects on special stability of chelate complexes have been studied and it has been established that 5-membered ring chelates are very stable.
- Kinetic studies of complexes show that reactions of complexes are only approximate to $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ and that the reactions mechanisms are influenced by solvent, ion-pair formation and pH.

6.0 TUTOR-MARKED ASSIGNMENT (TMA)

Questions

1. Identify the ligand that will give most stable complex with reason
 - i. a. NH_3 b. ethylenediamine c. 1,3-propylenediamine
 - ii. a. R-COOH b. $^-\text{OOC-COO}^-$ c. $^-\text{OOC-CH}_2\text{-COO}^-$
 - iii. a. $\text{Na}_2\text{EDTA}^{2-}$ b. EDTA^{4-} c. H_4EDTA
 - iv. a. pyridine b. 2, 2' bipyridine c. pyrole

- Given that $\text{Cd}^{2+} + 4\text{CH}_3\text{NH}_2 \rightleftharpoons [\text{Cd}(\text{NH}_2\text{CH}_3)_4]^{2+}$ has $\Delta H = 57.3\text{KJ/mol}$ and $\beta = 10^{6.53}$ calculate the ΔG and ΔS for the reaction
- Given that $\text{Cd}^{2+} + 2\text{en} \rightleftharpoons [\text{Cd}(\text{en})_2]^{2+}$ has $\Delta H = 56.4\text{KJ/mol}$ and $\beta = 10^{10.58}$ calculate the ΔG and ΔS for the reaction, gas constant, R , is 8.314J/Kmol
- Comment on the results obtained in 2 and 3 in relation to chelate effect
- Write the equations and stepwise formation constants for the reaction in question 2
- Explain the techniques used in kinetic studies briefly

7.0 REFERENCES/FURTHER READINGS

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