Indira Gandhi National
Open University
School of Sciences

BCHCT-137

COORDINATION CHEMISTRY, STATES OF MATTER AND CHEMICAL KINETICS

Block

2

COORDINATION CHEMISTRY

Course Design Committee

Prof. Gurmeet Singh,
Department of Chemistry,
University of Delhi, Delhi

Dr. Sushmita Choudhury (Retd.),
Gargi College, University of Delhi
New Delhi

Dr Pritam Mukhopadhyay ,
Associate Professor, School of Physical Sciences, Jawaharlal Nehru University.
New Delhi

Dr. Vijay Sarda (Retd.)
Department of Chemistry
Zakir Husain Delhi College
University of Delhi, Delhi

Prof. B. S. Saraswat (Retd.)
School of Sciences, IGNOU,
New Delhi

School of Sciences,
IGNOU, New Delhi 110068

Prof. M.S. Nathawat
Prof. Sunita Malhotra
Prof. B.I. Fozdar
Prof. Javed A. Farooqi
Prof. Sanjiv Kumar
Prof. Lalita S. Kumar
Prof. Kamalika Banerjee

Block Preparation Team

Prof. Kamalika Banerjee
School of Sciences, IGNOU
New Delhi

Dr. Sushmita Choudhury (Retd.) (Editor)
Deptt. of Chemistry, Gargi College,
University of Delhi

Course Coordinator: **Prof. Kamalika Banerjee**

PRINT PRODUCTION

Mr. Sunil Kumar
AR(P), SOS, IGNOU

Acknowledgements: Sh. Sarabjeet Singh for word processing and CRC preparation;
Sh. Deepak Kumar for word processing.
The utilisation of some contents of Inorganic Chemistry (CHE-02) course (Unit 12, 13 and 14) is gratefully acknowledged

July, 2021

ISBN:

Further information on Indira Gandhi National Open University courses may be obtained from the University's office at Maidan Garhi, New Delhi-110068 or IGNOU website www.ignou.ac.in

Printed and published on behalf of Indira Gandhi National Open University, New Delhi by the Registrar, MPDD, IGNOU.

Printed at:

BLOCK 2: COORDINATION CHEMISTRY

In the previous block of this course you have learnt about transition and inner-transition metals. You have been introduced to complex formation properties of transition metals.

In this block you will study about the coordination compounds and the crystal field theory.

Unit 4 deals with Werner's coordination theory and thereafter definitions of various terms relate to coordination chemistry are discussed. A detailed discussion on how to name the coordination compounds according to the latest IUPAC rules have been included.

In Unit 5 you will study the details of isomerism in coordination compounds. The theories of bonding related to coordination compounds, namely, the valence bond theory, as well as the inner and outer orbital complexes of some transition metals have been discussed.

Unit 6 deals with the crystal field theory, specially in octahedral complexes. Factors affecting the magnitude of crystal field splitting energy and the spectrochemical series are discussed here.

In Unit 7 the concepts of crystal field theory have been extended to tetrahedral as well as square planar complexes. Tetragonal distortion of octahedral geometry, square planar coordination and some common applications of complexes have been discussed.

Expected Learning Outcomes

After studying this block, you should be able to:

- understand Werner's coordination theory;
- define the terms complex, coordination compounds, coordination entity, central atom, ligand, oxidation state, chelation, coordination polyhedron and coordination number;
- know the IUPAC rules for naming coordination compounds;
- name the coordination compounds according to IUPAC rules;
- write the formulae of coordination compounds if the systematic names are provided;
- describe the types of isomerism in coordination compounds;
- discuss the theories (valence bond theory) of bonding as applied to coordination compounds;
- discuss the inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu;
- discuss the crystal field theory;
- describe the crystal field splitting in octahedral complexes and calculate the crystal field stabilization energy (CFSE);

- discuss the crystal field effects in weak and strong fields;
- come to know about the factors affecting the magnitude of crystal field splitting energy;
- get introduced to the spectrochemical series;
- understand crystal field splitting in tetrahedral complexes;
- compare the crystal field stabilization energy(CFSE) for octahedral and tetrahedral complexes;
- understand the tetragonal distortion of octahedral geometry(Jahn-Teller distortion);
- learn about formation of square planar complexes and note the crystal field splitting in such cases; and
- learn about some common applications of complexes including their magnetic behaviour.

UNIT 4

COORDINATION COMPOUNDS-I

Structure

4.1 INTRODUCTION

In Units 1 and 2 of the previous block you have learnt about transition metals and their tendency to form coordination compounds or complexes. In this unit we shall study such complexes in greater detail. It is appropriate to state that their chemistry is interesting and their importance in chemical and biochemical processes is rapidly increasing.The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry; they have a wide variety of physical and chemical properties which are quite different from normal salts. These differences arise due to the differences in their structures and nature of bonding.

Chlorophyll, haemoglobin and vitamin B_{12} are coordination compounds of magnesium, iron and cobalt respectively. A variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

We should also remember about the differences between double salts and coordination compounds. Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. Carnallite and potassium alum are addition compounds containing two salts. Now there are two types of addition compounds. If they lose their identity in solution they are known as double salts, but if they retain their identity in

solution they are known as complexes. When crystals of potassium alum are dissolved in water, it shows the properties of K^+, Al^{3+} and SO_4^{2-} ions. So it is an example of double salt which exists only in the crystalline state. But, when coordination compounds dissolve they do not form simple ions – Cu^{2+}, or Fe^{2+} and CN^- - but instead their complex ions remain intact. Thus the cuproammonium ion $[Cu(NH_3)_4(H_2O)_2)]^{2+}$ and the ferrocyanide ion $[Fe(CN)_6]^{4-}$ exist as distinct entities both in the solid and in solution. In view of a special mode of bonding called 'coordination' being involved in the formation of complexes, they are also termed as coordination compounds. In this unit we shall briefly look at some of the basic definitions related to coordination compounds, classification of these compounds and the basic rules for naming these compounds. In the next unit we will be dealing with isomerism in coordination compounds and also about the theories of bonding related to these compounds.

Expected Learning Outcomes

After studying this unit, you should be able to:

- understand Werner's coordination theory;
- define the terms complex, coordination compounds, coordination entity, central atom, ligand, oxidation state, chelation, coordination polyhedron and coordination number;
- know the IUPAC rules for naming coordination compounds;
- name the coordination compounds according to IUPAC rules; and
- write the formulae of coordination compounds if the systematic names are provided.

4.2 COORDINATION CHEMISTRY: WERNER'S COORDINATION THEORY

In 1913, Alfred Werner received the Nobel prize for discoveries in the field of inorganic chemistry for his work on the linkage of atoms and the coordination theory.

In the early period of development of the chemistry of complexes, a number of theories were put forward in order to explain in a simple manner the formation of a new compound by the combination of two or more stable and apparently saturated compounds. Even though these early theories were not fully successful in many ways, but chemists were motivated to perform new experiments in order to prove or disprove a proposed theory. Thus more experimental data were generated which helped those who were interested to understand the nature of the chemical bond. Werner did pathbreaking work in 1893 and proposed a theory which explained a number of experimental facts. Though the modern theories are more encompassing in nature yet the basic postulates introduced by Werner are still valid to this day. In the next section we shall discuss Werner's theory in the context of coordination chemistry.

4.2.1 Werner's Theory

Based on the study of a large number of compounds, Werner gave the following postulates:

- Metal atoms in complexes possess two types of valencies namely, principal or primary and auxiliary or secondary. In modern terminology primary valency is the oxidation state and the secondary valency the coordination number. (The definition of coordination number is given later in section 4.3).
- A metal satisfies both types of valencies. Primary valencies are always satisfied by anions but the secondary valencies can be satisfied either by anions and/or neutral molecules.
- Every metal atom has a fixed number of auxiliary valencies.
- The secondary valencies show directional properties. In other words secondary valencies are directed in space around the central ion.

Werner showed that his postulates are consistent with experimental observations. He made use of basically three kinds of experiments to justify his conclusions. Let us look at some of these experiments.

1. It is a well-known fact that a weaker base in a compound is replaced on reacting with a stronger base. For example, ammonia is released from ammonium salts in reaction with a strong base like NaOH. However, when a complex containing ammonia molecules like $[Co(NH_3)_6]^{3+}$ is treated with NaOH, no ammonia is released. It is not released even on treatment with strong acids under mild conditions. A reasonable conclusion would be that the ammonia molecules are bound in a different manner to the metal ion.
2. The qualitative and quantitative presence of halogen in ionic form can be established by treating the compound with silver nitrate which would give a precipitate of silver chloride. Example, a compound with a composition $CoCl_3.5NH_3$ on treatment with $AgNO_3$ gives two moles AgCl precipitate per mole of the compound. From this observation the obvious conclusion is that one chlorine is bound to metal in a different way from the other two. Let us understand this in detail.

   Cobalt has a primary valency (oxidation state) of three and exhibit secondary valency (coordination number) of 6.

   - **$CoCl_3.6NH_3$ Complex:** In this compound, the coordination number of cobalt is 6 and all the 6 secondary valencies are satisfied by NH_3 molecules. The 3 primary valencies are satisfied by chloride ions. On the addition of silver nitrate, these chloride ions are instantaneously precipitated. The total number of ions in this case is 4, three chloride ions and one complex ion. The central ion and the neutral molecules or ions satisfying secondary valencies are written in a square bracket while writing the formula of the compound. Hence the complex may be written as **$[Co(NH_3)_6]Cl_3$** .(Nomenclature will be dealt in detail in section 4.4.)
   - **$CoCl_3.5NH_3$ complex:** In this compound the coordination number of cobalt is also 6 but the number of NH_3 molecule is decreased

to 5 from 6 and one remaining position is now occupied by chloride ion. So one chloride ion serves the dual purpose of satisfying the primary as well as secondary valency. Thus the nature of bonding of one chloride ion is different from the othere two and when treated with silver nitrate only two chloride ions will be precipitated as silver chloride.The complex is formulated as $[Co(NH_3)_5Cl]Cl_2$.

- **$CoCl_3.4NH_3$ complex:** In this compound, two chloride ions exhibit dual behaviour of satisfying both primary and secondary valencies. This compound will give precipitate of only one Cl^- ion when treated with silver nitrate and so the total number of ions in this case is 2. So the formula is **$[Co(NH_3)_4Cl_2]Cl$**.

- **$CoCl_3.3NH_3$ complex:** In this compound, three chloride ions satisfy primary as well as secondary valency. No Cl^- will be precipitated on the addition of silver nitrate at room temperature. Therefore, the complex compound behaves as neutral non conducting molecule. The formula may be depicted as **$[Co(NH_3)_3Cl_3]$**.

So from the above discussions, you will be able to follow that the same chloride ion can bind in different ways with the metal in a coordination compound.

3. Measurement of molar conductance of a salt solution of approximately 10^3 *M* concentration can tell us the number of ions present in solution. For instance a molar conductance value of around 520 ohm^{-1} mol^{-1} cm^2 indicates the presence of five ions in solution whereas values around 400, 230 and 100 ohm^{-1} mol^{-1} cm^2 indicate 4, 3 and 2 ions respectively. Werner analysed a series of platinum ammine complexes and arrived at correct formulation in each case on the basis of molar conductance measurements. These are given in Table 4.1.

Table 4.1: Molar conductance values of platinum complexes

Formula of the compound on the basis of analysis	Molar conductance ($ohm^{-1}mol^{-1}$ cm^2)	Number of ions indicated	Werner's formulation of the compound
$PtCl_4.6NH_3$	523	5	$[Pt(NH_3)_6]Cl_4$
$PtCl_4.4NH_3$	229	3	$[Pt(NH_3)_4Cl_2]Cl_2$
$PtCl_4.3NH_3$	97	2	$[Pt(NH_3)_3Cl_3]Cl$
$PtCl_4.2NH_3$	0	0	$[Pt(NH_3)_2Cl_4]$
$PtCl_4.NH_3.KCl$	109	2	$K[Pt(NH_3)Cl_5]$
$PtCl_4.2KCl$	257	3	$K_2[PtCl_6]$

4. Werner argued that since the secondary valencies have a definite orientation in space, complexes should show stereoisomerism. In the case of a six coordinated complex three geometrical shapes are possible namely, planar, prismatic or octahedral.

Werner argued that a disubstituted complex of the type Ma_4b_2 would give three isomers if its structure is either planar or prismatic but only two if it is octahedral as shown in Fig. 4.1.

In all the compounds with the formula Ma_4b_2 synthesised by Werner, he could isolate only two isomers. This indicated that the structure was probably octahedral. For example, he could isolate only two geometrical isomers for the complex $[Co(NH_3)_4Cl_2]Cl$ clearly indicating an octahedral geometry, the *cis*- and *trans*- forms of which are illustrated in Fig. 4.2.

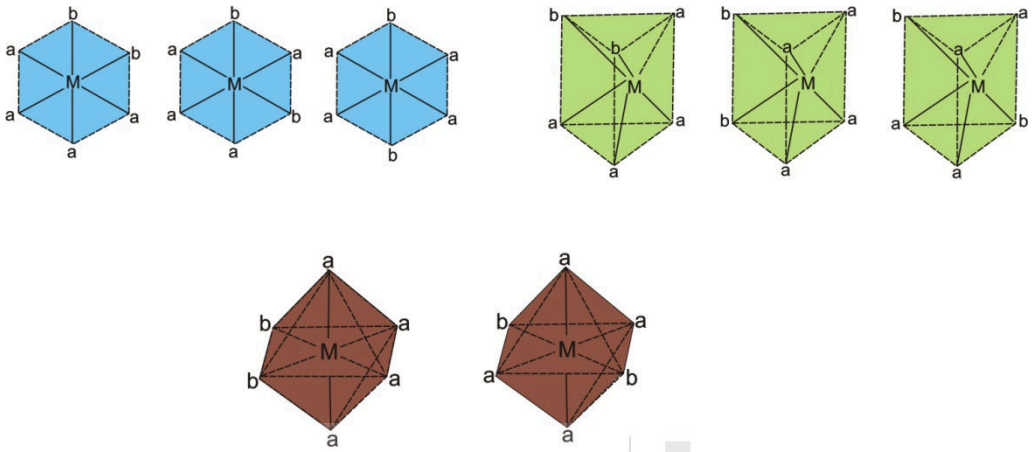


Fig. 4.1: Three possible geometries of a 6-coordinated Ma_4b_2 complex.

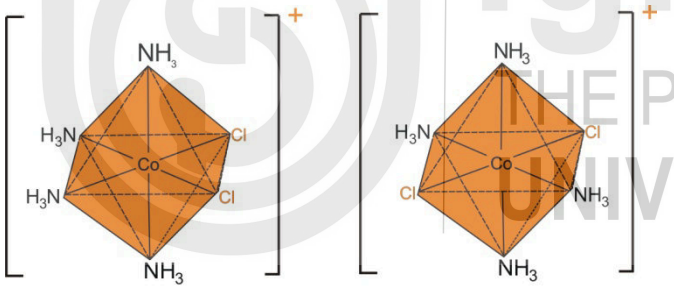


Fig. 4.2: Possible number of isomers for the octahedral complex ion $[Co(NH_3)Cl_2]^+$.

The final confirmation of the directional properties of auxiliary valencies and of the predicted geometry of a molecule came in the form of isolation of optical isomers for a number of complexes. Two such examples are shown in Fig. 4.2.

One of the main objections raised at the time when Werner introduced these ideas was that there was no theoretical justification for arbitrarily introducing two types of valency– primary and secondary. However, this was soon overcome when Lewis introduced his idea on covalency and electrovalency. It was thus realised that Werner's primary and secondary valencies were just alternative names for electrovalent and covalent bonds, respectively.Thus, the properties assigned to primary and secondary valencies become a natural consequence of bond properties given by Lewis.

However, there were inherent limitations with such a simple approach. For example, the following experimental facts cannot be explained on the basis of such a simple model:

Those complexes which exchange their ligands within a short time of mixing the reactants are known as labile complexes while others are referred to as inert complexes.

- certain metal ions show stronger tendency to form complexes compared to others;
- certain metal ions can form complexes with different coordination numbers as well as in different oxidation states;
- some metal complexes are very reactive and exchange ligands in typical substitution reactions whereas others do not;
- a particular geometrical shape appears to be preferred by some metals;
- most of the transition element complexes are coloured.

The above developments can also be cited as a typical example of the manner in which scientific theories grow and are refined in any particular field. Although Werner's theory could explain most of the observations and facts known at that time, yet many observations made by him and later by other workers indicated the need for further improvements in the theory of complex compounds. However Werner's theory still remains a simple theory to be introduced to understand these compounds.

The next major step in understanding the nature of bond in complexes was the application of the well-known concepts of valence bond theory developed by Pauling. Valence bond theory places main emphasis on the atomic orbitals of the metal ion which are involved in the bond formation. Once these were identified, the stereochemistry, geometry and the magnetic properties could be better interpreted in terms of suitable combinations of these orbitals.

We have used atom in a general sense which could equally mean an ion.

4.3 SOME BASIC DEFINITIONS

Coordination chemistry was pioneered by Nobel Prize winner Alfred Werner. Inorganic chemistry was not a prominent field until Werner studied the several forms of metal-ammine complexes such as $[Co(NH_3)_6Cl_3]$. He tried to distinguish ionized chloride from the coordinated chloride formulated by the complex formula and explained structure of the cobalt complexes. Thereafter the concept of coordination complexes came up. Werner's coordination theory became the base of modern coordination chemistry.

Some of the terms which we use in connection with coordination compounds carry specific meaning and thus form a kind of language for coordination chemistry. Let us discuss them one by one. We will start with the definition of a coordination compound which is more commonly called a complex compound or simply a complex.

$KAl(SO_4)_2, 12H_2O$ is a mixture of K_2SO_4 and $Al_2(SO_4)_3$, which have crystallised together with water of crystallisation.

Complex: A very general definition of complex is, 'A compound that results from the combination of a central atom or ion and a group of atom/ions/molecules surrounding it'. But we will avoid such a broad definition and define a complex as:

"A compound that results when a central metal atom or ion is chemically bonded to a group of ions or/and molecules such that the normal valency of the central atom is exceeded".

These compounds are usually formed by the donation of pair of electrons to the central metal ion by the group of ions or molecules. The bond so formed is called a coordinate bond and hence the name coordination compound. But you will not find this simple donor-acceptor bond approach for all types of coordination compounds. In this unit we will discuss those complexes where the central atom or ion is a metal or more specifically a transition metal. Double salts, addition products and organometallic compounds are not discussed here. A complex shows different properties from the original constituents and generally does not dissociate into component ions. For example, $[Co(NH_3)_6]Cl_3$, here it dissociates as $[Co(NH_3)_6]^{3+}$ and chloride ions. A complex compound could be neutral, cationic or anionic depending upon the total charge carried by the complex species. For example, neutral - $[Cd(CN)_2(en)_2]$, cationic- $[Cu(H_2O)_6]^{2+}$, anionic - $[Fe(CN)_6]^{4-}$.

Organometallic compounds are those compounds where the central metal atom or ion is directly attached to at least one carbon atom of an organic molecule.

Coordination Entity: A coordination compound is any compound that contains a coordination entity. It is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of other atoms or groups of atoms, each of which is called a ligand. While writing a formula for a complex, the charged or uncharged coordination entity is enclosed in square brackets.

Classically, a ligand was said to satisfy either a secondary or a primary valence of the central atom and the sum of these valencies (often equal to the number of ligands) was called the coordination number.

Examples: $[Co(NH_3)_6]^{3+}$, $[PtCl_4]^{2-}$, $[Fe_3(CO)_{12}]$

Central Atom: The central atom is the atom in a coordination entity which binds other atoms or groups of atoms (ligands) to itself. It has the central position in the coordination entity. Can you say which are the central atoms in $[Ni(H_2O)_4Cl_2]$, $[Co(NH_3)_6]^{3+}$ and $[PtCl_4]^{2-}$? Yes, they are nickel, cobalt and platinum, respectively.

The **coordination sphere** consists of the central metal ion or atom and its attached ligands. When you write the formula, you have to enclose the coordination sphere within brackets.

The root of the word ligand is often converted into other forms, such as to ligate, meaning to coordinate as a ligand, and the derived participles, ligating and ligated. The terms 'ligating atom' and 'donor atom' are used interchangeably.

Ligand: The ions and/or molecules which are directly attached to the central atom/ion are called ligands. A ligand could be an ion, an atom or a neutral molecule but should contain at least one atom which can donate a pair of electrons to the metal ion for the bond formation. Since the ligands are directly attached to the metal ion, they are said to be in the first coordination sphere of the central atom. Remember that the dentate character is a property of a ligand representing a number of coordinating atoms. Now we will discuss the different types of ligands based on their denticity.

All coordination complexes contain a metal atom or ions as the central part of the structure. Bonded to the metal are molecules or ions called **ligands** (from the Latin verb *ligare,* meaning 'to bind").

Monodentate Ligands: The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the centre through only one atom. Examples:

Ions	when it is a ligand
chloride	chlorido
water	aqua
hydroxide	hydroxido
ammonia	ammine

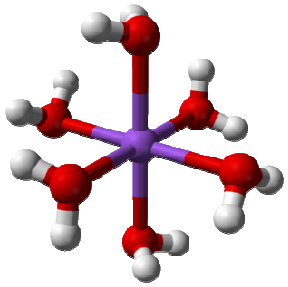


Fig. 4.3: Central atom with six monodentate ligands attached.

Bidentate (Didentate) Ligands: Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Eg.,1,2-diaminoethane which was earlier referred to as ethylenediamine (en), oxalate ion (ox), CO_3^{2-}, SO_4^{2-}, H_2NCH_2COOH (glycine). In Fig. 4.4 you can see the nitrogen atoms on the edges of 1,2- diaminoethane. Each have two free electrons that can be used to bond to a central metal atom or ion.

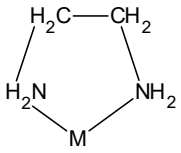


Fig. 4.4: 1,2-diaminoethane (en) is an example of a bidentate ligand.

Polydentate Ligands: They range in the number of atoms used to bond to a central metal atom or ion. Example EDTA, a hexadentate ligand as shown in Fig. 4.5 which can bind a metal via multiple "teeth".

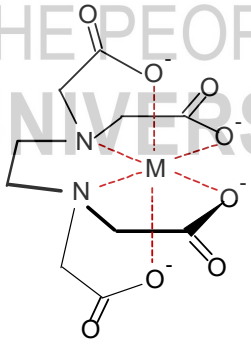
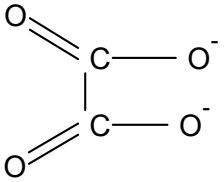
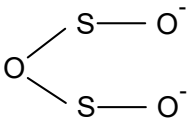
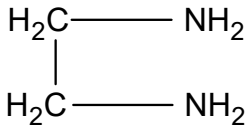
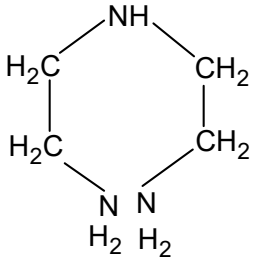
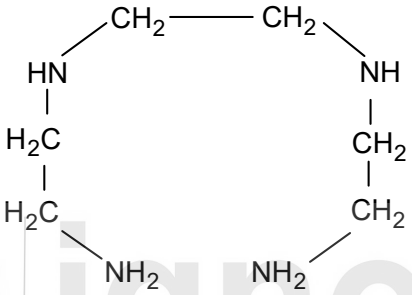
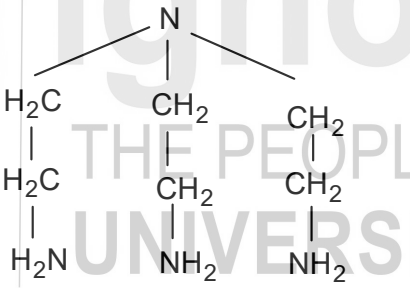
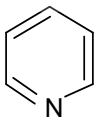
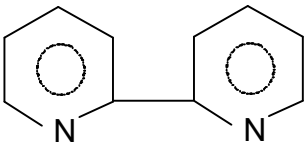
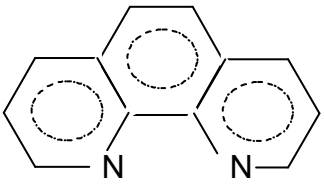
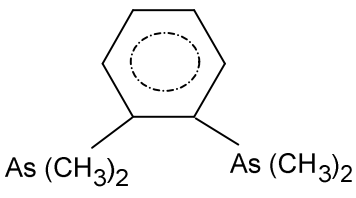


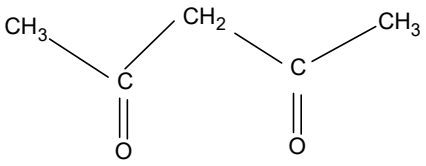
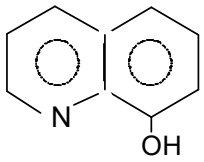
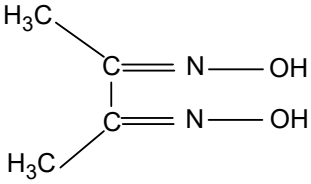
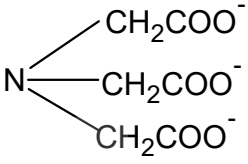
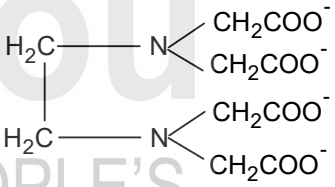
Fig. 4.5: EDTA bound to a generic transition metal.

Table 4.2 gives a list of ions molecules commonly used as ligands.

Table 4.2: List of ions/molecules commonly used as ligands

Name	Abbreviation	Structure
Oxalate anion	ox	
Thiosulphate anion	$S_2O_3^{2-}$	

Thiocyanate anion	---	SCN^-
Cyanate anion	---	OCN^-
Ethylenediamine or 1,2- diaminoethane	en	
Diethylenetriamine	dien	
Triethylenetetraamine	trien	
tris(2-aminoethyl) amine	tren	
Pyridine	py	
2,2'-Bipyridine	bipy	
1,10-Phenanthroline	phen	
1,2-Phenylenebis (diarsine)	diars	

Acetylacetone	acacH	
8-Hydroxyquinoline	oxineH	
Dimethylglyoxime	dmgH	
Glycinate anion	gly	$H_2NCH_2COO^-$
Nitrilotriacetate anion	nta	
Ethylenediamine-tetraacetate anion	edta	

The 'κ convention' is the latest one in which the letter κ (Kappa) is used to indicate the atom of ligation.

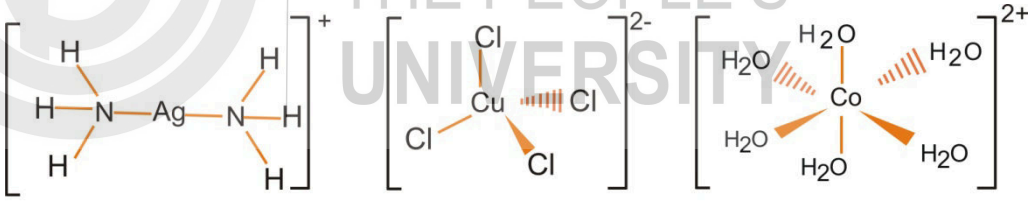


Fig. 4.6: The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[CuCl_4]^{2-}$ and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively.

$[Fe(H_2O)_5NO]^{2+}$ is responsible for the brown ring test for NO_3^- ion.

Ambidentate ligands: Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. They have two donor atoms but both are not used simultaneously. An example of this is thiocyanate, −SCN−, which can attach at either the sulfur atom or the nitrogen atom. If it attaches to a metal atom by the N atom, it gives thiocyanato-κ*N* complexes (old name is isothiocyanato) and if by the S atom, it gives thiocyanato-κ*S* complexes (old name is thiocyanato). NO_2^- is one more example, as M-NO_2^- the ligand is nitrito-κ*N* (old name is nitro) and as M-ONO it is nitrito-κ*O* (old name is nitrito).

Oxidation State: Oxidation state of an atom is defined as an apparent or formal charge on that particular atom in a molecule. The oxidation state of a central atom in a coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. A Roman numeral is used to denote it. In majority of the cases it is easily identified. For example, a complex $[Cu(NH_3)_4]Cl_2$ has the

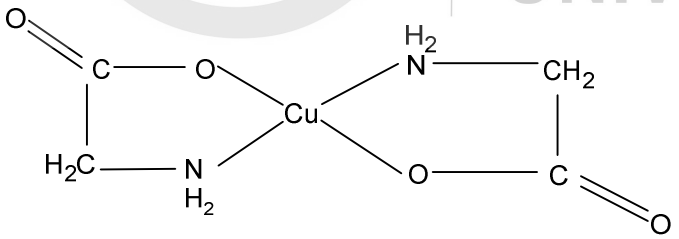
copper ion in the oxidation state of +2 since NH_3 molecules are neutral or do not carry any net charge. Note that the valency is not the same as oxidation state. We can say that in the above complex, it may not be easy to find out the oxidation state of the metal ion from the knowledge of the formula of the complex only. Suppose we consider a complex like $[Fe(H_2O)_5NO]^{2+}$. We also know that NO can exist as a neutral entity having no charge or as NO^- or NO^+. Now if in the above compound NO is acting as a neutral molecule, the oxidation state of the metal is +2. Finally if it is present in the form of NO^+, Fe would have +1 oxidation state. Thus substantial information is required before the oxidation state of the metal ion can be decided.

In certain cases, the formalism does not give acceptable central atom oxidation states. Because of such ambiguous cases, the net charge on the coordination entity is preferred in most nomenclature practices. Let us follow the examples given below:

	Formula	Ligands	Central Atom Oxidation State
1.	$[Co(NH_3)_6]^{3+}$	$6NH_3$	III (+3)
2.	$[CoCl_4]^{2-}$	$4Cl^-$	II (+2)
3.	$[Co(CN)_5H]^{3-}$	$5CN^- + 1H^-$	III (+3)
4.	$[Fe(CO)_4]^{2-}$	$4CO$	–II (-2)

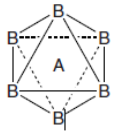
Chelation

Chelation is a process in which a polydentate ligand binds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent.



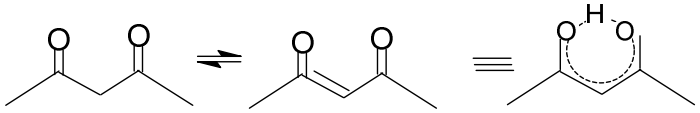
Oxidation state is an index derived from a simple and formal set of rules and it is not a direct indicator of electron distribution.

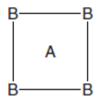
Finally, a multidentate ligand which combines with a metal ion through two or more atoms on the ligand simultaneously, is called a chelating agent. The resulting complex is called a chelate compound. Consider the example of copper glycinate complex where two glycinates are combined with one copper ion as shown above. The glycinate ion is joined through N and O to the copper ion simultaneously, Here, glycinate is acting as chelating agent.



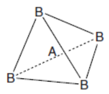
Octahedral coordination polyhedron

Chelating and cyclic ligands: **Acetylacetonate** ($acac^-$) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. With divalent metal ions, $acac^-$ forms neutral, volatile complexes such as $[Cu(acac)_2]$ and $[Mo(acac)_2]$.





Square planar coordination polygon



Tetrahedral coordination polyhedron

- **Crown ethers** such as 18-crown-6 2,2'Bipyridine are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.

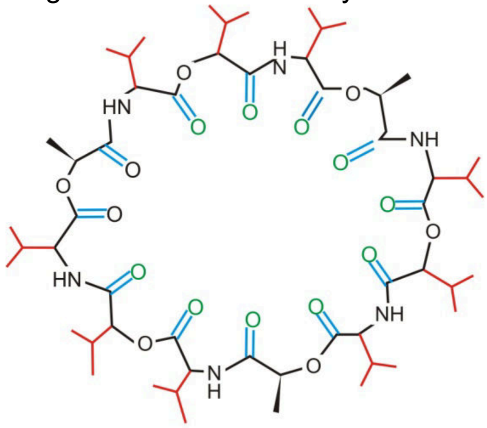


Fig.4.7: 18-crown-6 2,2'-Bipyridine.

Coordination Polyhedron

It is standard practice to regard the ligand atoms directly attached to the central atom as defining a coordination polyhedron (or polygon) about the central atom. Thus $[Co(NH_3)_6]^{3+}$ is an octahedral ion and $[PtCl_4]^{2-}$ is a square planar ion. In such cases, the coordination number will be equal to the number of vertices in the coordination polyhedron. This may not hold true in cases where one or more ligands coordinate to the central atom through two or more atoms which lie near to each other. Atoms which lie adjacent are treated as a single ligand occupying one vertex of the coordination polyhedron.

Coordination Number

Coordination Number is the number of atoms, ions, or molecules that a central atom or ion holds as its nearest neighbours in a complex or coordination compound or in a crystal. So, the coordination number of the central metal ion or atom is the number of donor atoms bonded to it. e.g.:

- The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two.
- For copper(+2) ion in $[CuCl_4]^{2-}$, coordination number is four.
- Cobalt(+2) ion in $[Co(H_2O)_6]^{2+}$ has coordination number six.
- Copper (+2) ion in $[Cu(en)_2]^{2+}$ has coordination number 4.

You may try the following SAQ which is based on the above definitions.

SAQ 1

Determine the coordination number and the oxidation state of the transition metal ion in each of the following complex:

(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Pt(NH_3)_2Cl_2]$ (d) $[CuF_4]^{2-}$

4.4 NOMENCLATURE

The 2004 IUPAC draft recommends that anionic ligands will end with –ido so that chloro would become chloride, etc.

In this section we will learn the rules for nomenclature i.e. naming the complexes. You have learnt about development of coordination theory by Werner in section 4.2. As it was based on coordination theory, coordination compounds were considered to be formed by addition of independently stable compounds to a simple central compound. The same additive principle was used for naming them. Thus names of the added compounds and the central simple compound were combined.

Example: Addition of ligands to a central atom, $Ni^{2+} + 6H_2O$ gives $[Ni(OH_2)_6]^{2+}$, name: hexaaquanickel(II)

A summary of the rules of nomenclature as recommended by the International Union of Pure and Applied Chemistry (IUPAC) is given below:

- If the complex is a salt, the cation is named first followed by the name of the anion. For example, in naming $K_2[PtCl_6]$ we shall name potassium first followed by the name of the anion. In another example of $[Cu(NH_3)_4]Cl_2$, the name of the cation, $[Cu(NH_3)_4]^{2+}$, will be placed before chloride ion. The cation is named first in both positively and negatively charged coordination entities.
- For the complex entity, whether it is in cationic, anionic or neutral form, the name of the ligand(s) is put before the name of the metal atom. But you have to follow the reverse order while writing the formula of the compound. For example in $[Cu(NH_3)_4]Cl_2$, we shall name the four ammonia molecules first followed by copper and finally the presence of chloride is mentioned; but in writing the formula, copper is written before ammonia molecules.

$[Re_2Cl_8]^{2-}$ is octachloridodirhenate(III)

- Systematic and alternative names for some common ligands are given in Tables 4.2 contains the names of common organic ligands whereas Table 4.3 contains the names of other simple molecules and ions that may act as ligands. The general features are as follows:
  - Names of anionic ligands, whether inorganic or organic, are modified to end in ‘o’. In general, if the anion name ends in ‘ide’, ‘ite’ or ‘ate’, the final ‘e’ is replaced by ‘o’, giving ‘ido’, ‘ito’ and ‘ato’, respectively. In particular, alcoholates, thiolates, phenolates, carboxylates, partially dehydronated amines, phosphanes, etc. are in this category. Also, it follows that halide ligands are named fluorido, chlorido, bromido and iodido, and coordinated cyanide is named cyanido. In its complexes, except for those of molecular hydrogen, hydrogen is always treated as anionic. ‘Hydrido’ is used for hydrogen coordinating to all elements including boron.
  - Names of neutral and cationic ligands, including organic ligands, are used without modification (even if they carry the endings ‘ide’, ‘ite’ or ‘ate’).
  - Enclosing marks are required for neutral and cationic ligand names, for names of inorganic anionic ligands containing multiplicative prefixes

(such as triphosphato), for compositional names (such as carbon disulfide), for names of substituted organic ligands (even if there is no ambiguity in their use), and wherever necessary to avoid ambiguity. However, common ligand names such as aqua, ammine, carbonyl, nitrosyl, methyl, ethyl, etc., do not require enclosing marks, unless there is ambiguity when they are absent. For example:

1. $[Co(NH_3)_5Cl]Cl_2$
   pentaamminechloridocobalt(III) chloride
2. $[AuXe_4]^{2+}$
   tetraxenonidogold(II)

Some ligands and their endings are given below:

Table 4.3: Some ligands and their endings.

S. No.	Ligands	Endings
1.	Cl^-	chlorido
2.	CN^-	cyanido
3.	H^-	hydrido
4.	D^- or $^2H^-$	deuterido or [^{2}H] hydrido
5.	F^- (fluoride)	fluorido
6.	O^{2-} (oxide)	oxido
7.	$PhCH_2CH_2Se^-$	2-phenylethane-1-selenolato
8.	$MeCOO^-$	acetato
9.	Me_2As^-	dimethylarsanido
10.	$MeCONH_2$	acetamide (*not* acetamido)
11.	$MeCONH^-$	acetylazanido or acetylamido (*not* acetamido)
12.	$MeNH_2$	methanamine

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds.

- The number of ligands is indicated by adding prefixes di-, tri-, tetra-, penta-, hexa-, etc. for two, three, four, five, six, etc. entities of the ligands. For example, $[Co(NH_3)_6]Cl_3$ will be called hexamminecobalt chloride.

  If the ligands are complicated groups or if the name of the ligand itself has such a prefix like tri phenylphosphine, instead of di-, tri-, tetra-, penta- prefixes we use bis-, tris-, tetrakis-, pentakis- etc. and the ligand is enclosed in parentheses. For instance $[Cu(CH_3COCHCOCH_3)_2]$ is called bis (acetylacetonato) copper(II).

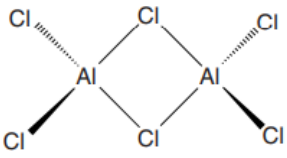
- In any complex species, the ligands are quoted in alphabetical order, without regard to charge, before the name of the central metal atom. Numerical prefixes indicating the number of ligands are not considered in determining that order. For example, a compound like $[CoCl(en)_2(NO_2)]Cl$ will be called chloridobis(1,2-diaminoethane)

(nitrito–κ*O*)cobalt(III) chloride or chloridobis(1,2-diaminoethane) (nitrito–κ*N*)cobalt(III) chloride.(The Kappa convention is explained later in this section).

- The oxidation state of the metal ion in a complex is indicated by Roman (I), (II),(III) etc. or an Arabic (O) and placed in parenthesis is immediately after the name of the metal. If, however, the complex species is an anion, the oxidation state of the metal is mentioned at the end of the name of the complex.
- The name of the complex anion always ends in 'ate' and the Latin name of the metal atom is used. No specific ending is used for neutral or cationic complex species. For example, $K_2[PtCl_6]$ is called potassium hexachloridoplatinate(IV) and $K[Ag(CN)_2]$ is named as potassium dicyanidoargentate(I).
- A little space is given between the name of the cation and the anion. No space or hyphen is used anywhere else.
- Once the complex entity is completely identified according to the above rules, no mention of the number of cations or anions used for charge balancing is required. For example. $[Co(NH_3)_6]Cl_3$ is called hexaamminecobalt(III) chloride and not hexaamminecobalt(III) trichloride. Similarly, $K_2[PtCl_6]$ is named potassium hexachloridoplatinate(IV) and not dipotassium hexachloridoplatinate(IV).

μ-mu
$[(H_3N)_5CoOCo(NH_3)_5]^{4+}$
μ-oxido-bis
(pentamminecobalt)
(III)

- Bridging ligands, as far as they can be specified, are indicated by the Greek letter '*μ*' appearing before the ligand symbol or name and separated from it by a hyphen. A ligand can also act as a bridging group, by forming bonds to two or more central atoms simultaneously in polynuclear species. Bridging ligands link with central atoms and thereby form coordination entities which have multiple central atoms. The number of central atoms joined into a single coordination entity by bridging ligands or direct bonds between central atoms is indicated by using the terms dinuclear, trinuclear, tetranuclear, etc. Bridging can be through one atom or through a longer array of atom. Example,



$[Al_2Cl_4\ (\mu\text{-}Cl)_2]$ or $[Cl_2Al(\mu\text{-}Cl)_2AlCl_2]$
di-*μ*-chlorido-tetrachlorido-1κ^2*Cl*,2κ^2*Cl*-dialuminium

In names, the whole term, e.g. *μ*-chlorido, is separated from the rest of the name by hyphens, as in ammine-*μ*-chlorido-chlorido, etc., unless the bridging ligand name is contained within its own set of enclosing marks.

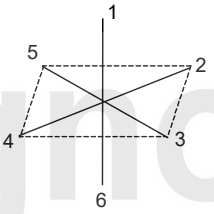
Prefixes are used when the bridging ligand occurs more than once, as in tri-*μ*-chlorido-chlorido. Bridging ligands are listed in alphabetical order together with the other ligands, but in names a bridging ligand is cited before a corresponding non-bridging ligand, as in di-*μ*-chlorido-

tetrachlorido. Whereas when you have to write the formulae, you have to place the bridging ligands after terminal ligands of the same kind. Example,

$[(H_2O)_5Cr(\mu\text{-}OH)_2Cr(H_2O)_5]Cl_4$ which is *μ*-dihydroxido bis {pentaaquachromium(III)} chloride.

The bridging index *n*, the number of coordination centres connected by a bridging ligand, is placed as a right subscript. Usually the bridging index 2 is not indicated. Multiple bridging is listed in descending order of complexity, e.g. μ_3-oxido-di-*μ*-oxido-trioxido. For ligand names requiring enclosing marks, *μ* is contained within those marks.

- Structural information may be given names and formulas by prefixes such as cis- trans- etc. $[Pt(NH_3)_2Cl_2]$ can be written as cis-diamminedichloridoplatinum(II) or trans-diamminedichloridoplatinum(II), respectively.
- In an octahedral compound with different ligands the positions of the ligands are specified as shown below:



- **The kappa convention**

  Single ligating atoms are indicated by the italicized element symbol preceded by a Greek letter kappa, κ. These symbols are placed after the portion of the ligand name that represents the ring, chain or substituent group in which the ligating atom is found, e.g., $[NiBr_2(Me_2PCH_2CH_2PMe_2)]$ which is dibromido[ethane-1,2-diylbis(dimethylphosphane-κ*P*)]nickel(II)

  Let us go through more examples:

  Thiocyanato-κ*N* is used for nitrogen-bonded NCS and thiocyanato-κ*S* for sulfur-bonded NCS. Nitrogen-bonded nitrite is named nitrito-κ*N* and oxygen-bonded nitrite is named nitrito-κ*O*, as in pentaamminenitrito-κ*O*-cobalt(III). For ligands with several ligating atoms linearly arranged along a chain, the order of κ symbols should be successive, starting at one end. The choice of end is based upon alphabetical order if the ligating atoms are different, e.g. cysteinato-κ*N*,κ*S*; cysteinato-κ*N*, κ*O*.

Now let us go through the following simple examples for naming complexes:

a) $[Pt(NH_3)_4Cl_2]^{2+}$ - overall charge = +2, oxidation number of Pt = +4

Keeping alphabetical order rules the name is:

Tetraamminedichloridoplatinum(IV)

b) $[Ni(CO)_3(py)]$ – here CO and py are neutral, oxidation number of Ni = 0

Name of complex: tricarbonylpyridinenickel(0)

The above rules are simple but you need practice. You should be able to answer the following SAQ.

SAQ 2

(a) Write down the names of the following complexes:

(i) $[Cr(NH_3)_3(NO_2)_3]$ ……..…….

(ii) $[Co(NH_3)_5(H_2O)]Cl_3$ …….

(iii) $[Cr(NH_3)_6][Cr(SCN)_6]$ ……..…….

(iv) $K_3[Al(ox)_3]$ …….

(v) $[Pt(py)_4][PbF_4]$ ……..…….

(vi) $[[(H_2O)_4Cr(NH_2)Cr(H_2O)_4]Cl_3$

(b) Write down the formula for each of the following compounds.

(i) Hexaamminecobalt(II) chloride …….

(ii) Potassium trioxalatoferrate(III) ……..

(iii) μ-dihydroxidobis{tetramminecobalt(III)} nitrate…….

4.5 SUMMARY

This unit includes an introduction to the coordination chemistry with special emphasis on the Werner's theory. In this we have learnt about the basic definitions of the terms used in the study of coordination compounds. Also we have learnt the rules for naming these compounds according to IUPAC systems of nomenclature.

4.6 TERMINAL QUESTIONS

1. Label the following ligands as monodentate, bidentate, ambidentate or polydentate:

   (i) Trimethyl phosphine (PMe_3); (ii) ($H_2NCH_2CH_2NH_2$)1, 2-diaminoethane or en; (iii) NO_2^- (iv) $(C_5H_4N)_2$ (v) H_2O (vi) SO_4^{2-}.

2. How would you proceed to establish the formulations given to the following compounds?

   $[Co(NH_3)_6]Cl_3$, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]$ $[PtCl_4]$, $[Co(acac)(en)_2]Cl$.

3. Write the formulae of the following complexes:

   i. Pentammine(nitrito-κO)cobalt(III) chloride

   ii. Dichloridobis(1,2-diaminoethane)rhodium(III) ion

   iii. Diamminediiodidocobaltate(III) ion

   iv. Potassium tetracynanidonickelate(II)

4. Write down the names of the following species

a) $K[CrF_5O]$ b) $[Cr(en)_2(H_2O)(NCS)]^+$

c) $[Co(en)_3]\,[Fe(CN)_6]$ d) $[Cr(H_2O)Cl_3(C_5H_5N)_2]H_2O$

4.7 ANSWERS

Self-Assessment Questions

1. The coordination number and oxidation state of the metal ion in (a) to (d) are given below:

a) 6, +2, b) 6, +3, c) 4, +2, d) 4, +2

2. a) i) triammine(trinitrito-κ*O*)chromium(III) or triammine(trinitrito-κ*N*)chromium(III)

ii) Pentaammineaquacobalt(III) chloride

iii) Hexaamminechromium(III) (hexathiocyanato-κ*S*)chromate(III) or Hexaamminechromium(III) (hexathiocyanato-κ*N*)chromate(III)

iv) Potassium trioxalatoaluminate(III)

v) Tetrapyridineplatinum(II) tetrafluoridoplumbate(II)

vi) μ-amido-μ-imidobis{tetraaquachromium(III)} chloride

b) i) $[Co(NH_3)_6]Cl_3$ ii) $K_3[Fe(ox)_3]$

(iii) $[(NH_3)_4Co(OH)_2Co(NH_3)_4](NO_3)_4$

Terminal Questions

1. (i) monodentate (ii) bidentate (iii) ambidentate (iv) bidentate (v) monodentate (vi) bidentate.

2. $[Co(NH_3)_6]Cl_3$, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]\,[PtCl_4]$, $[Co(acac)(en)_2]Cl$. By treating the above with $AgNO_3$, the presence of halogen in the ionic form can be done both qualitatively and quantitatively. The number of moles of AgCl precipitate obtained from per mole of the above compound ds will be 3, 0, 0 and 1 respectively.

3. i) $[Co(NH_3)_5(NO_2)]Cl_2$ ii) $[RhCl_2(en)_2]^+$

iii) $[Co(NH_3)_2I_2]^{3+}$ iv) $K_2[Ni(CN)_4]$

4. a) Potassium pentafluridooxidochromate(VI)

b) bis(1,2-diaminoethane-κ*O*)aqua(thiocyanato-κ*N*)chromium(II)

c) tris(1,2-diaminoethane-κ*O*)cobalt(III)hexacyanidoferrate(III)

d) aquatrichloridodipyridinechromium(III) monohydrate

Source of Figure

Fig. 4.3: Wikimedia Commons, Creative Commons CCO License; CC-SA.

UNIT 5

COORDINATION COMPOUNDS-II

Structure

5.1 INTRODUCTION

In the previous unit you have studied about the development of coordination chemistry, the basic terms involved in it and how to name the complexes. In the beginning of this unit we will discuss about isomerism in such compounds. You are familiar with isomerism in organic compounds but you will see that metal complexes too display isomerism. In this context, if you look at your hands or legs you will see that, though both the left and right hand or leg look similar, you will not be able to replace your left hand or leg with your right hand or leg. You will note the same for your left shoe and the right one. You will come across similar cases in the molecular world. This concept will be particularly useful for understanding the concept of isomers. Thereafter we will discuss the theories of bonding as applied to metal complexes and finally you will be introduced to inner and outer orbital complexes of some metals.

J. von Liebig (1823) first showed that the silver salt of fulminic acid, Ag–O–N=C, and silver isocyanate, Ag–N=C=O, have the same composition but different properties. But J. Berzelius first gave the name 'isomerisation' in 1830.

Expected Learning Outcomes

After studying this unit you should be able to:

- describe the types of isomerism in coordination compounds;
- discuss the theories (valence bond theory) of bonding as applied to coordination compounds and
- discuss the inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu.

5.2 ISOMERISM IN COORDINATION COMPOUNDS

Compounds having the same chemical formula but different structural arrangements are called isomers. In this section we will discuss the different types of isomerism in coordination compounds along with their explanation and some examples. Due to a wide variety of geometries and coordination numbers, the metal complexes show a variety of isomerism. These isomers may undergo rapid interconversions. The speed of the instrumental technique employed to detect the isomers should be faster than that of the interconversions of isomers. The latest analytical instruments have made the discovery of new isomers possible. The isomers may or may not show the same physical and chemical properties. If you look at the complex $[Pt(NH_3)_2(Cl)_2]$(platin) which has two isomers; you will see that the *cis*-platin isomer, is found to be very effective against tumours, but the *trans*-isomer is not. So it is very important to know how to synthesize a desired isomer for a particular purpose. There are different methods (physical and chemical) for determination of structures of isomers, X-ray diffraction has been found to be particularly useful.

CLASSIFICATION OF ISOMERISM

A detailed classification of isomerism in metal complexes is given in Fig. 5.1.

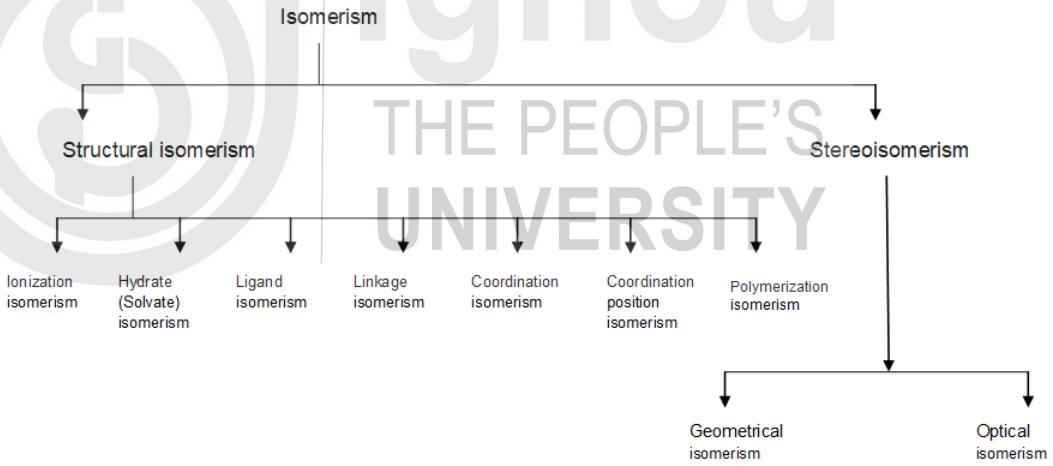


Fig. 5.1: Classification of isomerism in metal complexes.

The two principal types of isomerism known among coordination compounds are structural isomerism and stereoisomerism. These can be further subdivided as follows:

(a) Structural isomerism

(i) Ionization isomerism (ii) Hydrate (Solvate) isomerism (iii) Ligand isomerism (iv) Linkage isomerism (v) Coordination isomerism (vi) Coordination position isomerism (vii) Polymerization isomerism

(b) Stereoisomerism

(i) Geometrical isomerism (ii) Optical isomerism

Let us discuss them one by one.

5.2.1 Structural Isomerism

(i) Ionization Isomerism

Isomers that give different ions in the solution are called ionization isomers. Coordination compounds may have the same empirical formula but yield different ions in solution. This arises due to exchange of anionic ligand in the coordination sphere with an ion outside it. An example is provided by the ionization isomers $[Co(NH_3)_5(SO_4)]Br$ (red) and $[Co(NH_3)_5Br]SO_4$ (violet). These two isomers can be easily identified by performing tests for sulphate and bromide ions in their aqueous solutions respectively. Aqueous solution of $[Co(NH_3)_5Br]SO_4$ with barium chloride gives a white precipitate.

$$[Co(NH_3)_5Br]SO_4 \rightarrow [Co(NH_3)_5Br]^{+2}(aq) + SO_4^{2-}(aq)$$

While $[Co(NH_3)_5SO_4]Br$ gives pale yellow precipitates of silver bromide with an aqueous solution of silver nitrate, it does not give the tests for sulphate ion.

$$[Co(NH_3)_5SO_4]Br \rightarrow [Co(NH_3)_5SO_4]^{+1}(aq) + Br^{-}(aq)$$

A few more examples of ionization isomers are;

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4Cl(NO_2)]Cl$

(ii) Hydrate (Solvate) Isomerism

The general name for this isomerism is solvate isomerism. Specifically in aqueous solutions, the isomerism is referred to as hydrate isomerism. The isomers in which coordinated ligands are replaced by water (solvent) molecules are known as hydrate (solvate) isomers.

In a compound, water molecules are either in the form of coordinated one or they are as water of crystallization in the lattice. In the case of coordination, the water molecules have direct attachment to the metal ion, but when they occupy the lattice sites in a crystal they may not have such direct link to the metal ion.

Some examples of hydrate isomers are given in Table 5.1. You may see that the physical/chemical properties of hydrate isomers are quite different.

Table 5.1: Hydrate Isomers of Aquated Chromium(III) Chloride

$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2.H_2O$	$[Cr(H_2O)_4Cl_2]Cl.2H_2O$
Violet	Blue green	Dark green
Gives three chloride ions in aqueous solution	Gives two chloride ions in aqueous solution	Gives one chloride ion in aqueous solution

(iii) Ligand Isomerism

When an isomeric ligand such as, $CH_3CH_2CH_2NH_2$ coordinate to form complexes then ligand isomerism arises. 1,2-diaminopropane and 1,3-diaminopropane form complexes showing ligand isomerism, as shown in Fig. 5.2:

(a) (b)

Fig.5.2: (a) 1,3-diaminopropane and (b) 1,2-diaminopropane ligand isomer complexes.

Other examples of ligand isomerism are:

$[Ag(pic)_2]^-$ and $[Ag(nic)_2]^-$, where pic = picolinate ion (pyridine 2-carboxylate), nic = nicotinate ion (pyridine 3-carboxylate);

$[CoCl_2(pn)_2]Cl$ and $[CoCl_2(tn)_2]Cl$, where pn = propylenediamine, tn = trimethylenediamine.

(iv) Linkage Isomerism

In the previous unit (Unit 4) you have learnt about ambidentate ligands. They are responsible to give rise to linkage isomerism. The isomers formed when ambidentate ligands use different coordinating atoms for binding the metal ion are known as linkage isomers. Such a pair of isomeric complexes with a NO_2^- ligand is shown in Fig.5.3.

A simple example is provided by complexes containing the thiocyanate ligand, SCN^-, which may bind through the nitrogen to give M–NCS (as discussed in previous unit, the modern nomenclature is with κ-*N*) or through sulphur as discussed in previous unit, the modern nomenclature is with κ-*S*) to give M–SCN. Jørgensen (who was Werner's contemporary) discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO) called as nitrito (as discussed in previous unit, the modern nomenclature is with κ-*O*), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($–NO_2$) which is named as nitro compound (as discussed in previous unit, the modern nomenclature is with κ-*N*).

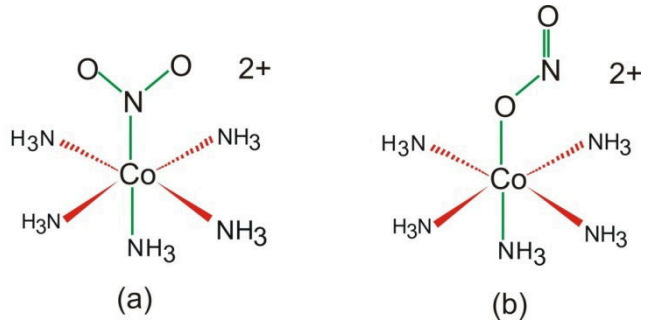


Fig.5.3: (a) $[Co(NO_2)(NH_3)_5]^{2+}$ and (b) $[Co(ONO)(NH_3)_5]^{2+}$.

SAQ 1

Cr(III)-SCN bonded thiocyanato complexes (κ-*S* compound) slowly rearrange to give the N-bonded Cr(III)-NCS isothiocyanato complex (κ-*N* compound). Comment.

(v) Coordination Isomerism

Whenever a complex is formed which has both cation and anion as complex ions then coordination isomerism may arise. There may be interchange of ligands between cationic and anionic entities present in the complex forming coordination isomers. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}. The pair

$$[Cr(NH_3)_6]^{+3}[Cr(SCN)_6]^{-3} - [Cr(NH_3)_4(SCN)_2]^{+}[Cr(NH_3)_2(SCN)_4]^{-}$$

involves the same metal ion (Cr^{+3}) in both the cationic and anionic complex ions but the arrangement of ligands with respect to the metal centres vary in the two isomers.

While the pair $[Co(NH_3)_6]^{+3}[Cr(CN)_6]^{-3} - [Cr(NH_3]_6^{+3}[Co(CN)_6]^{-3}$ illustrate coordination isomerism involving complexes with different metal ions. Some more simple examples are given below:

$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

$[Cr(NH_3)_6][Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2][Cr(NH_3)_2(SCN)_4]$

$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(vi) Coordination position isomerism

If in a multinuclear complex the distribution of ligands around the metal centres changes it will result in a different isomer. Such an isomerism is called coordination position isomerism. Some typical examples are:

$$[(NH_3)_4Co<\begin{matrix}NH_2\\O_2\end{matrix}>Co(NH_3)_2Cl_2]Cl_2$$

and

$$[Cl(NH_3)_3Co<\begin{matrix}NH_2\\O_2\end{matrix}>Co(NH_3)_3Cl]Cl_2$$

$$[(R_3P)_2Pt<\begin{matrix}Cl\\Cl\end{matrix}>PtCl_2] \text{ and } [Cl(R_3P)Pt<\begin{matrix}Cl\\Cl\end{matrix}>Pt(R_3P)Cl]$$

(vii) Polymerization isomerism

This term is used to describe compounds having same empirical formula but different molecular compositions. The difference from normal polymerization is that here we have differences in arrangements of group as well as multiplication of molecular weight. This is exemplified by $[Co(NH_3)_3(NO_2)_3]$ which may be formulated as A. Now look at the compounds listed below, they have same empirical formula as A but the molar mass is a multiple of A. Thus A may be referred to as the monomer and the six compounds listed are polymerization isomers.

Formula	Molecular Weight
$[Co(NH_3)_6][Co(NO_2)_6]$	Double
$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	Double
$[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]_2$	Triple
$[Co(NH_3)_6)][Co(NH_3)_2(NO_2)_4]_3$	Quadruple
$[Co(NH_3)_4(NO_2)_2]_3[Co(NO_2)_6]$	Quadruple
$[Co(NH_3)_5(NO_2)_3][Co(NO_2)_6]_2$	Quintuple

5.2.2 Stereoisomerism

Stereoisomers have similar metal ligand bonding sequence but the arrangement of atoms in space is different. Stereoisomerism can be divided into two kinds: geometrical and optical.

(i) Geometrical isomerism occurs when ligands can assume different positions around the metal ion. For example, the compound $[Pt(NH_3)_2Cl_2]$ has a square planar structure. The two possible arrangements are shown in Fig. 5.4.

In the *cis*-isomer the two ammonia molecules are next (*cis*) or adjacent to each other whereas in the trans-isomer the two ammonia molecules are across (trans) to each other.

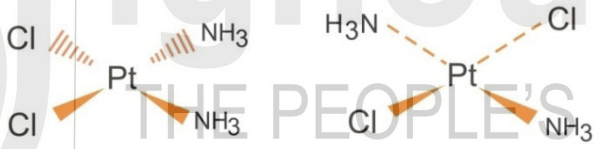
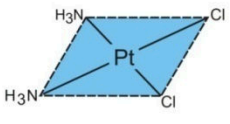
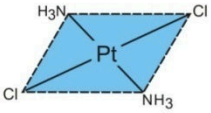
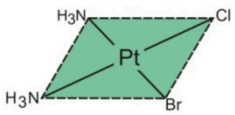
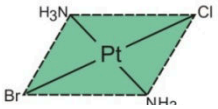
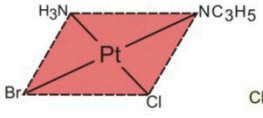
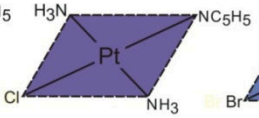
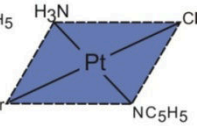


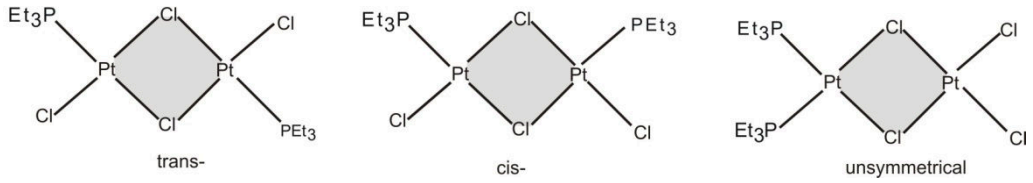
Fig. 5.4: *cis*- and *trans*- isomers of diamminedichloridoplatinum(II).

This type of isomerism is not possible for complexes with coordination number 2 (linear molecule), 3 (trigonal planar) and 4 (tetrahedral geometry).

For square planar complexes Ma_4, Ma_3b or Mab_3 where a and b are monodentate ligands, geometrical isomerism is not possible. However, square planar complexes of the type Ma_2b_2, Ma_2bc. Mabcd and $M(AA)_2$, $M(AB)_2$–where AA and AB represent symmetrical and unsymmetrical bidentate ligands respectively – do give geometrical isomers. A few examples are given below:

Type	Compound	Isomers
Ma_2b_2	$[Pt(NH_3)_2Cl_2]$	 
Ma_2bc	$[Pt(NH_3)_2Br\ Cl]$	 
Mabcd	$[Pt(NH_3)I)(C_5H_5N)]]$	  

Bridged binuclear planar complexes like $[PtCl_2I_2(Pet_3)]$ may exist in three isomeric forms:



Six-coordinated octahedral complexes of the type Ma_4b_2, Ma_3b_3, Ma_3b_2c, Ma_3bcd, Ma_2b_2cd, Ma_2bcde, Mabcdef would all give geometrical isomers. Systems with one or two bidentate ligands along with monodentate ones would also give geometrical isomers. Thus we see that with octahedral geometry a large number of isomers are possible; whether they can be separated or not is a different question which depends on many factors. As we increase the number of different ligands, the possible number of isomers increases. For example, Ma_2b_2 type of complex would give only two isomers *cis*- and *trans*-. Similarly for Ma_3b_3 type of complex we again get two isomers facial (fac-) and meridional (mer-) isomers. In the former (fac-) three ligands of one type form one triangular face of the octahedron and the other three are on the opposite face, as shown in Fig. 5.5(a). In the latter (mer-).one set of these ligands are arranged around an edge of the octahedron whereas the other set occupies the opposite edge as shown in Fig. 5.5(b).

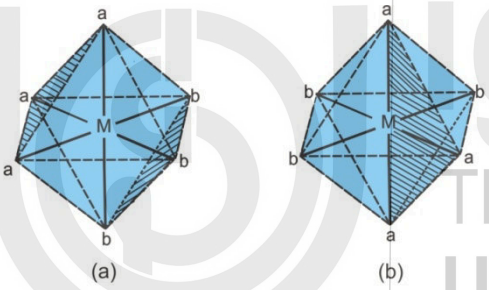


Fig. 5.5: (a) facial and (b) meridional isomers of Ma_3b_3 complex.

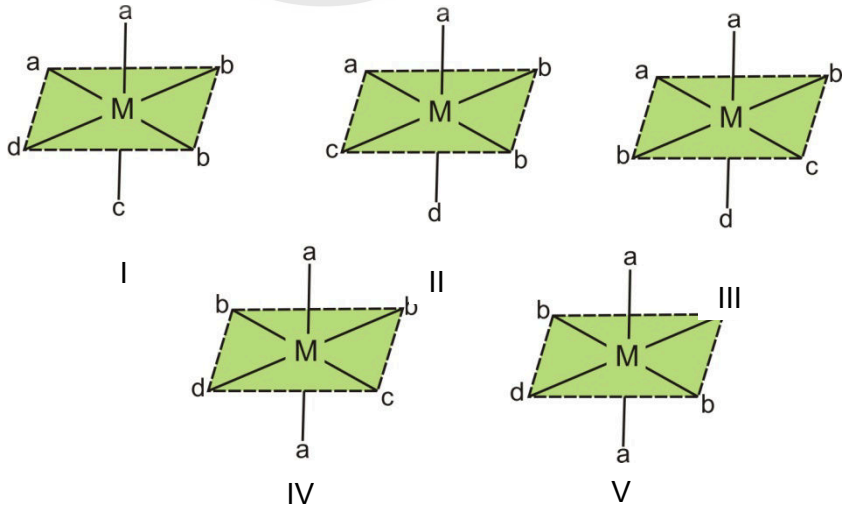


Fig. 5.6: Geometrical isomers of Ma_2b_2cd complex.

When writing the geometrical isomers you must make sure that the relative positions of the ligands must be different in each configuration and it is not just a rotation of the molecule as a whole. The trick in writing these configurations is that you fix the position of some ligands initially and rotate the other ligands, then for the isomer write the configuration with the changed positions of the

ligands which were fixed earlier. For example, in the above case we have fixed the *cis* position for the two ligands 'a' and wrote all possible configurations I, II and III. Once that is over then we put the two 'a' ligands in trans-positions and again rotate other ligands in all possible ways to get a different configuration. Finally you must remember that there is no formula available which can predict the number of possible isomers for any particular compound and hence, you have to try writing down all possible configurations in each and every case (which of course, requires a lot of patience and practice).

(ii) Optical Isomerism: Two isomers which have almost identical physical and chemical properties like melting point, boiling point, density, colour etc. but differ in the way they rotate the plane-polarised light are called optical isomers. Such optically active compounds exist in pairs and are known as stereoisomers or enantiomers. These isomers are non-superimposable mirror images of each other just like your right hand is the mirror image of your left hand. Any molecule which contains either a centre of symmetry or a plane of symmetry will not show optical isomerism. Optical isomerism is rarely observed in square planar complexes. Tetrahedral complexes of the type $[M(AB)_2]$ where (AB) is an unsymmetrical bidentate ligand give optical isomers as shown in Fig. 5.7 especially where M = Be, B.

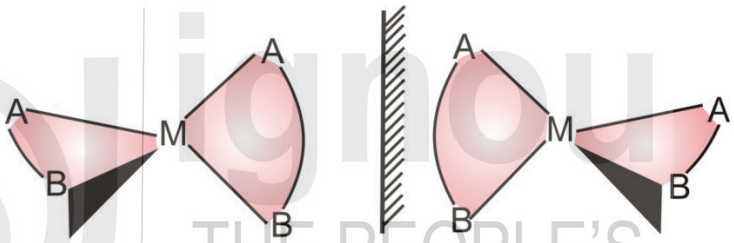


Fig. 5.7:Optical isomers of $M(AB)_2$ complex.

However, optical iomerism is very common with octahedral complexes of the type $M(AA)_3$, $M(AA)_2ab$, $M(AA)a_2b_2$, $M(AA)(BB)a_2$ etc. A few typical examples are shown in Fig. 5.8.

It is customary to symbolize a chelating agent as a curved line with the abbreviation for the ligand in the middle. Thus en could be used to represent NH_2CH_2-CH_2NH_2.

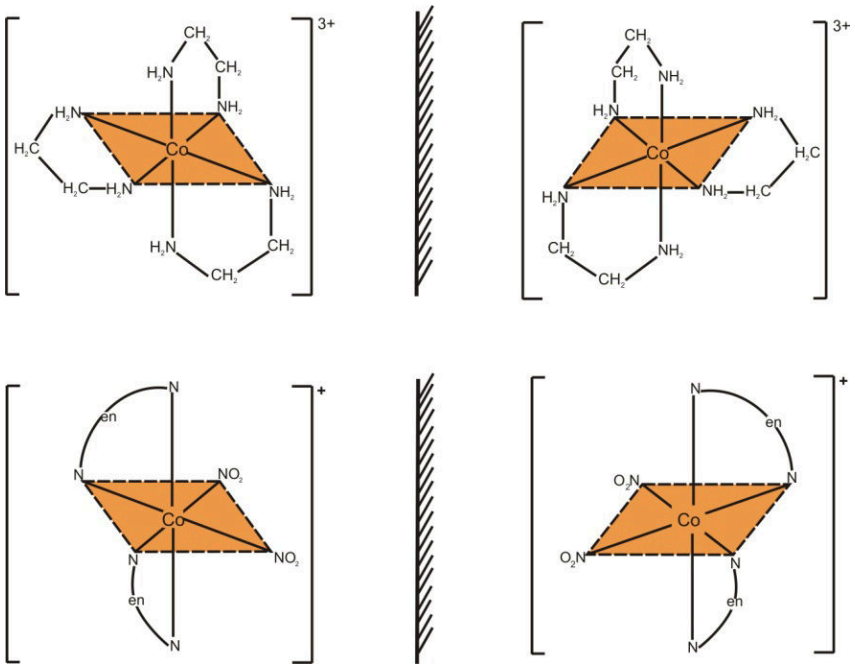


Fig. 5.8: Optical isomers of $[Co(en)_3]^{3+}$.

In the next section we shall study the theories to explain the bonding in complexes. However, after reading this section you should be able to solve the following SAQ.

SAQ 2

Write down all possible isomers of $[CoCl_2(en)_2(NO_2)$ and give their names.

5.3 THEORIES OF BONDING AS APPLIED TO COORDINATION COMPOUNDS

In the early period of development of the chemistry of complexes, a number of theories were put forward in order to explain in a simple manner the formation of a new compound by the combination of two or more stable and apparently saturated compounds. Though these early theories were not fully successful in many ways, yet they served their purpose of encouraging the workers in the field to perform new experiments in order to prove or disprove the proposed theory. The slow accumulation of experimental data helped to understand the nature of the chemical bond by the later workers.

However, the real credit goes to Werner who in 1893 introduced bold new ideas which explained a number of experimental facts. Though the modem theories are more encompassing in nature yet the basic postulates introduced by Werner are still valid to this day which we have already discussed in Unit 4 of this course.

In the next subsection we shall discuss the valence bond theory as applied to coordination compounds.

5.3.1 Valence Bond Theory

This theory, proposed by Pauling, starts with the assumption that the bond between the metal ion and the ligand is basically covalent in nature. In order to form a chemical bond the central metal ion must have enough vacant orbitals to accept the lone pairs of electrons from the ligands. The number of bonds formed is thus directly related to the number of vacant orbitals on the metal ion. At this stage Pauling introduced the concept of hybridized atomic orbitals. Accordingly, the vacant atomic orbitals on the metal ion combine to give a set of hybridized orbitals.

For hybridization only those orbitals are used which have the correct orientation in space and whose energy values are very near to each other. These hybridized orbitals overlap with the ligand orbitals to share the lone pairs of electrons from the ligands. Since these hybridized orbitals show a definite orientation in space, the geometry of the molecule is determined by the kind of hybridization involved.

Once the geometry of the molecule is known, the suitable combination of atomic orbitals can be found but the reverse process is not always possible.

The correct combinations of the atomic orbitals have been worked out as shown in Table 5.2.

Table 5.2: Suitable Atomic Orbitals for Hybridization

Coordination Number	Vacant atomic orbitals on the metal ion	Hybridized orbitals	Geometry of the molecule	Example
2	s,p	sp	linear	$[Ag(NH_3)_2]^+$
3	$s,(2)p$	sp^2	Trigonal planar	$[HgI_3]^-$
	$s,(3)p$	sp^3	tetrahedral	$[Zn(NH_3)_4]^{2+}$
4	d_{xy}, d_{yz}, d_{xz} and s	d^3s	tetrahedral	$[MnO_4]^-$
	$d_{x^2-y^2}, s, (2)p$	dsp^2	square planar	$[Ni(CN)_4]^{2-}$
5	$d_{z^2}, s, (3)p$	dsp^3	Trigonal bipyramid	$[CuCl_5]^{3-}$
	or			
	$d_{x^2-y^2}, s, (3)p$	dsp^3	square pyramid	$[VO(acac)_2]$
6	$d_{x^2-y^2}, d_{z^2}, s, (3)p$	d^2sp^3	octahedral	$[Co(NH_3)_6]^{3+}$
	or			
	$s, (3)p, d_{x^2-y^2}, d_{z^2}$	sp^3d^2	octahedral	$[CoF_6]^{3-}$

In cases where paramagnetic ions are very close together they interact with each other and result in more intense form of magnetism known as ferromagnetism and antiferromagnetism. However, we shall not be concerned with these types of magnetism in our discussions since in complexes the paramagnetic metal ions are never too close.

In Table 5.2, the numbers shown in parenthesis represent the number of specific orbitals involved in hybridization. They do not indicate either the principal quantum number or the number of electrons in a particular orbital.

Pauling showed that there is a direct correlation between the type of hybridization and the magnetic properties of the complex. In order to understand this relationship, you should recapitulate the basic concepts of magnetism. The orbital motion and the spinning of the electron give rise to a certain angular momentum to an atom. This angular momentum causes the atom to acquire magnetic moment. The magnetic moment due to spin angular momentum is much greater in comparison to magnetic moment arising out of orbital angular momentum. Further, if there are two electrons in an orbital having opposite spins, the magnetic moment due to spin angular momentum will be zero. However, if there are unpaired electrons in an atom its magnetic moment is given by the expression:

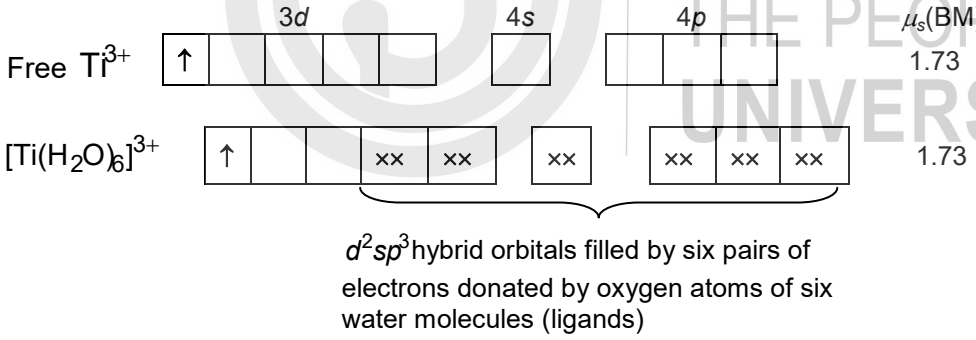
$\mu_s = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons and BM is the unit of magnetic moment. It is called Bohr Magneton and abbreviated as BM. The formula is known as spin-only formula for the calculation of magnetic moment since in its derivation we have omitted the contribution due to orbital angular momentum. If all the electrons in an atom/ion have paired spins they will not give rise to any magnetic moment. Such substances are called

diamagnetic and when put in an external magnetic field they are slightly repelled by the field. On the other hand an atom/ion having unpaired electrons gives rise to magnetic moment. Such substances are called paramagnetic and when placed in an external magnetic field are pulled towards the field. Table 5.3 gives the number of unpaired electrons and the associated magnetic moment.

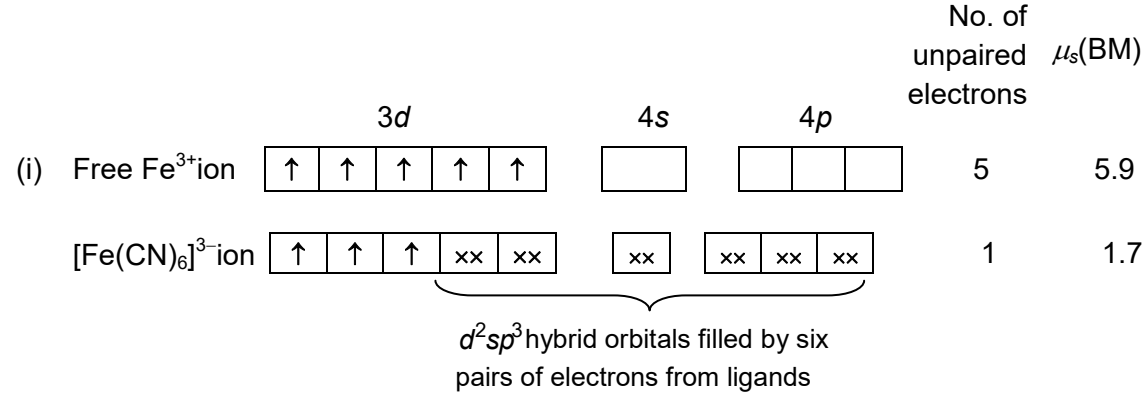
Table 5.3: Correlation between Number of Unpaired Electrons and Expected Magnetic Moment

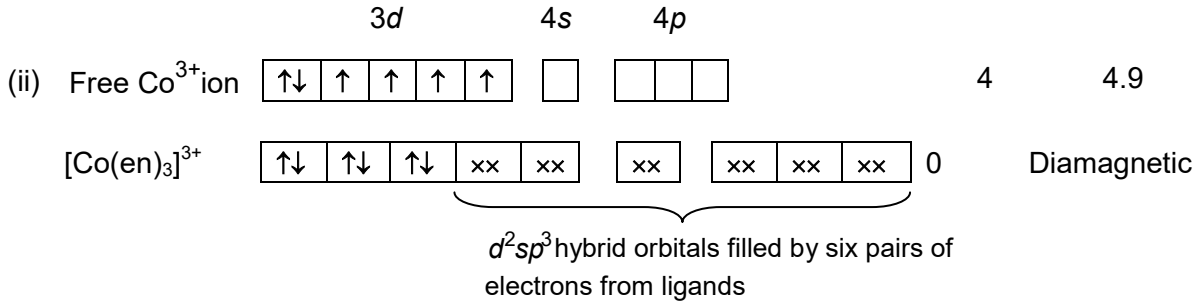
Number of unpaired electrons, *n*	**Magnetic moment (BM)** $\mu_s = \sqrt{n(n+2)}$
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

Let us now turn our attention to the complexes having transition metal ion with d^1, d^2 or d^3 electrons. With these configurations, there are enough vacant orbitals available to accept the pairs of electrons from four or six ligands to form tetrahedral, square planar or octahedral compound. The magnetic moment of the complex will be the same as free ion value as shown in the diagram given below:



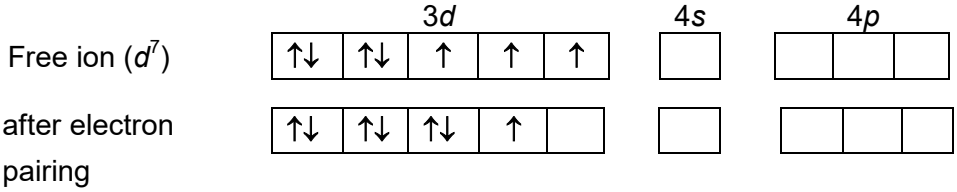
When the number of *d* electrons is greater than three and up to six as in d^4, d^5, d^6 systems, there is still a possibility of forming octahedral complexes using d^2sp^3 hybridized orbitals by forcing some of the electrons to pair up. Following two examples should make the point clear.





In majority of the cases the decrease in the number of unpaired electrons agrees well with the magnetic moment values obtained experimentally. However, it does not hold true for a number of complexes. For example a complex ion like $[FeF_6]^{3-}$ gives a magnetic moment value equal to five unpaired electrons indicating thereby that the electronic distribution on the Fe^{3+} ion remains the same as in free ion state. Pauling suggested that instead of using the inner orbitals (3*d*, 4*s*. 4*p*), iron can use outer orbitals (4*s,* 4*p*, and 4*d*) for d^2sp^3 hybridization leaving the electronic distribution the same as in free ion state.

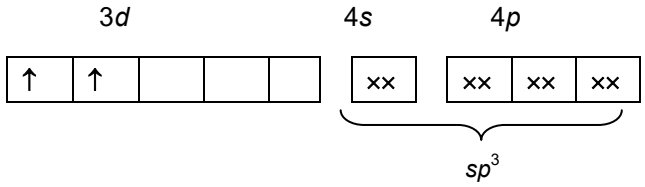
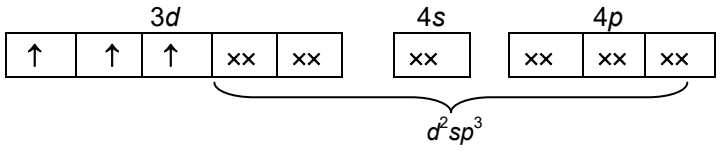
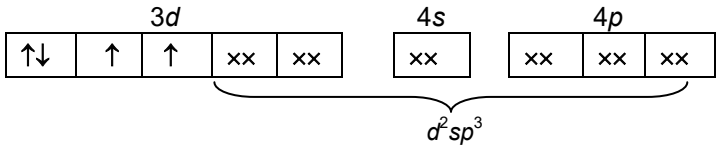
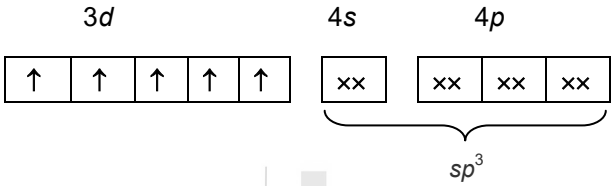
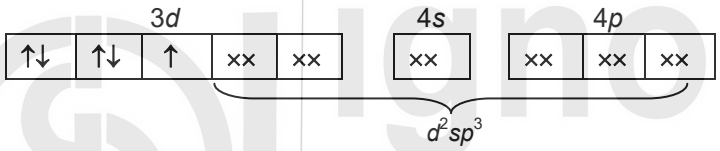
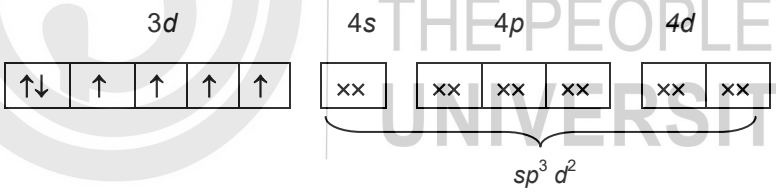
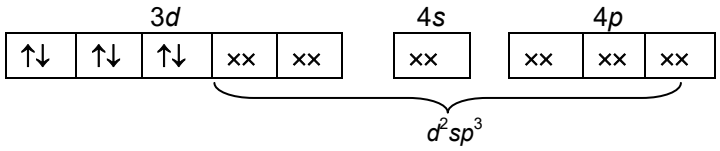
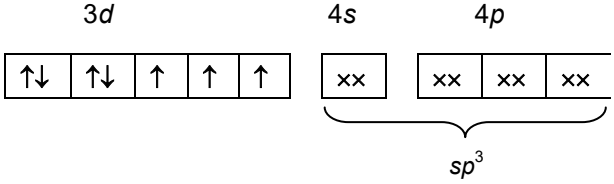
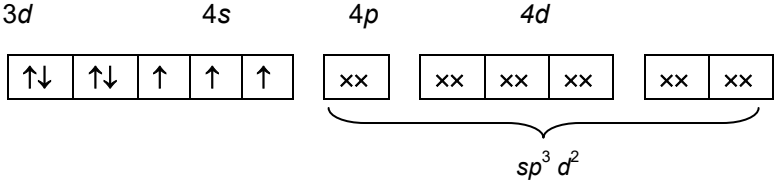
Craig showed that highly electronegative ligands tend to form spin-free complexes. Although the valence bond theory suggests two correct alternatives in low spin and high spin, yet it does not help in making the choice. However, it indirectly suggests that the low spin complexes should be relatively less reactive. It has also been shown that a d^6 high spin octahedral complex will be more stable than four coordinated complexes which do not require outer d^6 orbitals for hybridization. Turning our attention to systems having d^7 to d^{10} electronic configuration, we find that even forcing all the *d* electrons to pair up in the inner orbitals it still does not leave two vacant *d*-orbitals for hybridization; hence d^2sp^3 hybridization is not possible in such cases as shown below:

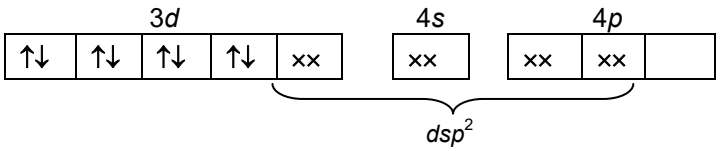
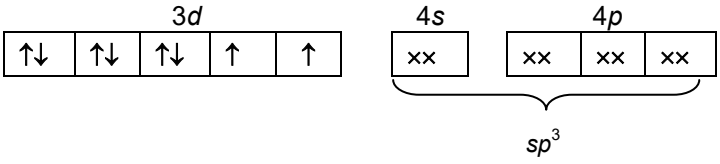
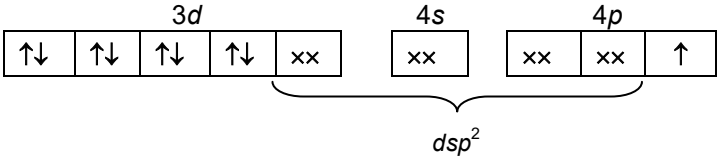
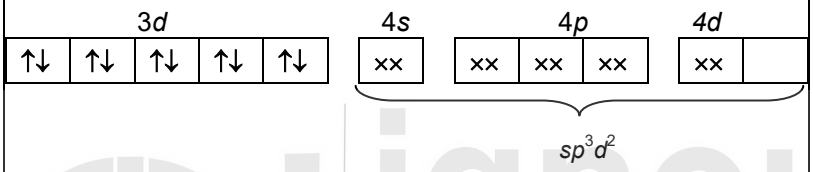
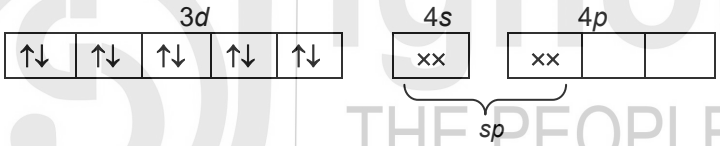


In complexes of this type, we are left with just one choice of forming high spin octahedral complex or else metal ion should form complexes with lower coordination number. Table 5.4 gives examples of a number of compounds having different geometries and different number of unpaired electrons.

Table 5.4: Hybridized orbitals and the corresponding geometries of some complexes

No. of *d* electrons in ion	Complex	Hybrid orbitals and electronic distribution	No. of unpaired electrons	Geometry
d^1	$[Ti(H_2O)_6]^{3+}$	3d 4s 4p; d^2sp^3	1	Octahedral

d^2	$[CrF_4]$		2	Square planar
d^3	$[Cr(NH_3)_6]^{3+}$		3	Octahedral
d^4	$[Mn(CN)_6]^{3-}$		2	Octahedral
d^5	$[MnCl_4]^{2-}$		5	Square planar
	$[Fe(CN)_6]^{3-}$		1	Octahedral
d^6	$[CoF_6]^{3-}$		4	Octahedral
	$[Co(en)_3]^{3+}$		Nil	Octahedral
d^7	$[CoCl_4]^{2-}$		3	Square planar
	$[Co(NH_3)_6]^{2+}$		3	Octahedral

d^8	$[Ni(CN)_4]^{2-}$		Nil	Square planar
	$[Ni(Cl)_4]^{2-}$		2	Tetrahedral
d^9	$[Cu(NH_3)_4]^{2+}$	 one electron is shifted from 3*d* to 4*p* orbital	1	Square planar
d^{10}	$[Zn(NH_3)_6]^{2+}$		Nil	Octahedral
	$[Ag(CN)_2]^-$		Nil	Linear

*Hybrid orbitals are always occupied by lone pairs of electrons from ligands.

As you can see this theory is not only easy to apply but it also gives more information about the complexes and became more acceptable initially. However, its limitations also became obvious very soon. Let us consider a few of these in detail:

- It gives no idea whether a particular metal ion would prefer to have any particular, geometry say, an octahedral or tetrahedral with a given ligand.
- Even if we know that a complex formed is four coordinated we cannot decide whether it would be tetrahedral or square planar. It is only after measuring the magnetic moment that we can decide the correct geometry. For example, in the case of the two tetracoordinated compounds of Ni(II), $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ the former is a square planar compound the other is tetrahedral.
- The VBT fails for four coordinated complexes of Cu(II). Cu(II) is a d^9 system and it is expected that for a complex of $[Cu(CN)_4]^{2-}$ the geometry will be tetrahedral based on sp^3 hybridization. However the tetrammine complex of Cu(II) is found to be square planar with dsp^2 hybridization. This is explained by promoting the 9th electron from 3*d* to 4*p* thereby vacating one *d* orbital for the electron pair of the ligand. Now if

it is so easy to promote an electron from 3*d* to 4*p* then surely by supplying some energy it should be possible to remove this electron, or in other words, Cu(II) should be readily oxidized to Cu(III), but this is not the case. Thus this example is considered to be a major limitation of VBT.

- The important role ligands play in deciding the geometry of the resultant complex is not taken into account by this theory.
- It gives only an approximate magnetic moment value which in some cases may differ considerably.
- Besides magnetic property, it does not throw any light on other physico-chemical properties of complexes like-spectral, stability, reactivity etc.

Thus we see the need for a more comprehensive theory which could explain the observed properties and if possible, predict the formation of new compounds. Even if such a theory may not be all comprehensive, it should at least be able to recognize the factors responsible for the typical properties of complexes. Crystal field theory is such an attempt and in the next two units we shall deal with this new theory. However, before proceeding any further, you may try to solve the following SAQ based on valence bond theory.

SAQ 3

Classify each of the following complexes as either high or low spin. Explain your answers.

$[Co(H_2O_6)]^{2+}$, μ = 4.6 BM; $[Co(CN)_6]^{4-}$, μ = 1.9 BM

$[Fe(NO_2)_6)]^{4-}$, μ = 0.0 BM; $[Fe(H_2O)_6]^{3+}$, μ = 5.94 BM

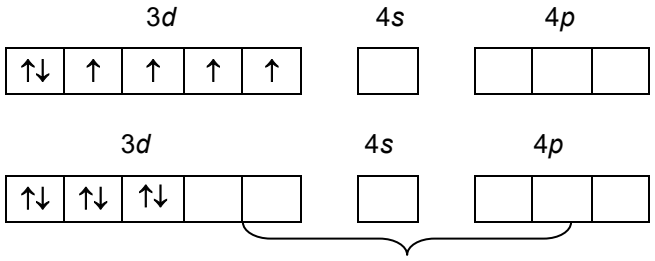
5.3.2 Inner and Outer Orbital Complexes of Cr, Fe, Co, Ni and Cu

In this subsection we are going to discuss the inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu. The most important point to be understood here is that in an inner-sphere complex, the ligands are attached directly to a central metal ion. An outer-sphere complex happens when cation and anion associate in solution or ionic solid. Let us understand the difference between the two terms with the case of an aqueous solution of $[Mn(OH_2)]^{2+}$ and $[SO_4^{2-}]$ ions, where the equilibrium concentration of the outer-sphere complex $[Mn(OH_2)_6]^{2+}\{SO_4^{2-}\}$can, depending on the concentration, exceed that of the inner-sphere complex $[Mn(OH_2)_5SO_4]$where the ligand SO_4^{2-} is `directly attached to the metal ions. A complex is said to be outer orbital when outer *d* orbitals (having the same principal quantum number as *s* and *p* orbitals) are used in bonding. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2. They have octahedral shape. When *d* orbitals of (n – 1) shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3. They are also octahedral in shape.

1. **6 – ligands** (unidentate), **octahedral entity.**

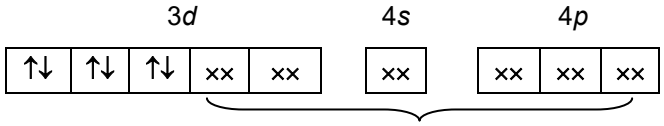
(i) Inner orbital complex $[Co(NH_3)_6]^{3+}$

Orbitals of Co^{3+} ion



d^2sp^3 hybridised orbitals of Co^{3+}

Orbitals of $[Co(NH_3)_6]^{3+}$ ion

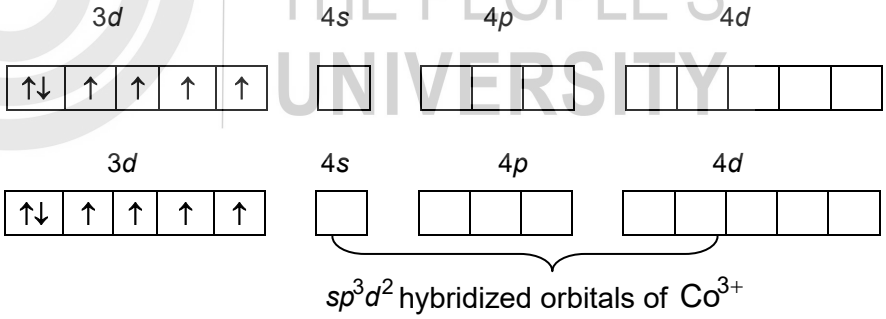


Six pairs of electrons from six NH_3 molecules (d^2sp^3 hybridisation)

As the electrons are paired, therefore complex will be diamagnetic in nature.

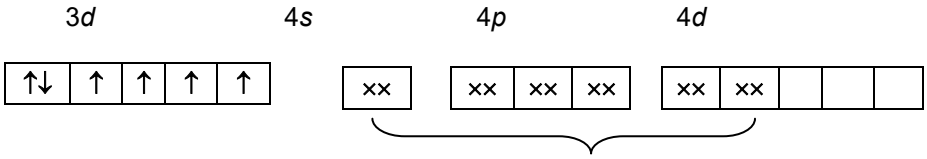
(ii) Outer orbital complex, $[CoF_6]^{3-}$

Orbitals of Co^{3+} ion



sp^3d^2 hybridized orbitals of Co^{3+}

Orbitals of $[CoF_6]^{3-}$ ion



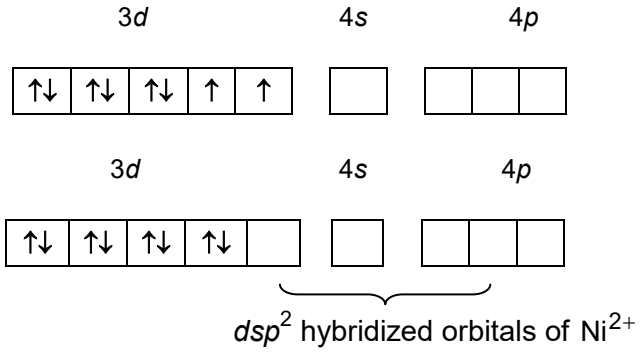
six pairs of electrons from six F^- ligands (sp^3d^2 hybridization)

The complex has unpaired electrons, therefore, it will be paramagnetic in nature.

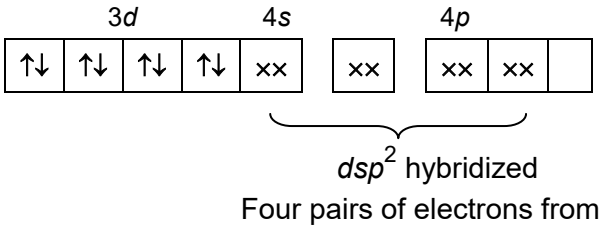
2. **4-ligands** (unidentate) **tetrahedral entity.**

(i) Inner orbital complex, $[Ni(CN)_4]^{2-}$

Orbitals of Ni^{2+} ion



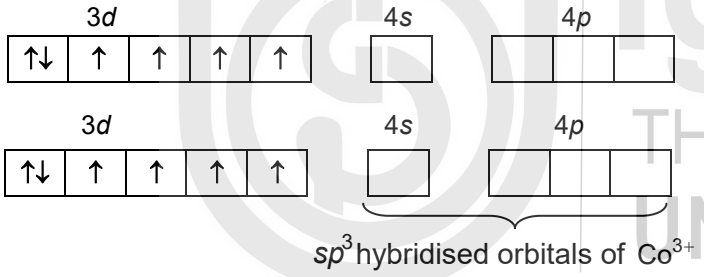
Orbitals of $[Ni(CN)_4]^{2-}$ ion



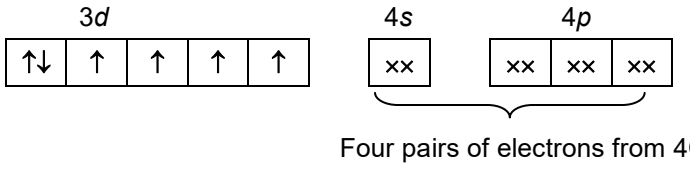
All electrons are paired so complex will be diamagnetic in nature.

(ii) Outer orbital complex, $[CoCl_4]^-$

Orbitals of Co^{3+} ion

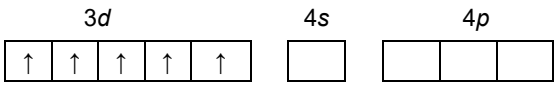
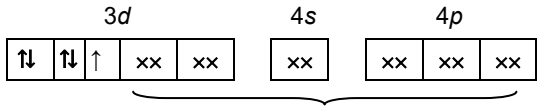
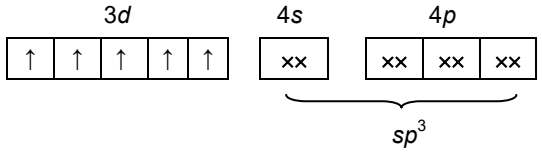
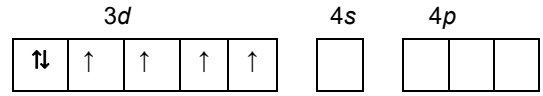
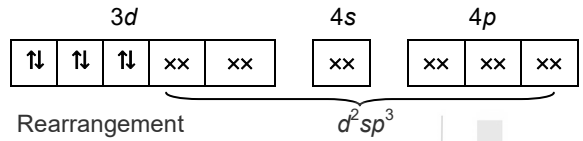
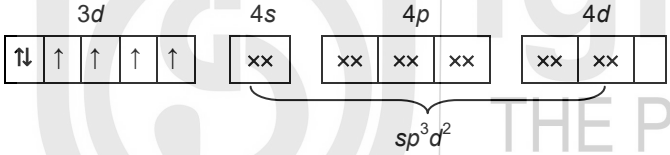
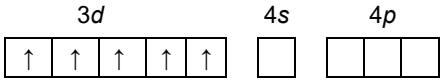
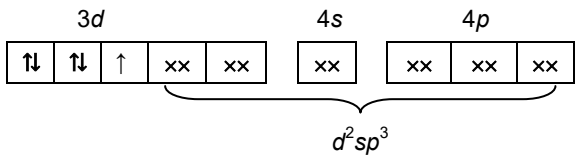
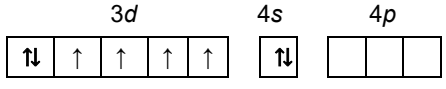
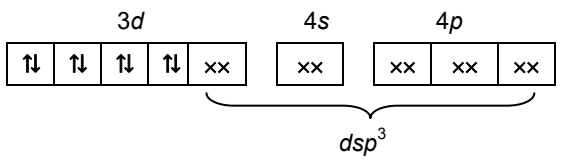


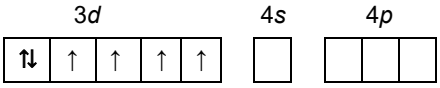
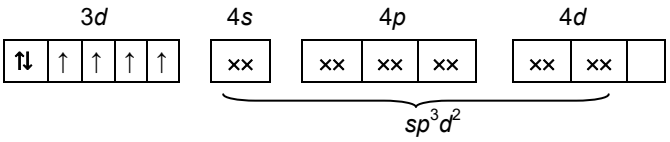
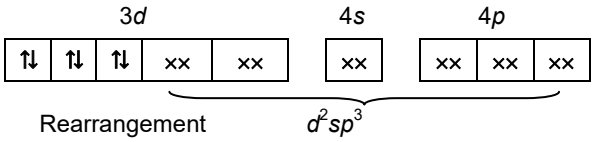
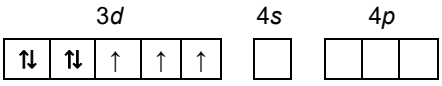
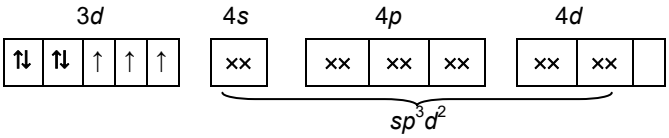
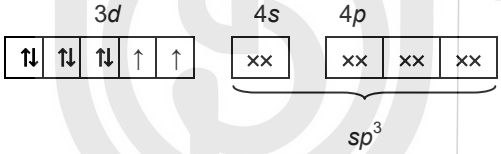
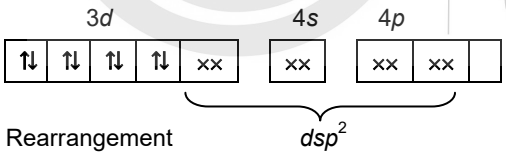
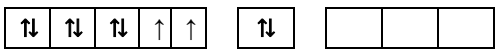
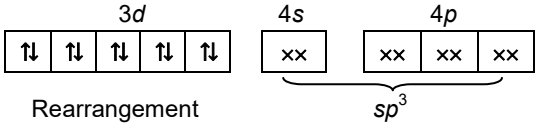
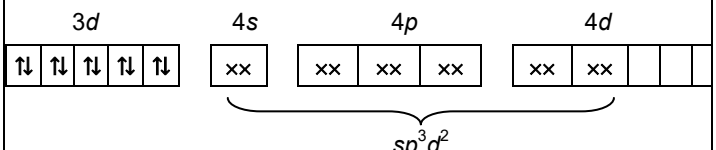
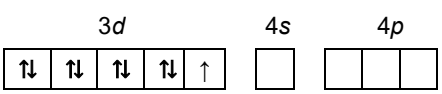
Orbitals of $[CoCl_4]^-$ ion

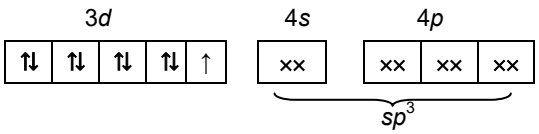
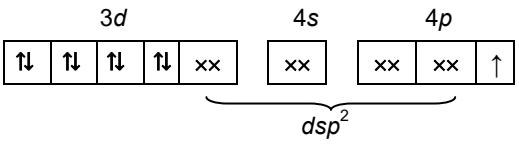


Since the complex has unpaired electrons. So it will be paramagnetic in nature. Some other examples of inner and outer orbital complexes are given below.

Ion (No. of *d* electrons)	Electronic distribution	Oxidation state	Hybridisation	Geometry	UP	Magnetic property
$Cr^{3+}(d^3)$	3d 4s 4p ↑ ↑ ↑	+3			3	Para-magnetic
$[Cr(NH_3)_6]^{3+}$	3d 4s 4p ↑ ↑ ↑ ×× ×× ×× ×× ×× ×× d^2sp^3	+3	d^2sp^3 (inner)	Octahedral	3	Para-magnetic

$Mn^{2+}(d^5)$		+2			5	Para-magnetic
$[Mn(CN)_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	1	Para-magnetic
$[MnCl_4]^{2-}$		+2	sp^3	Tetrahedral	5	Para-magnetic
$Fe^{2+}(d^6)$		+2			4	Para-magnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3 (inner)	Octahedral	0	Dia-magnetic
$[Fe(H_2O)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	4	Para-magnetic
$[Fe(NH_3)_6]^{2+}$	Same	+2	sp^3d^2 (outer)	Octahedral	4	Para-magnetic
$Fe^{3+}(d^5)$		+3		Octahedral	5	Para-magnetic
$[Fe(CN)_6]^{3-}$		+3	d^2sp^3 (inner)	Octahedral	1	Para-magnetic
$Fe(d^6s^2)$		0			4	Para-magnetic
$Fe(CO)_5$		0	dsp^3 (inner)	Trigonal bipyramid	0	Dia-magnetic

$[Co^{3+}(d^6)]$		+3			4	Para-magnetic
$[CoF_6]^{3-}$		+3	sp^3d^2 (outer)	Octahedral	4	Para-magnetic
$[Co(NH_3)_6]^{3+}$		+3	d^2sp^3 (inner)	Octahedral	0	Dia-magnetic
$Co^{2+}(d^7)$		+2			3	Para-magnetic
$[Co(H_2O)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	3	Para-magnetic
$[Ni^{2+}(d^8)]$		+2			2	Para-magnetic
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Para-magnetic
$[Ni(CN)_4]^{2-}$		+2	dsp^2	Square planar	0	Dia-magnetic
$Ni(d^8s^2)$		0			2	Para-magnetic
$[Ni(CO)_4]$		0	sp^3	Tetrahedral	0	Dia-magnetic
$Ni(NH_3)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	2	Para-magnetic
$Cu^{2+}(d^9)$		+2			1	Para-magnetic

$[CuCl_4]^{2-}$		+2	sp^3	Tetrahedral	1	Para-magnetic
$[Cu(NH_3)_4]^{2+}$	 one electron is shifted from 3*d*- to 4*p*-orbital	+2	dsp^2	Square planar	1	Para-magnetic

UP = Unpaired Electrons

We have given various examples of inner and outer orbital complexes. Before proceeding any further, you may try to solve the following SAQ.

SAQ 4

Give the differences between inner and outer orbital complexes.

5.4 SUMMARY

This unit includes the different types of isomerism in coordination compounds. Also the Valence Bond Theory (VBT) to explain the nature of the metal ligand bond is discussed along with inner and outer orbital complexes of Cr, Fe, Co, Ni and Cu.

5.5 TERMINAL QUESTIONS

1. Assuming monomeric and also dimeric formulations what different types of isomerism are possible in the following cases:

   $[Pt(NH_3)_2Cl_2]$; $[Pt(NH_2-CH_2-COO)_2]$;$[Pt(NH_2-(CH_2)_2-NH_2)$;
   $[Cu(NH_3)_4][PtCl_4]$; $[Co(NH_3)_5(NO_2)](NO_3)_2$

2. How do you account for the indicated molecular geometry for the following compounds in terms of valence bond theory:

   $[AuCl_4]^-$ – Square planar; $[Fe(CN)_6]^{3-}$ – Octahedral;

   $[GaCl_4]^-$ – Tetrahedral; $[NiCl_4]^{2-}$ – Tetrahedral;

3. The complex $[PdCl_2(PPh_3)_2]$ gives geometrical isomers and is found to be diamagnetic whereas an analogous Ni compound $[NiCl_2(PPh_3)_2]$ does not give any geometrical isomers and is found to be paramagnetic. Can you explain these observations?

4. For which of the following complexes are optical isomers possible? Give reasons for your answer.

   (a) $[Fe(CN)]_6^{3-}$ (b) $[Co(NH_3)_2(en)_2]^{3+}$

   (c) $[Cr(C_2O_4)_3]^{3-}$

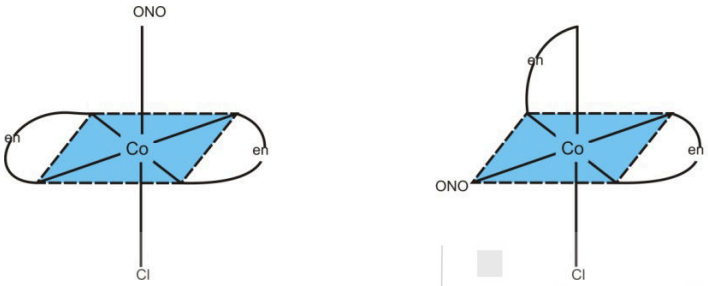
5. Pentacarbonyliron (0) is a diamagnetic complex. Examine the structure according to valence bond model.

5.6 ANSWERS

Self-Assessment Questions

1. Cr(III)-SCN , since they are linkage isomers with ambidentate ligands.

2. The compound $[Co(en)_2Cl_2]NO_2$ may have $[Co(en)_2(NO_2)Cl]Cl$ as an ionization isomer. This ionization isomer in turn may give a linkage isomer, $[Co(en)_2(ONO)Cl]Cl$. These three isomers would thus constitute what are known as structural isomers. All three structural isomers can exist as *cis*- and *trans*-isomers, one such pair is given below:



3. Consider the two compounds $[Co(H_2O)_6]^{2+}$ and $[Co(CN)_6]^{4-}$ each of which contains Co^{2+} ion in an octahedral field. Obviously the compound $[Co(H_2O)_6]^{2+}$ is high spin having a magnetic value of 4.6 BM whereas $[Co(CN)_6]^{4-}$ is low spin with a magnetic moment value of 1.9 BM. The complex $[Fe(NO_2)_6]^{4-}$ contains Fe^{2+} contains Fe^{2+} which belongs to a d^6 system. As the magnetic moment of the complex is zero, it indicates that all the six *d*-electrons are paired up. Hence the compound is low spin. On the other hand, the magnetic moment of 5.94 BM for the complex $[Fe(H_2O)_6]^{3+}$ corresponds to five unpaired moment of 5.94 BM for the complex $[Fe(H_2O)_6]^{3+}$ corresponds to five unpaired electrons in Fe^{3+}. It indicates that there is no pairing of *d*-electrons of Fe^{3+} ion, hence the complex is high spin.

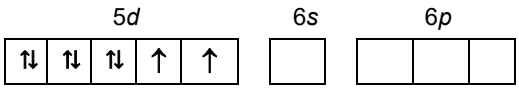
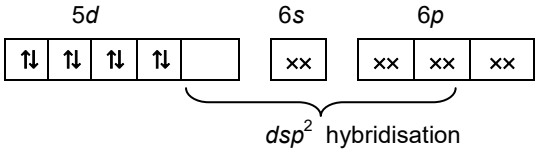
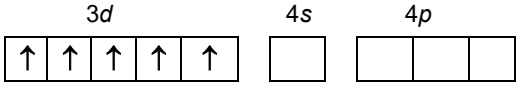
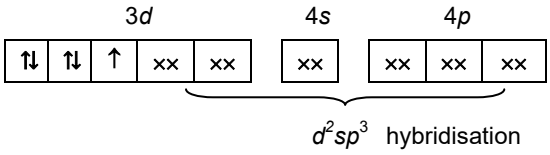
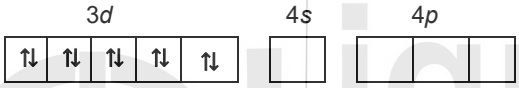
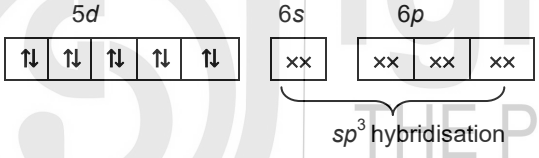
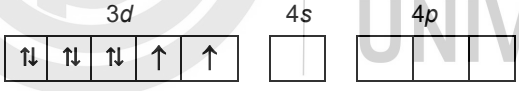
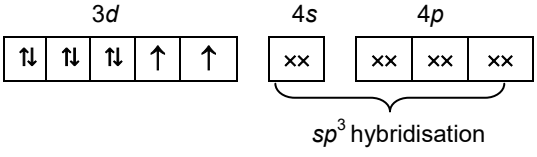
4.

S. No.	Inner Orbital Complexes	Outer Orbital Complexes
a)	Strong field or low spin ligands	Weak field or high spin ligands
b)	Hybridisation is dsp^2 (where one orbital of 3*d*, one orbital of 4*s* and two orbitals of 4*p*)	Hybridisation in sp^3 (where one orbital of 4*s* and three orbitals of 4*p*)
c)	Square planar shape	Tetrahedral shape

Terminal Questions

1. Stereoisomerism (Geometrical); linkage, optical,coordination, ionization.

2. According to valence bond theory, the geometry of any species is guided by the hybrid orbitals available on the central ion for bond formation. Electronic configuration and type of hybrid orbitals used for different anions are given below:

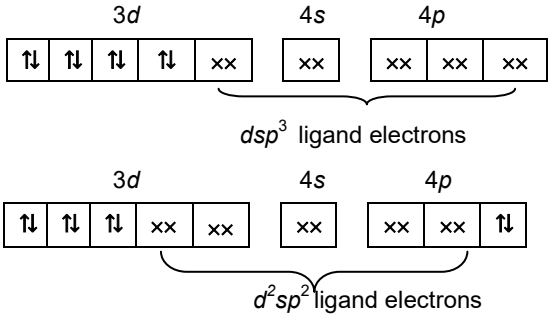
$Au^{3+}5d^8$	
$[AuCl_4]^-$	
$Fe^{3+}\ 3d^5$	
$[Fe(CN)_6]^{3-}$	
$Ga^{3+}\ 3d^{10}$	
$[GaCl_4]^-$	
$Ni^{2+}3d^8$	
$[NiCl_4]^{2-}$	

3. Since $[PdCl_2(PPh_3)_2]$ is a four coordinated complex and gives geometrical isomers, it must have square planar geometry. It will also be diamagnetic. Though $[NiCl_2(PPh_3)_2]$ Is also four coordinated and belongs to a d^8 system just like the first compound, yet it does not give geometrical isomers. This indicates a tetrahedral geometry for the compound which will also be paramagnetic.

4. Since, compound (a) is a completely symmetrical molecule, it will not give optical isomers. Trans-isomers of (b) and (c) will also be symmetrical and, therefore, will not give optical isomers. Only the *cis* forms of (b) and (c) which do not have any plane or centre of symmetry will give optical isomers.

5. Atomic number of iron is 26. Iron(0) retains all these electrons. These are distributed in different orbitals as given below;

Iron(0) is a d^8 system. The carbonyl groups are monodentate and hence iron(0) has a coordination number five in the complex. VBT predicts a dsp^3 hybridisation when the geometry is trigonal bipyramidal and a d^2sp^2 hybridisation when the geometry is square pyramidal. Electrons from the carbonyl ligands will occupy these hybrid orbitals. The options are thus:



In the case of dsp^3 hybridisation all the eight electrons will remain paired in the four 3*d* orbitals of iron supporting the diamagnetic character of the complex. On the other hand in d^2sp^2 hybridisation case, eight electrons of iron cannot be accommodated in the 3*d* orbitals. So, two electrons have to be promoted from 3*d* to 4*p* which is not much favoured. Promotion to higher energy outer orbitals may lead to oxidation. So the trigonal bipyramidal geometry may be preferred.

UNIT 6

CRYSTAL FIELD THEORY-I

Structure

6.1 INTRODUCTION

In the previous units 4 & 5 you have been introduced to various concepts of coordination compounds. In Unit 4 you have studied "Werner's Coordination Theory", the basic definitions of the terms used in the study of coordination compounds and the IUPAC system of their nomenclature. In Unit 5 you learnt about isomerism in coordination compounds and the theories of bonding as applied to complexes with special reference to the "Valence Bond Theory". The terms inner and outer orbital complexes were introduced and specific examples of such complexes of some transition metals were discussed. This unit will incorporate a very important theory of bonding, the "Crystal Field Theory". This theory, first proposed by Hans Bethe in 1929 to explain the colour and magnetic properties of some solid crystalline salts of metals, was originally based on purely electrostatic interaction between a metal ion and the ligands. This is quite an unrealistic situation as it is known that all metal-ligand bonds do show some degree of covalency. However the merit of this theory is that it helps us to explain many special features of transition metal complexes. Later in 1935 van Vleck modified it to allow some covalent interaction. So now let us start our discussions on this theory in this unit and it will continue in the next unit too.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ discuss the crystal field theory;
- ❖ describe the crystal field splitting in octahedral complexes;
- ❖ calculate the crystal field stabilization energy (CFSE);
- ❖ discuss the crystal field effects in weak and strong fields;
- ❖ come to know about the factors affecting the magnitude of crystal field splitting energy; and
- ❖ get introduced to the spectrochemical series.

6.2 CRYSTAL FIELD THEORY

Let us first start with the principal qualitative aspects of the crystal field theory (CFT). It is a hypothetical model and this theory is based on two main assumptions which are given below:

(i) Firstly you have to imagine that the ligands are point negative charges (this may be either from the net negative charge on the ligand or from the negative end of the ligand dipole arising from the lone pair of electrons on its donor atom). So you see the size and shape of ligands are not considered here.

(ii) Secondly, the theory considers only the electrostatic interaction between a metal and the ligands. This may be considered in two steps: (a) electrostatic attraction between the positive nucleus of the metal and the negatively charged electrons of the ligands (imagined as point charges); (b) electrostatic repulsion force between the electrons in the valence shell of the metal and the ligand electrons.

With these assumptions, the crystal theory sets on to find the effect of these point charges (ligands) on the energy levels (*s*, *p*, *d*, *f*) of the metal ion.

Crystal Field Theory (CFT) was first used to explain the properties of crystalline substances and hence is named thus. You can also apply it to any other system in which the interacting particles have a regular arrangement, e.g., in an isolated complex species. The ligand electrons (assumed point charges) are assumed to constitute an electrostatic field around the metal ion, just as in an ideal ionic crystal. Before understanding the details of crystal field splitting in complexes of various types of geometry we need to have a look at the different orbitals of the metal involved in bond formation. Let us start with *s* orbitals; as they are spherically symmetrical, any effect due to mutual repulsions between the *s* electrons and the negatively charged ligands will be the same in all directions. The net result of such an interaction would be to increase the total energy of the system, which comprises both the metal and ligand. The same will happen for the completely filled *p* orbitals of a transition metal ion.

Before going to the interactions for *d* orbitals of the metal ion, one must understand the description of the lobes of *d* orbitals:

- d_{xy}: lobes lie in-between the *x* and the *y* axes.
- d_{xz}: lobes lie in-between the *x* and the *z* axes.
- d_{yz}: lobes lie in-between the *y* and the *z* axes.
- $d_{x^2-y^2}$: lobes lie on the *x* and *y* axes.
- d_{z^2}: there are two lobes on the *z* axis and there is a donut shaped ring that lies on the *xy* plane around the other two lobes.

Thus the *d* orbitals can be divided in two groups – the d_{xy}, d_{xz} and d_{yz} orbitals whose lobes point between the Cartesian axes and the $d_{x^2-y^2}$ and d_{z^2} orbitals whose lobes lie along the Cartesian axes. It is worthwhile to note that the lobes represent the regions where the probability of finding the electron is maximum.

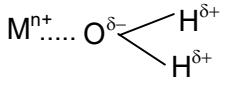
These are shown in Fig. 6.1. In a free metal ion the five *d* orbitals are degenerate, or they have the same energy. However their energy is affected in the presence of an external field. If the external field is spherically symmetrical then the *d* orbitals are affected equally, that is they are still degenerate. However, in a metal complex the ligands approach from specific directions and due to the differences in their orientation, all the five *d* orbitals are not effected equally by the presence of ligands and their degeneracy is lifted and they split into two sets.

The interactions of the orbitals and the extent of splitting will naturally depend on the strength of the field exerted by the ligands; this, in turn, will depend on the distance and intensity of attraction between the central atom and the ligands. Since the *p* orbitals of a metal are usually full and equally populated, splitting of the *p* orbitals will not have any net effect on the energy of the system. The *d* orbitals are the most affected in presence of the ligands. (Such effects will also be negligible for *f* orbitals because the fields are too small, particularly with the 4*f* orbitals which are well shielded by the outer electrons. The 5*f* orbitals give rise to larger splitting. In an octahedral field, the *f* orbitals are expected to be split into three sets).

Now we consider how the *d* orbitals are affected in different geometries, particularly in the octahedral environment of ligands which is most common among complex compounds. Thus, depending upon the position of the ligands the interaction between the *d* electrons will not be uniform and the five *d* orbitals will no more be equal in energy. When complex formation takes place we say that the degeneracy of the orbitals has been removed due to the presence of ligands. Crystal field theory accounts for the properties of complexes in terms of splitting of the *d* orbitals into different energy levels. In the next section we shall consider the octahedral complexes and see how the splitting of the orbitals takes place in this case.

The point charges of CFT (ligands) create an electric fleld, which is responsible for the changes in the energy levels of the metal ion. The electric field is usually referred to as crystal field or ligand field.

Even a neutral molecule can be considered as a source of negative charges. Negative end of the dipole points towards the metal ion as in



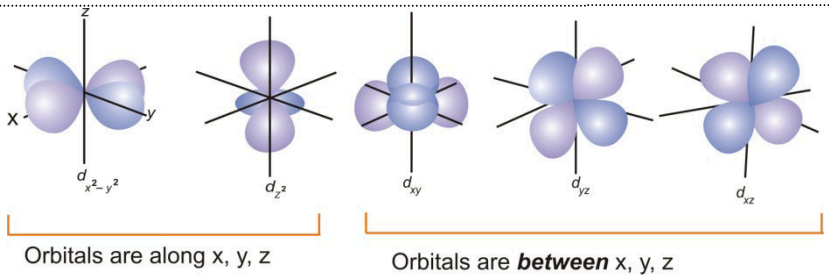


Fig. 6.1: The directional properties of the five *d* orbitals in a free transition metal ion.

SAQ 1

a) Draw the $d_{x^2-y^2}$ orbital giving proper axes.

b) What can you say about direction of its lobes?

6.3 CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEXES

In this section, we are going to discuss about the crystal field splitting in octahedral complexes. Let us consider an octahedral complex, **ML_6,** where M is a metal ion and L stands for a ligand. This **complex** can be represented as shown in Fig. 6.2 a). Here four ligands lie in one plane and the other two in a plane perpendicular to the first plane. Six ligands are at the comers of a regular octahedron and they all lie along the three perpendicular axes, *x*, *y* and *z*. Thus we see that all those orbitals which lie in the direction of these axes will experience a stronger force of repulsion as compared to the orbitals which lie between the axes (Fig. 6.2). So the $d_{x^2-y^2}$ and d_{z^2} orbitals which lie along the axes will be repelled more by the ligands and will be higher in energy than d_{xy}, d_{yz} and d_{xz} set of orbitals.

d_{z^2} orbital actually is a combination of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ which means, it is $d_{2z^2-x^2-y^2}$.

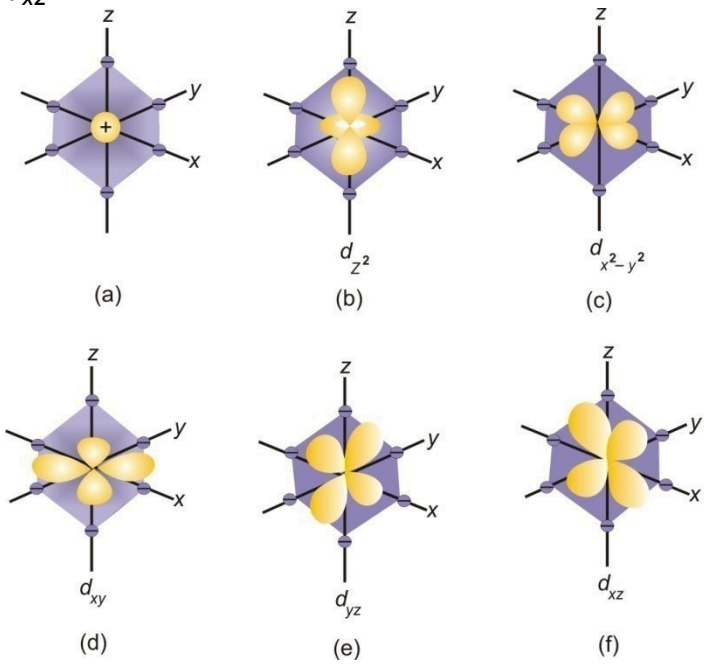


Fig. 6.2: a) An octahedral arrangement of negative charges approaching a metal ion. (b-f) The orientations of the *d* orbitals relative to the negatively charged ligands.

But just a redistribution of the spherical charge cannot alter the energy of the system, so it may be concluded that the energy of these three *d* orbitals will be lowered to keep the total energy of the system constant. Hence, the total increase in the energy of the four electrons in $d_{x^2-y^2}$ and d_{z^2} should be equal to the total decrease in energy of the six electrons in d_{xy}, d_{yz} and d_{zx} orbitals (referring to the hypothetical spherical field). The splitting is thus said to conserve the barycentre or "centre of gravity" of the orbitals. These results are shown diagrammatically in Fig. 6.3.

The idea of barycentre is quite general and applies to any geometry.

The situation may now be generalized for any complex of the type ML_6 with six identical ligands in an octahedral environment around a central metal ion with any number of *d* electrons. The set of three lower energy degenerate orbitals are classed as t_{2g} while the two higher energy orbitals are labeled e_g set of orbitals from their symmetry consideration. The subscript '*g*' (for gerade) applies as the octahedral field is centrosymmetric.

Experimentally Δ_O values are obtained from electronic spectra.

The separation between the t_{2g} and e_g levels is conventionally represented by Δ_O. The term Δ_O is preferred over the older term 10 Dq as it clearly specifies octahedral geometry. Conservation of "centre of gravity", as explained just now, requires that the rise in energy of the two e_g orbitals and the drop in energy of the three t_{2g} orbitals will be in the ratio 6:4 (referred to the average energy of the orbitals in the hypothetical spherical field).

Thus each of the three t_{2g} orbitals is lowered in energy by $0.4\Delta_O$ causing a total lowering of $1.2\ \Delta_O$. Each of the two e_g orbitals are raised in energy by $0.6\Delta_O$ causing a total raise of $1.2\Delta_O$. The sum total of these two thus becomes zero. The Δ_O values are generally in the range of 100-250 kJ mol^{-1}. All this is represented diagrammatically in Fig. 6.3.

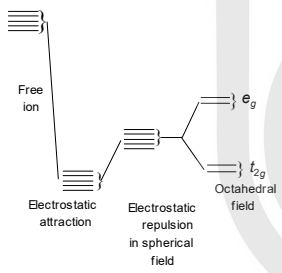


Fig. 6.3 may give an erroneous impression that *d* orbitals in degenerate state are lower in energy than in the complex. This arises since we are considering only the repulsive forces between the *d* orbitals and the ligands. The real state of affairs may be depicted by the above diagram.

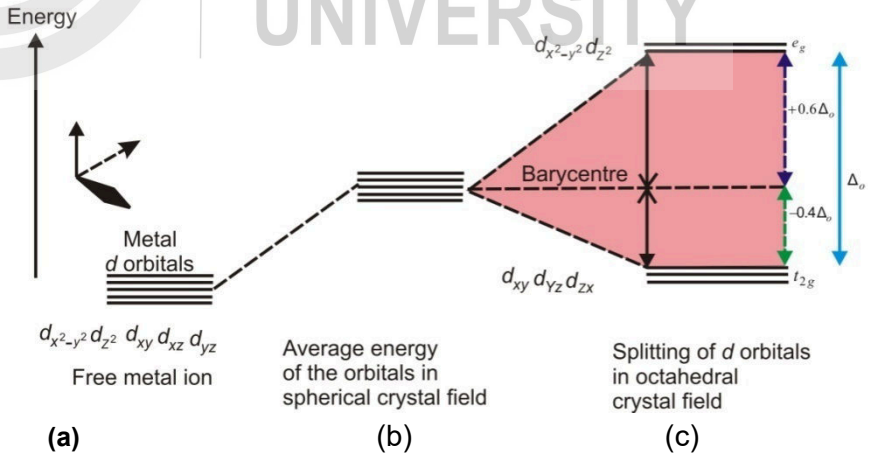


Fig. 6.3: (a) *d* orbital energy level in degenerate state, (b) in an uniform field of six negative charges and (c) in an octahedral crystal field.

Δ_o is delta octahedral.

Next, you will learn how to calculate about crystal field stabilization energy (CFSE). Before that try the following SAQ.

SAQ 2

What is meant by the barycentre in case of crystal field splitting?

6.3.1 Crystal Field Stabilization Energy (CFSE)

We will now discuss how to calculate crystal field stabilization energy (CFSE), for the octahedral complexes .

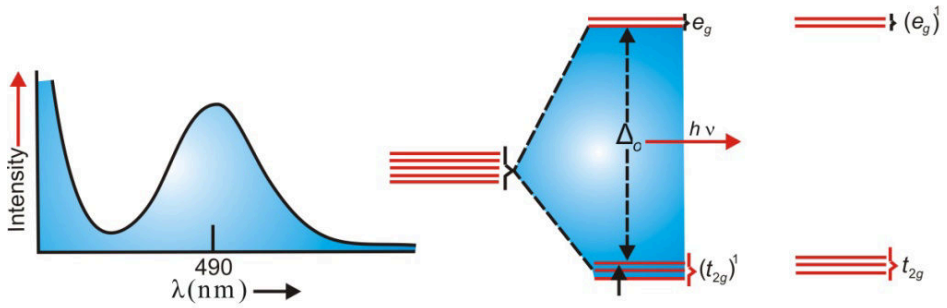
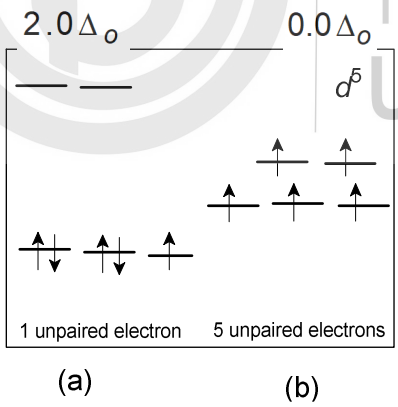


Fig. 6.4: The nature of absorption spectrum of $[Ti(H_2O_6]^{3+}$ ion (visible region).(a) Absorption spectra of $[Ti\ (H_2O)_6]^{3+}$ corresponding to (b) the electron transition $(t_{2g})^1 \rightarrow (e_g)^1$

The magnitude of Δ_O in this case can be estimated from the observed spectrum of the complex $[Ti(H_2O)_6]^{3+}$ The single *d* electron is expected to be promoted to the higher e_g level by absorption of energy equal to Δ_O: $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$ (Fig. 6.4).

Consider a complex, $Fe(+3)L_6$, which belongs to the d^5 system. In a Fe^{3+} ion in a spherically uniform field the five *d* electrons will occupy five different orbitals with parallel spins according to Hund's rule. However, when it is surrounded by six ligands, the five *d* electrons will distribute themselves in either of the following two ways as shown in Fig. 6.5:



Raise in energy is given a positive sign and hence, the lowering is given a negative sign.

Fig. 6.5: Possible configurations of a d^5 system in an octahedral field: (a) low spin (b) high spin

Let us consider a complex in which the metal has only one *d* electron, for example the $[Ti(H_2O)_6]^{3+}$, which exist in aqueous solution. In its ground state, the single *d* electron will occupy the orbital of lowest available energy. The octahedral environment of the six H_2O ligands should split the *d* orbitals into lower energy t_{2g} and higher energy e_g sets and in its ground state, the electron occupies one of the t_{2g} orbitals (t_{2g}^1 configuration). This will lower the energy of the electron by $0.4\Delta_O$ in comparison to that in a hypothetical spherical field of the ligands at the same distance. The complex may then be said to have gained crystal-field stabilization energy (CFSE) to the extent of $0.4\Delta_O$. The energy of the electron with reference to the barycentre will be $-0.4\Delta_O$.

Can you now find out what will be the CFSE if there are two electrons present in t_{2g} set of orbitals? Yes, the CFSE would be equal to $2\times(-0.4\Delta_O)$ or $-0.8\ \Delta_O$. So in this way the CFSE for any complex may be calculated if the electronic distribution is given.

Apart from the d^{10} configuration. all other configurations in an octahedral field would have e_g set of orbital incompletely filled. Under the circumstances electrons from t_{2g} orbitals can jump to e_g orbitals, if the correct amount of energy is supplied to the complex.

In the case of transition metal complexes the energy required for the electronic transition from ground state to the excited state generally falls in the visible part of the electromagnetic radiation. A plot of absorbance versus the wavelength of light for the compound is known as absorption spectrum of the complex. If the complex absorbs the red portion of the white light, the blue part will pass through the compound and the compound will appear blue to our eyes.

When light associated with energy $h\nu$, such that $\Delta_O = h\nu$, is passed through a solution of $[Ti(H_2O)_6]^{3+}$, absorption of light takes place and the lone electron from ground state is raised to the excited state. Experimentally, it is found that the energy for this absorption is around 20,400 cm^{-1}. Hence, we can write Δ_O = 20,400 cm^{-1} and CFSE = $-2/5 \times 20{,}400$ or $-8{,}160$ cm^{-1} or approximately -98 kJ mol^{-1}.

So, in this section you have learnt about crystal field stabilization energy (CFSE) and its calculations. In the next section we will be discussing about the crystal field effects.

SAQ 3

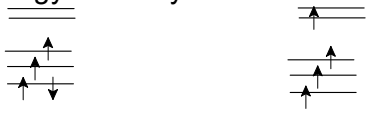
Calculate the CFSE of an octahedral complex with three electrons in the *d* orbitals.

6.4 CRYSTAL FIELD EFFECTS

In this section we are going to discuss about crystal field effects. We will start our discussion with weak and strong fields.

6.4.1 Weak and Strong Fields

To understand the crystal field effects in weak and strong fields we have to start with a d^4 complex, the fourth *d* electron may either (i) doubly occupy a t_{2g} orbital at the cost of the pairing energy *P* or (ii) enter one of the e_g orbitals at the cost of destabilization by an amount Δ_O. The actual configuration adopted will correspond to lowest energy of the system:



d^4	$\Delta_O > P : t_{2g}^4$	$\Delta_O < P : t_{2g}^3 e_g^1$
	CFSE = - 1.6 Δ_O + *P*	CFSE = - 0.6 Δ_O

In the first case ($\Delta_O > P$), the complex has only two unpaired electrons and is said to be *low-spin complex* while in the second case ($\Delta_O < P$), the complex has four unpaired electrons; it is said to be a *high-spin complex.* Strong ligand fields cause greater splitting, making Δ_O high. Hence low-spin complexes are also referred to as strong-field complexes while high-spin complexes are called weak-field complexes.

The decision as to which of the two configurations, i.e., high-spin or low-spin is more stable is rather easy to make. If the pairing energy is greater than Δ_O, then the two electrons will prefer to go in different orbitals with parallel spins giving a high-spin complex. The reverse is true for low-spin complexes. Thus, we can write

if $P > \Delta_O$------- high-spin complex

$P < \Delta_O$------- low-spin complex

$P = \Delta_O$------- the two states are in equilibrium

Pairing energy, *P*, depends mainly on the electronic distribution of the central metal ion and its value can be obtained from the atomic spectra of the element. Δ_O is obtained from the molecular spectra of the complex. It depends on the metal ion, ligand and the geometry of the complex. Once these two values are known for any complex, you will know whether it will be high-spin or low-spin and you will also be able to calculate the CFSE.
Table 6.2 gives the pairing energy values for d^4 to d^7 ions of first row transition elements as well as Δ_O values for a few complexes. In d^1, d^2, d^3, d^8, d^9 and d^{10} systems only one configuration of each is possible.

Table 6.1: *P* and Δ_O, value for octahedral complexes of some first row transition elements

d^n	Ion	Pairing energy *P* (cm^{-1})	complex	Δ_o(cm^{-1})
d^4	Cr^{2+}	20,425	$[Cr(H_2O)_6]^{2+}$	13,900
	Mn^{3+}	25,215	$[Mn(H_2O)_6]^{3+}$	21,000
d^5	Mn^{2+}	23,825	$[Mn(H_2O)_6]^{2+}$	7,800
	Fe^{3+}	29,875	$[Fe(H_2O)_6]^{3+}$	13,700
d^6	Fe^{2+}	19,150	$[Fe(H_2O)_6]^{2+}$	10,400
			$[Fe(CN)_6]^{4-}$	33,000
	Co^{3+}	23,625	$[Co(H_2O)_6]^{3+}$	18,200
			$[Co(NH_3)_6]^{3+}$	22,900
			$[Co(CN)_6]^{3-}$	33,500
d^7	Co^{2+}	20,800	$[Co(H_2O)_6]^{2+}$	9,300

The CFSE for configurations $d^1 - d^{10}$ ions in strong and weak octahedral fields are computed below by taking account of *P*. (There will be no splitting of the *d* orbitals in a d^0 case).

Table 6.2: Crystal Field Stabilization Energy (CFSE) for Octahedral Complex

Weak field				Strong field		
d^n	Configuration	No. of Unpaired electrons	CFSE	Configuration	No. of Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$-0.4\Delta_o$	t_{2g}^1	1	$-0.4\Delta_o$
d^2	t_{2g}^2	2	$-0.8\Delta_o$	t_{2g}^2	2	$-0.8\Delta_o$
d^3	t_{2g}^3	3	$-1.2\Delta_o$	t_{2g}^3	3	$-1.2\Delta_o$
d^4	$t_{2g}^3\ e_g^1$	4	$-0.6\Delta_o$	t_{2g}^4	2	$-1.6\Delta_o + P$
d^5	$t_{2g}^3 e_g^2$	5	$0.0\Delta_o$	t_{2g}^5	1	$-2.0\Delta_o + 2P$
d^6	$t_{2g}^4\ e_g^2$	4	$-0.4\Delta_o$	t_{2g}^6	0	$-2.4\Delta_o + 2P$
d^7	$t_{2g}^5\ e_g^2$	3	$-0.8\Delta_o$	$t_{2g}^6\ e_g^1$	1	$-1.8\Delta_o + P$
d^8	$t_{2g}^6\ e_g^2$	2	$-1.2\Delta_o$	$t_{2g}^6\ e_g^2$	2	$-1.2\Delta_o$
d^9	$t_{2g}^6 e_g^3$	1	$-0.6\Delta_o$	$t_{2g}^6\ e_g^3$	1	$-0.6\Delta_o$
d^{10}	$t_{2g}^6\ e_g^4$	0	$0.0\Delta_o$	$t_{2g}^6\ e_g^4$	0	$0.0\Delta_o$

The pairing energy may be ignored for many practical purposes. Here it has been computed by taking into account the number of unpaired electrons present in the free ion. For example, a d^6 metal ion already contained one pair of electrons in a *d* orbital. The extra destabilization in a t_{2g}^6 configuration therefore comes from two more paired electrons. However, the "pairing energy" also includes a major contribution from the loss of exchange energy when electrons with parallel spins are forced to adopt antiparallel spins.

The CFSEs comprise only about 2% to 10% of the total binding energy of a given complex and hence not the main source of binding energy in a complex. However, the CFSEs may be important in explaining many properties of complex species, as we shall encounter soon. So we have, discussed in the next section we will discuss the factors affecting the magnitude of crystal field splitting energy.

SAQ 4

What would be the CFSE for an octahedral complex of a d^7 ion in weak field and strong field?

6.5 FACTORS AFFECTING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING ENERGY

In this section we are going to discuss the factors affecting the magnitude of crystal field splitting energy.

What do you observe about the relation between Δ_O and ligands from Table 6.1?

1. For a given ligand, Δ_O does not vary much along the metal ions in the first transition series in the same oxidation state. So you will find that Δ_O for hexaaqua complexes of Mn^{2+} and Ni^{2+} are comparable.

2. For a given ligand, Δ_O increases with the oxidation state of the metal. The hexaaqua complex of Fe^{2+} complex has Δ_O values which are less than the corresponding complex of Fe^{3+}.

3. For a given ligand and same stereochemistry, the magnitude of Δ_O increases by about 30% to 50% on passing from the first transition series (3*d* series) to the second transition series (4*d* series) and again by about the same amount from the second transition series to the third transition series(5*d* series). Thus Δ_O for the three hexaammines increases as $[Co(NH_3)_6]^{3+}$: 23,000 cm^{-1}; $[Rh(NH_3)_6]^{3+}$: 34,000 cm^{-1}, $[Ir(NH_3)_6]^{3+}$: 41,000 cm^{-1}. The reason behind this may be higher effective nuclear charge and greater spatial distribution of the larger *d* orbitals.

4. For a given ligand and stereochemistry, the metal ions can be arranged according to increasing order of Δ_O:

   $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$

6.5.1 Spectrochemical Series

As you can see from Table 6.1, there is a large variation in Δ_O values as you change the ligand. It is possible to list most common ligands in order of increasing field strength, Δ_O. Such an arrangement, known as spectrochemical series(as the data came from spectral studies the series is referred to as the spectrochemical series) is given below:

$$I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < H_2O < NCS^- < NH_3 < en < bipy < phen < NO_2^- < CN^-$$

This series helps us to find out the reason behind the differences in the spectral properties of complexes. As the strength of the crystal field created by the ligands increases, the frequency of absorption of light by the complex would also increase. Absorption of high frequency radiations means that light of lower frequency will be transmitted and will be responsible for the particular colour of the complex. It thus explains as to why the colours of a series of complexes of one particular metal ion, in the same oxidation state having the same geometry, could be different. For example, four octahedral compounds of Co^{3+} ion show different colours (Table 6.3) which are in accordance with spectrochemical series.

Table: 6.3: The Δ_o values of octahedral compound of Co^{3+} in cm^{-1}.

Complex	$\Delta_O(cm^{-1})$	Colour
$[Co(C_2O_4)_3]^{3-}$	18,000	Dark green
$[Co(H_2O)_6]^{3+}$	18,200	Blue
$[Co(NH_3)_6]^{3+}$	22,900	Golden-brown
$[Co(CN)_6]^{3-}$	33,500	Yellow

The spectrochemical series can sometimes be helpful in making certain prediction about the complex. For instance, if we know that a particular metal ion gives a low spin complex with ammonia ligands, then it is certain that its analogous compound with CN^- ligands would also be low spin, since CN^- creates much stronger crystal field than NH_3. Similarly, if a metal forms a low-spin complex with say, 1,2-diaminoethane, it will form low-spin complexes with ligands farther right to it in the series, that is, bipyridyl or cyanide ions. However, these predictions are purely qualitative in nature and many a times the order may be reversed for adjacent ligands in the spectrochemical series.

From previous courses you must have studied that atomic spectra are obtained when electrons are excited from one energy level to another. The energy of the light absorbed or emitted is related to the energy levels of the atom or ion under study. Look at the Fig. 6.6, which shows how to use colour disks to analyze colours.

You will not be able to interpret the spectrochemical series form electrostatic effects alone, e.g., neutral water molecules has a stronger ligand field than the negatively charged hydroxyl ion. Also, H_2O has a greater dipole moment than NH_3, but the latter has a stronger ligand field.

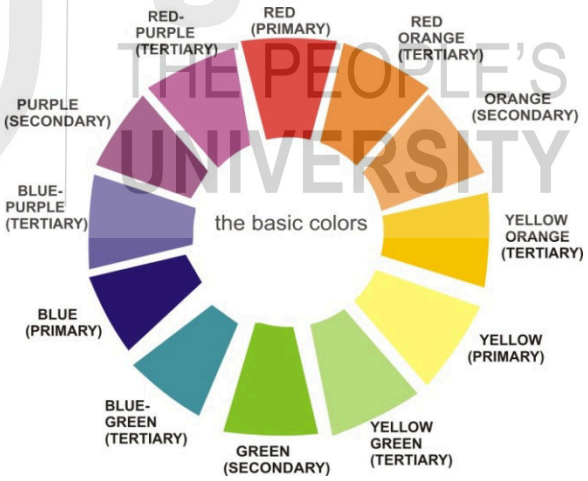


Fig. 6.6: Using colour disks to analyze colours.

The three primary colours are red, blue, and yellow. Adding light of two primary colors gives the secondary colours purple (red + blue), green (blue + yellow). Combining the three primary colours results in white light.

In coordination complexes, the splitting between *d* orbitals often corresponds to the energy of visible light, so light in the visible region of the spectrum is absorbed when electrons move from a lower-energy *d* orbital to a higher-energy *d* orbital. When the electron moves between two orbitals having different energies in a complex, it is referred to a *d-d* transition. The colours of a solution is due to the colours of the light *not* absorbed by the solution. For example, solution of Ni^{2+} ion in water absorbs red and blue light and so appears green.

At the end of this section, you should try the following SAQ first and then move to the next section.

SAQ 5

If pairing energy *P* for Fe^{3+} ion is 29,875 cm^{-1} and Δ_O for $[Fe(H_2O)_6]^{3+}$ is 13,700 cm^{-1}, find out

(i) whether the complex is high spin or low spin

(ii) the number of unpaired electrons

(iii) whether the complex is coloured or not?

6.6 SUMMARY

In this unit we have discussed the crystal field theory along with a description of the crystal field splitting in octahedral complexes. We have also learnt how to calculate the crystal field stabilization energy (CFSE). Thereafter, a discussion on the crystal field effects in weak and strong fields was done. The factors affecting the magnitude of crystal field splitting energy were discussed in details. Finally the spectrochemical series was discussed.

13

6.7 TERMINAL QUESTIONS

1. An octahedral complex $[CoA_6]^{3+}$ is red and the complex $[CoB_6]^{3+}$ is green. Which ligand, A or B, produces the large crystal field splitting energy, Δ_O? Explain your answer.
2. Is the complex $[CoF_6]^{4-}$ more likely to be low-spin or high-spin?
3. Sketch the *d* orbital energy levels for $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$ and predict the number of unpaired electrons in each.
4. For an octahedral complex of each of the following metal ions, draw a crystal field energy diagram that shows the electron occupancy of the various *d* orbitals:

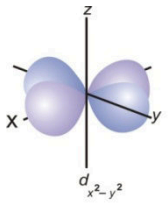
   a) Mn^{2+} b) Cr^{2+} c) Co^{2+}

   If appropriate, show both the high-spin and low-spin configurations.

6.8 ANSWERS

Self Assessment Questions

1. a)

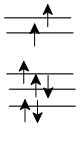


   b) The lobes lie on the x and y axes.

2. The barycentre is the "centre of gravity" of the orbitals which is observed in case of crystal field splitting.

3.  t_{2g}^3 CFSE $= -1.2\Delta_o$

4.

Weak field	Strong field
 $t_{2g}^5\ e_g^2$	 $t_{2g}^6\ e_g^1$
high spin	low spin
Net energy stabilization in weak field: $= -5(0.4)\Delta_o + 2(0.6)\Delta_o$ $= -\ 0.8\Delta_o$ CFSE $= -\ 0.8\Delta_o$	Net energy stabilization in strong field: $= [-6(0.4)\Delta_o + 1(0.6)\Delta_o] + P$ $= -\ 1.8\Delta_o + P$ CFSE $= -\ 1.8\Delta_o + P$

5. i) Since P>>Δ_O, the complex should be high spin.

ii) Fe^{3+} in high spin state in $[Fe(H_2O)_6]^{3+}$ will have the following electronic configuration:

 $t_{2g}^3\ e_g^2$

Hence, the number of unpaired electrons is 5.

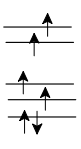
iii) Yes, it should be coloured. Since the e_g orbitals are not completely filled, the electrons from t_{2g} set of orbitals can be excited to e_g orbitals. Such a transition would absorb light in the visible region and hence the compound would appear coloured.

Terminal Questions

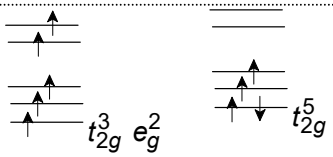
1. $[CoA_6]^{3+}$, the red coloured complex produces the larger crystal field splitting energy Δ_O. This is because absorption of high frequency radiations means that light of lower frequency will be transmitted and will be responsible for the particular colour of the complex.

2. High spin, as F^- ligand is not a very strong ligand.

3.

$[Fe(OH_2)_6]^{2+}$	$[Fe(CN)_6]^{3-}$
Fe^{2+} d^6  $t_{2g}^4\ e_g^2$ Number of unpaired electrons = 4	Fe^{3+} d^5  t_{2g}^5 Number of unpaired electrons = 1

4. a) Mn^{2+} d^5



$t_{2g}^3\ e_g^2$ t_{2g}^5

b) Cr^{2+} d^4 $t_{2g}^3\ e_g^1$ t_{2g}^4

c) Co^{2+} d^7 $t_{2g}^5\ e_g^2$ $t_{2g}^6\ e_g^1$

UNIT 7

CRYSTAL FIELD THEORY-II

Structure

7.1 INTRODUCTION

One of the important theories of bonding in coordination compounds is crystal field theory which was introduced in the previous unit. A description of the crystal field splitting in octahedral complexes was explained; calculations of the crystal field stabilization energy (CFSE) and discussions on the crystal field effects in weak and strong fields were also covered. The factors affecting the magnitude of crystal field splitting energy were discussed in detail and you were introduced to the spectrochemical series. We will continue in this unit with our discussions on crystal field theory starting with crystal field splitting in tetrahedral complexes after which we will compare CFSE for octahedral and tetrahedral complexes. Subsequently tetragonal distortion of octahedral geometry along with Jahn-Teller distortion will be discussed and finally we will deal with crystal field splitting in square planar complexes.

Expected Learning Outcomes

After studying this unit and having the experiments performed, you should be able to:

- ❖ understand crystal field splitting in tetrahedral complexes;
- ❖ compare the crystal field stabilization energy(CFSE) for octahedral and tetrahedral complexes;
- ❖ understand crystal field splitting in tetrahedral complexes;

- ❖ compare the crystal field stabilization energy(CFSE) for octahedral and tetrahedral complexes;
- ❖ understand the tetragonal distortion of octahedral geometry (Jahn-Teller distortion);
- ❖ learn about formation of square planar complexes and note the crystal field splitting in such cases; and
- ❖ learn about some common applications of complexes including their magnetic behaviour.

7.2 CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEXES

Splitting of d orbitals in tetrahedral complexes

The tetrahedral geometry is a little more difficult to visualize than the octahedral geometry; however Fig. 7.1 gives a simplified picture. A tetrahedron is formed when the diagonally opposite corners of the top and bottom faces of a cube are joined to its centre.

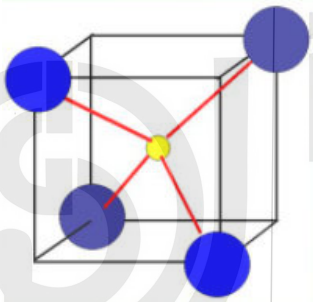


Fig. 7.1: Four opposite corners of a cube describe a tetrahedron.

So you see, a tetrahedral complex can be viewed as a part of cube where the metal ion occupies the centre of the cube and the four ligands are placed at four alternate corners of the cube (Fig. 7.1). From this figure you can see that none of the orbitals d_{xy}, d_{yz}, d_{xz} or $d_{x^2-y^2}$ and d_{z^2} point directly at the ligand.

But the first set of three orbitals approach the ligands more closely as compared to the last two orbitals. Hence, in this case the *d* orbital splitting will be as shown belowin Fig. 7.2.

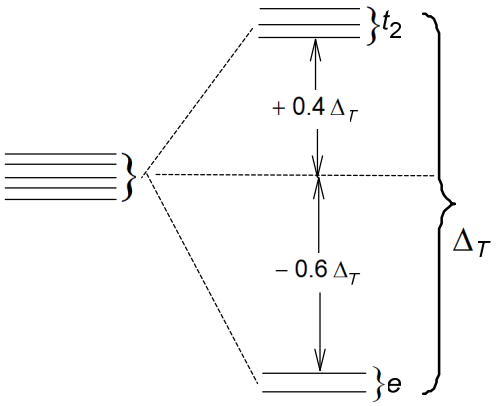


Fig. 7.2: Splitting of *d* orbitals in a tetrahedral crystal field

Now, the lower-energy $d_{x^2-y^2}$ and d_{z^2} orbitals are labeled '*e*' and the higher energy d_{xy}, d_{yz} and d_{zx} orbitals are labeled 't_2'. In the tetrahedral case, the subscript *g* is not applied as the tetrahedron does not possess a centre of symmetry. Please note this difference from the subscripts used in case of octahedral complexes. The difference in energy between the two sets of orbitals is denoted by Δ_T. Remembering the reasonings regarding conservation of energy of barycentre which we discussed in case of octahedral complexes, we find that each orbital of *e* set is lowered by $-0.6\Delta_T$ and each orbital belonging to the ' t_2 ' set is raised in energy by $+0.4\Delta_T$.

In a d^1 or d^2 system the electrons will always go in the '*e*' set of orbitals with the release of corresponding amount of energy (CFSE). For d^1 it will be $-0.6\ \Delta_T$ and for d^2 it will be $2(-0.6\ \Delta_T)$ or $-1.2\ \Delta_T$. These values can be converted in terms of Δ_O for comparison as explained in the next section. Again for systems from d^3 to d^6 there are two different configurations possible in each case as shown in Fig. 7.3.

From Table 6.1 in the previous unit, you can see that the pairing energies (*P)* and Δ_O for common ligands are of comparable order of magnitude. It is also true that Δ_T is almost one-half the value of Δ_O. Hence, we can say that pairing energy, *P*, is almost double the value of Δ_T or in other words, $P >> \Delta_T$. Under the circumstances all the electrons in any system in tetrahedral field will spread out in *e* and t_2 sets of orbitals rather than pair up in *e* orbitals. In other words it is said that the low spin tetrahedral complexes of the first row transition elements are not known.

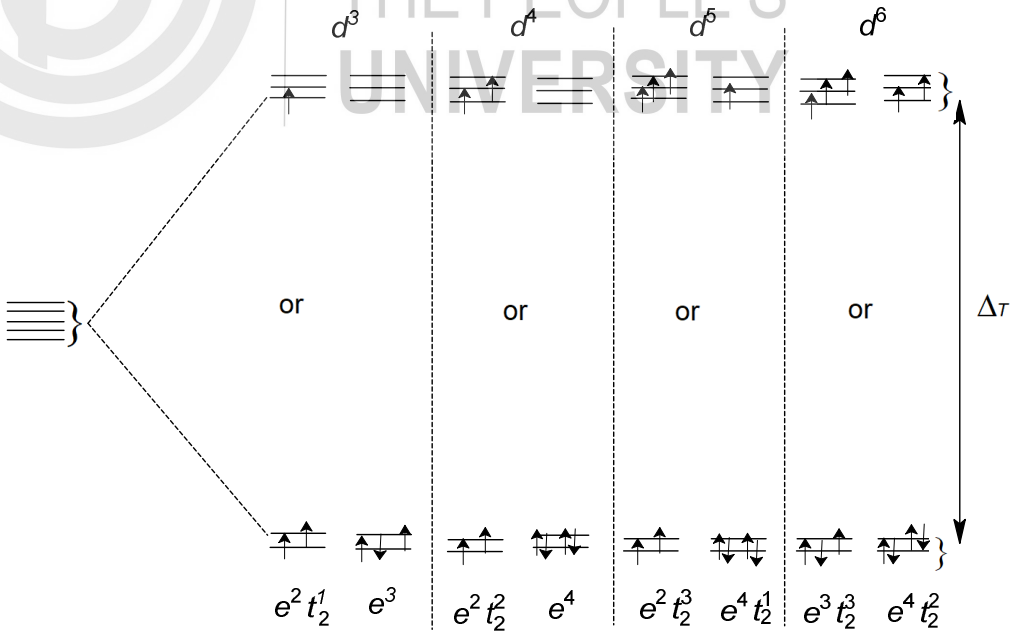


Fig. 7.3: Possible electronic configurations for d^3 to d^6 systems in a tetrahedral crystal field.

This section deals with the discussion of crystal field splitting in tetrahedral complexes. In the next section, we are going to compare the CFSE for the octahedral and tetrahedral complexes.

7.3 COMPARISON OF CFSE FOR O_H AND T_D COMPLEXES

We will now try to compare the CFSE for octahedral and tetrahedral complexes. There is an interesting question which can come to your mind- does a complex have a preferred geometry? Is octahedral coordination favoured over tetrahedral coordination or vice versa? The common geometries found in complex compounds are tetrahedral, square planar and octahedral coordination. An octahedral complex has six M-L bonding interactions and, in the absence of significant steric and electronic effects, this arrangement will have a lower energy than a tetrahedral complex with just four M-L bonding interactions (considering the steric bulk on a complex). Unless opposed by severe steric or electronic factors, the octahedral coordination, using the largest number of available sigma bonding orbitals on the metal, is the most stable one. As we have already seen, such complexes are also favoured by higher CFSE than tetrahedral complexes. However, certain metal ions in the first transition series exhibit a greater tendency than others to form tetrahedral complexes. The relative stabilities of octahedral and tetrahedral complexes of a metal naturally depend upon several factors in addition of CFSE. However, if we compare such trends in series of ions where all other factors contributing to ΔH^o vary uniformly, the effect of the difference between the CFSEs may be appreciated to some extent.

Δ_T is delta tetrahedral

The change in enthalpy of hydration (ΔH^o) data gives us a rough estimate of CFSE.

The separation between t_2 and e levels (Δ_T) in the tetrahedral case is much less than that in the corresponding octahedral field. If the same ligands approach the same metal ion from the same distance, we expect that the electrostatic effect of four point charges will be 2/3 of that produced by six point charges. Also, the ligands do not point directly towards the metal in a tetrahedral complex and this also reduces it by a further factor of 2/3. Detailed calculations show that

$$\Delta_T = \frac{2}{3} \times \frac{2}{3} \Delta_O = \frac{4}{9} \Delta_O$$

$$\Delta_T = \frac{4}{9} \Delta_O \qquad ...(7.1)$$

for the same metal ion and same ligands at same metal-ligand distances, in general terms, the magnitude of splitting for a tetrahedral complex is nearly half that for the corresponding octahedral complex. Tetrahedral complexes thus gain lower CFSE compared to octahedral complexes. Let us understand by considering the absorption spectra of VCl_4 and VCl_6^{2-}. Here assumption is made that VCl_4 according to the CFT is a tetrahedral complex of V(+4), d^1 system. The ground state configuration would then be $e^1 t_2^0$. Absorption of light results in the electronic transition $e \rightarrow t_2$ which corresponds to the broad absorption band of VCl_4 around 8000 cm^{-1}. So Δ_T for VCl_4 is equal to 8000 cm^{-1} which is nearly half the value of Δ_O observed with VCl_6^{2-} (15,400 cm^{-1}).

High spin tetrahedral complexes are much prevalent as their crystal field splittings are lower than the corresponding pairing energy. An exception is

$[Cr\{N(SiMe_3)_2\}_3NO]$ (Me = methyl) which is a low-spin complex with a distorted tetrahedral structure; it contains Cr(+2) (d^4) coordinated by NO^+ and three $\bar{N}(SiMe_3)_2$. Then, if tetrahedral complexes are not favoured by large CFSE, why are they formed? Well, when the ligands are large or other stereochemistry is not favoured by high gain of CFSE then the tetrahedral complexes may be favoured. In case of large and bulky ligands steric effects may favour tetrahedral geometry.

Using the expression for CFSE in both tetrahedral and octahedral fields in terms of Δ_O (using Eq. 7.1), we can compare them. Thus, for a d^1 ion in tetrahedral field (e^1), the CFSE is $\frac{3}{5}\Delta_T = \frac{3}{5}\times\frac{4}{9}\Delta_O = 0.266\ \Delta_O$. The values of CFSE thus obtained for all the d^0 to d^{10} configurations may be similarly calculated. These are plotted against the number of d electrons together with the CFSE values of high spin octahedral complex in Fig. 7.4.

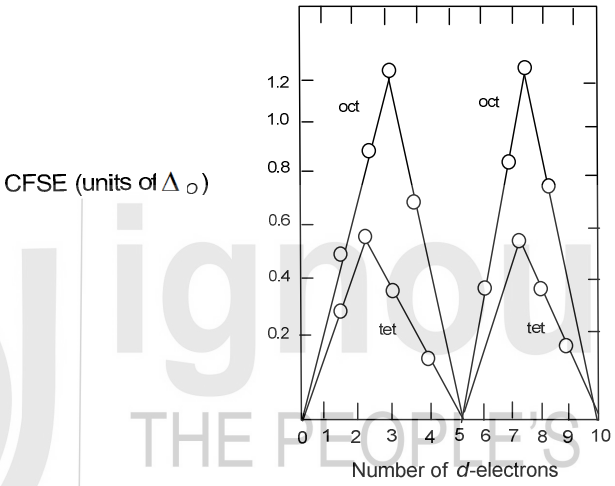


Fig. 7.4: CFSE for d^0 – d^{10} (high spin) ions in octahedral and tetrahedral fields.

The d^4 and d^9 configurations (for example Cr(+2) and Cu(+2)) gain a higher CFSE by adopting octahedral coordination). They undergo distortion and gain further stabilization, this will be discussed later. What about ions with d^1, d^2, d^6 and d^7 configurations? On passing from tetrahedral to octahedral coordination they will gain little additional CFSE and this may be the reason why they form many tetrahedral complexes. Thus V(+3)(d^2), unlike Cr(+3), forms tetrahedral VX_4^- species (X = Cl, Br, I). It similarly forms a larger number of tetrahedral complexes with both neutral and anionic ligands. V^{+2}(d^2) and Co^{+2}(d^7) form tetrahedral complexes ($[MX_4]^{2-}$) with chloride, bromide, and iodide ligands. d^0, d^5 (high spin) and d^{10} configurations have no crystal field stabilization either in tetrahedral or octahedral environment. From Fig. 7.4 can you say which configurations show preference for octahedral geometries? Chromium (+3) (d^3) and nickel (+2) (d^8) do indeed show an exceptional preference for octahedral geometries. So if you consider the CFSE then predictions can be made that d^3 and d^8 ions strongly prefer an octahedral geometry over a tetrahedral one; for other configurations the preference is less pronounced.

Now let us see the effect of the ligands on CFSE. Weak-field ligands will not give preference for octahedral coordination. With strong-field ligands, low-spin complexes might be preferred and although the situation is complicated by the pairing energy, the CFSE of a low-spin octahedral complex will be greater than

that of a high-spin complex. So, low-spin complexes will be preferably octahedral and not tetrahedral. This preference for octahedral over tetrahedral coordination plays an important role in the solid state by influencing the structures that are adopted by compounds of *d*-block metals. This influence is demonstrated by the ways in which the different metal ions A and B in spinels (of formula AB_2O_4) occupy the octahedral or tetrahedral sites.

Thus you have learnt how to compare the CFSE for the octahedral and tetrahedral complexes in this section. Before moving to the next section where we will discuss crystal field splitting in square planar complexes, please solve the following SAQ.

SAQ 1

Which electronic configuration of *d* orbitals does not have any CFSE either in tetrahedral or octahedral environment? Justify your answer.

7.4 CRYSTAL FIELD SPLITTING IN SQUARE PLANAR COMPLEXES

The next common geometry after octahedral and tetrahedral, encountered in transition metal complexes, is square planar. In this section, we will discuss crystal field splitting in such complexes. Prior to that, we will have a look at tetragonal distortion of octahedral geometry.

Tetragonal Distortion of Octahedral Geometry: Jahn-Teller Distortion

The Jahn-Teller effect basically gives an insight of distortion from perfect symmetry. We have noted earlier that the degeneracy of the five *d* orbitals is removed in a crystal field. Lifting of this degeneracy provides greater stability by way of crystal field stabilization energy. The system may become even more stable if this degeneracy is further removed. Certain electronic configurations facilitate such distortions from perfect geometries. Consider an octahedral high spin d^4 complex having $t_{2g}^3\, e_g^1$ distribution of electrons. In a regular octahedral environment, the e_g level is doubly degenerate: the electron can occupy either the $d_{x^2-y^2}$ or d_{z^2} orbital. If the e_g level is split as a consequence of some distortion in the regular geometry, the electron will now occupy the orbital with lower energy and get further stabilized. A rigorous and generalized statement of this situation was made by Jahn and Teller in 1937. The theorem states: *Any nonlinear molecule in a degenerate electronic state will undergo distortion to remove the degeneracy and to lower the energy.*

The theorem only tells us when a distortion is most likely to be expected; but it does not tell us anything about the direction or magnitude of distortion. However, it is seen that if the undistorted system has a centre of symmetry, this will be maintained in the equilibrium configuration after distortion. Examples of Jahn-Teller distortions are common among systems with unsymmetrically filled e_g level:

d^4 (high spin) : Cr(+2), Mn(+3)

d^7 (low spin) : Co(+2), Ni(+3)

d^9 : Cu (+2)

The structure of the $[Cu(H_2O)_6]^{2+}$ ion in the perchlorate salt is shown below. The unusually long axial Cu-O distances are noteworthy. Since the ion still retains a four-fold axis of symmetry, the distortion is referred to as *tetragonal distortion.* The $[Ni(H_2O)_6]^{2+}$ ion, in contrast, has a symmetric octahedral distribution of the ligands.

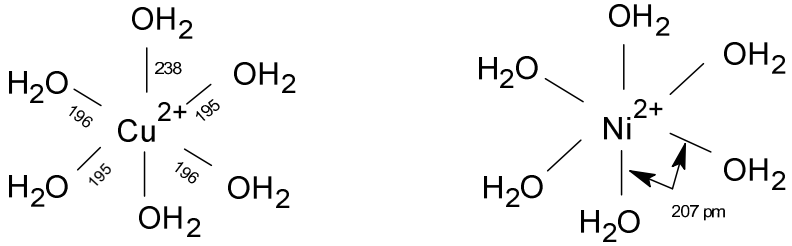


Fig. 7.5: Jahn-Teller distortion in octahedral Cu(+2). Tetragonally distorted octahedral structure of $[Cu(H_2O)_6]^{2+}$ in $[Cu(H_2O)_6]$ $[ClO_4]_2$ and the symmetric octahedral structure of $[Ni(H_2O)_6]^{2+}$ in $[NH_4]_2[Ni(H_2O)_6][SO_4]_2$.

Let us first understand Jahn-Teller distortion in a simple way with the $[Cu(H_2O)_6]^{2+}$ ion as an example. In an octahedral field, the d^9 ion has an electron distribution $t_{2g}^6 e_g^3$. So the following two cases are possible:

Case I: $d^1_{x^2-y^2}\, d^2_{z^2}$:

The ligands along the *x* and *y* axes will be less screened from the electrostatic attraction of Cu^{2+} ion than the two ligands on the z-axis. So, the four ligands in the *xy*-plane will be closer to the cation than the other two on the *z*-axis. This results in tetragonal distortion of the octahedron which is elongated along the *z*-axis (*z*-out). There are four short equatorial bonds and two long axial bonds.

Case 2: $d^2_{x^2-y^2}\, d^1_{z^2}$:

Here the four ligands in the *xy*-plane will be more screened from the electrostatic attraction of the Cu^{2+} ion than the two ligands on the z-axis. Thus, the two axial ligands are more closer to the metal ion than the other four and a tetragonally distorted octahedron contracted along the *z*-axis (*z*-in).

These two situations are illustrated in Fig. 7.6, where δ_1 is the difference in energy between the two e_g orbitals, and δ_2 is the difference in energy between the d_{xy} and the other two degenerate t_{2g} orbitals. For bivalent copper compounds, most experimental data indicate an elongated octahedron with two long and four short distance, as shown earlier for $[Cu(H_2O)_6]^{2+}$.

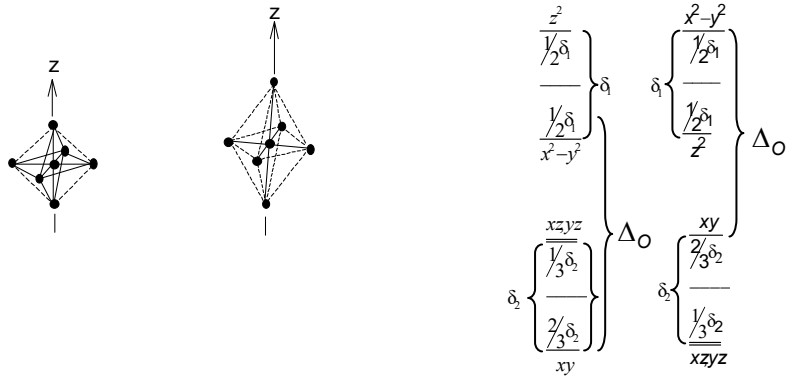


Fig. 7.6: Consequence of Jahn-Teller distortion in an octahedral complex:(a) z-in and (b) z-out situation. Drawing not to scale. $\delta_2 < \delta_1 << \Delta_O$.

An examination of Fig. 7.6 reveals that distortion (either z-in or z-out) results in a lower energy for the system, that is, causes stabilization. The centre of gravity rule holds for the tetragonal splitting and the system gains a net stabilization equal to $\frac{1}{2}\delta_1$. There is no net change in energy for the t_{2g} electrons.

So Jahn-Teller (J-T) distortion in complexes of metal ions is expected from those metal ions which have unsymmetrical electron distribution in e_g or the t_{2g} level. Thus, we also expect pronounced J-T distortion with ions of the following configurations (in addition to the $t_{2g}^6 e_g^3$ configuration discussed above).

$t_{2g}^3 e_g^1$: high-spin Cr(+2) and Mn(+3);

$t_{2g}^6 e_g^1$: low-spin Co(+2) and Ni(+3);

We should also expect J-T distortions when an octahedral complex has 1, 2, 4 or 5 electrons in the t_{2g} level. Since these orbitals are not oriented directly along the lines of approach of the ligands, the splitting of these consequent to distortion would be naturally very small and difficult to detect. Referring to Fig. 7.6, we expect a t_{2g}^1 species to be stabilized by $\delta_2/3$ on elongation along one axis flattening along one axis would cause stabilization by $2\delta_2/3$. Similar reasoning leads to expect distortion by elongation in case of t_{2g}^2 configuration (stabilization = $2\delta_2/3$) and distortion by flattening in the t_{2g}^5 case.

Since the energy difference involved is very small, there is little experimental evidence to confirm such distortions owing to partially filled t_{2g} configurations.

The Jahn-Teller theorem applies to excited states as well though this is more complicated due to short life of the excited state. When the first excited state of any species has partially filled e_g level, we expect Jahn-Teller distortion. Such effects are readily observed in the electronic spectra. In the previous unit we had seen that the electronic spectrum of the $[Ti(H_2O)_6]^{3+}$ ion shows a band. The ground state of the ion suggests a distorted octahedral structure with the single electron occupying the d_{xy} orbital, the *z*-in distortion providing more stabilization than the *z*-out distortion. The excited state has a singly occupied e_g orbital which is also susceptible to distortion; thus we expect two transitions:

Since the e_g group of orbitals lie directly along the lines of approach of the ligands in an octahedral field the distortion is much pronounced with unsymmetrical electron occupancy in the e_g level.

Whereas, t_{2g} orbitals do not point directly towards the ligands and so the distortion caused by unsymmetrical occupancy of these orbitals is much less

A tetragonal distortion can be expected when the ground electronic configuration of a complex is orbitally degenerate; the complex will distort so as to remove the degeneracy and achieve a lower energy.

$$d_{xy} \rightarrow d_{x^2-y^2};\ d_{xy} \rightarrow d_{z^2}$$

Due to two transitions the spectrum is in form of a band and not a sharp peak.

EXAMPLE 7.1: Six-coordinate d^9 complexes of copper (+2) usually depart considerably from octahedral geometry and show pronounced tetragonal distortions (Fig. 7.5). High-spin d^4 (e.g., Cr^{2+} and Mn^{3+} and low-spin d^7 six-coordinate complexes (e.g. Co^{2+} and Ni^{3+}) may show a similar distortion, but complexes of these ions are less common, and the distortions are less pronounced than those in copper (+2). Why?

SOLUTION: These distortions are manifestations of the Jahn-Teller effect. If one or three electrons occupy the e_g orbitals (as in high-spin d^4, low-spin d^7, and d^9 complexes) with configuration that would be $t_{2g}^6 e_g^3$ in octahedral), such a distortion leaves two electrons in the d_{z^2} orbital with a lower energy and one in the $d_{x^2-y^2}$ orbital with a higher energy.

As we discussed before, the Jahn-Teller effect does not predict the preferred distortion. For instance, with an octahedral complex it cannot predict whether axial or equatorial elongation will take place, the nature of distortion is a matter of energetics, not symmetry. However, because axial elongation weakens two bonds and equatorial elongation (axial compression) weakens four, axial elongation is more common than axial compression.

Before moving to the next section where you will study the crystal field splitting in square planar complexes, try out the following SAQ.

SAQ 2

Explain Jahn-Teller effect in the d^9 configuration of $CuCl_2$.

7.4.2 Square Planar Coordination

As mentioned earlier, the square planar geometry is quite common in certain transition metal complexes. We will now discuss the crystal field splitting in such complexes.

Square planar complexes

In order to find the *d* orbital splitting in a square planar complex, it is easier to start with an octahedral compound where splitting patterns are known and then imagine the formation of a square planar complex by slowly moving two trans ligands away from the metal. This would at first distort the molecule which is known as a tetragonally distorted octahedron. Moving the ligands further to such an extent that the interaction between the metal ion and the ligands is practically nil would result in a square planar compound. This situation is best described as square planar complex because the other two ligands are so far off that they can be considered to be unattached to the metal ion and are thus unable to form a true chemical bond. These situations are depicted in pictorial form in Fig. 7.7.

Let us see what happens to the energy value of *d* orbitals under these stages. We start with the energy level diagram of lower triplet (t_{2g}) and upper doublet (e_g) in an octahedral field. Fig. 7.7(I). When the two trans ligands placed along say, *z*-axis, are moved away the most affected orbital would be d_{z^2}. The repulsion between the orbital and the ligand will decrease, thus making it more stable compared to others. At the same time all other orbitals containing *z*-axis namely d_{xz}, d_{yz} will also be affected by the movement of the two ligands along the *z*-axis. However, these will experience less effect than the d_{z^2} orbital.

These two orbitals will become lower in energy by equal amount but less than d_{z^2} as indicated by different slopes in Fig. 7.7.

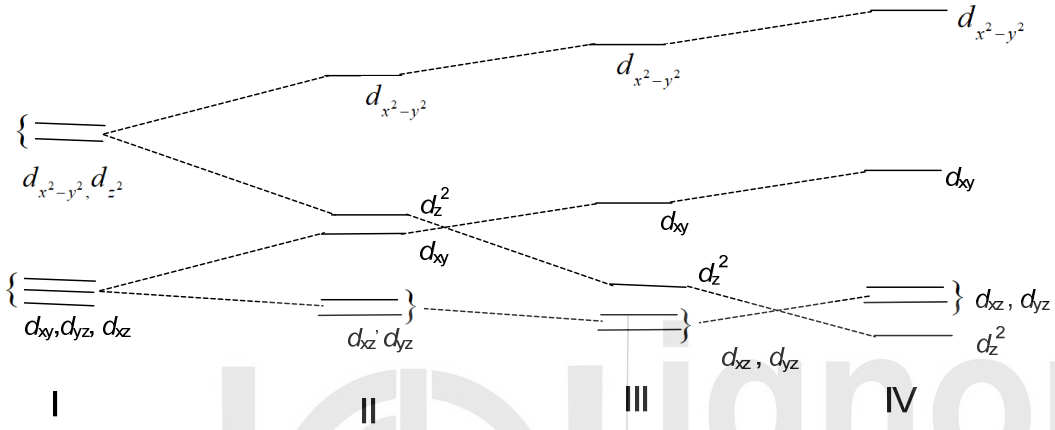


Fig. 7.7: Crystal field splitting of *d* orbitals in a tetragonally distorted field

For e_g set of orbitals, if d_{z^2} orbital is lowered in energy due to distortion, then $d_{x^2-y^2}$ must be raised in energy by an equal amount so that the net result is no change in energy.

Similarly, d_{xz} and d_{yz} are lowered whereas d_{xy} is raised in energy by such an amount that the net resultant is zero. Hence the energies of d_{z^2}, d_{xz} and d_{yz} will be lowe red. There will be corresponding increase in the energies of other orbitals, conserving the barycentre(Fig. 7.7).

Thus in a distorted octahedral molecule the orbitals in order of increasing energy or decreasing stability are: (d_{xz}, d_{yz}) degenerate), d_{xy}, d_{z^2}, $d_{x^2-y^2}$ as shown in Fig. 7.7 (II). A further distortion results in the formation of a square planar complex. Here, the energy of the d_{z^2} orbital is lowered so much t that it is almost equal in energy to that of the d_{xz}, d_{yz} orbitals as in Fig. 7.7 (III). The d_{xy} orbital is significantly high in energy and the least stable orbital or the one with the highest energy would be $d_{x^2-y^2}$. In a few rare instances the d_{z^2} orbital falls even below the d_{xz} and d_{yz} orbitals as in Fig. 7.7 (IV). Next let us discuss how we can calculate the orbital splitting energy in case of square planar complex. If only the electrostatic interactions are taken into consideration, then a square planar arrangement of ligands as in Fig. 7.7 (III) is found from which the orbital splitting energy for square planar complexes may be calculated as follows:

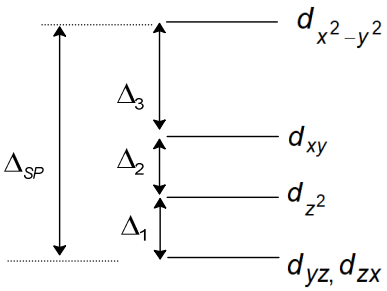


Fig. 7.8: The orbital splitting parameters for a square-planar complex.

The splitting energy (from highest orbital $d_{x^2-y^2}$ to lowest orbitals d_{xz} and d_{yz}) is Δ_{SP} ,which is the splitting energy of square planar complexes. So,

$\Delta_{SP} = \Delta_1 + \Delta_2 + \Delta_3$

Looking at Fig. 7.7 we can follow that $\Delta_1 = \Delta_O$, so Δ_{SP} is generally larger then Δ_O.

Based on these values we can calculate CFSE as well as the magnetic moment for any particular complex. Metal ions with d^8 configurations form square planar complexes which are favoured by high CFSE. A strong ligand field raises the energy of the $d_{x^2-y^2}$ orbitals which eventually remains unoccupied and the orbitals lowered in energy are occupied. Some common examples of square complexes of d^8 metal ions are $[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$, $[AuCl_4]^-$, $[Ag(OH)_4]^-$ and $[Pt(NH_3)_4]^{2+}$. It has been observed that the first row transition elements show greater tendency to form square planar rather than tetrahedral complexes. These observations are in line with the CFSE calculations for the two geometries.

We have thus come to the stage where we can appreciate that a simple electrostatic approach can lead to many useful applications of coordination compounds where the estimated theoretical values are pretty close to the experimentally determined values. We do not expect to get perfect results since our assumptions so far are imperfect. We are thus, left with two choices, either to discard the theory completely and look for a new approach or to modify it in such a way so as to account for the observed discrepancies.

Molecular orbital theory is a completely different approach. It starts with identifying the metal orbitals and the ligand orbitals (hybridized) which have the correct symmetry and energies for combination to yield molecular orbitals. The total electrons from the ligands and metal ion are placed into these molecular orbitals and the bond order, which is a measure of the covalency, is determined. Once the energy sequence of molecular orbitals in a complex is known, the properties of the complex can be explained. It does not start with any assumption regarding the type of bond involved in the complex; rather the bond type comes out as a natural consequence of the theory. Despite being much more comprehensive than the VBT or CFT the theory is not very popular. The reason for this is that the quantum mechanical calculations involved are too tedious and many a time cannot be solved. We shall not go into the details of this theory but would like to emphasize that this is the best and comprehensive approach; in all those cases where precise calculations have been possible, the applications of the molecular orbital theory on

coordination compounds are in almost perfect agreement with the experimental observations.

The second approach, though not as perfect, is more useful. Here we do all the calculations based on crystal field theory. The differences between the calculated values and the experimental results are accounted for on the basis of covalency. This is known as **adjusted crystal field theory** or sometimes referred to as 'ligand field theory'. Some authors prefer to call the molecular orbital theory as ligand field theory, though this is not a very accurate terminology.

In the next section we shall discuss very briefly a few applications of complexes. Try the following SAQ before proceeding to the next section.

SAQ 3

The difference in energy between the $d_{x^2-y^2}$ and d_{xy} orbitals in a square planar field is identical to the difference between the same orbitals in the octahedral field. Comment.

SAQ 4

The complex $[NiCl_4]^{2-}$ contains two unpaired electrons while $[Ni(CN)_4]^{2-}$ is diamagnetic. Propose structures for these two complex ions on the basis of Cystal Field Theory (CFT).

7.5 SOME COMMON APPLICATIONS OF COMPLEXES

In this section we are going to discuss some common applications of complexes. We begin our discussion with the magnetic properties of transition metal complexes. The crystal field theory helps us to explain the observed paramagnetism and diamagnetism of complex compounds in terms of ground state distribution of the metal *d* electrons among the energetically discriminated groups of *d* orbitals. From Fig. 7.9, it can be seen, how the ground state electron distribution is for various d^n. For d^1, d^2, d^3, d^8, d^9 and d^{10} configuration, the electrons can be distributed among the t_{2g} and e_g levels in only one way (Fig. 7.9). The calculated spin-only magnetic moment from the number of unpaired electrons for these configurations are also shown.

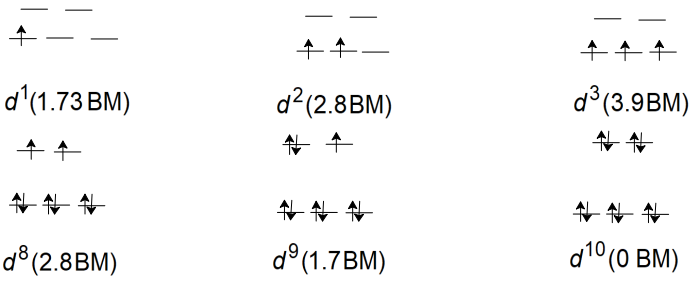


Fig. 7.9: Ground state electron occupancy of d^1, d^2, d^3, d^8, d^9 and d^{10} configurations in octahedral complexes. Expected spin-only magnetic moments are given in parentheses.

The remaining d^n configuration, that is, d^4, d^5, d^6, d^7, present two alternative electron distributions depending upon the relative magnitude of the crystal-field splitting parameter Δ_O may be less than the pairing energy (P) of an electron in the t_{2g} level, giving rise to low-spin or spin-paired complexes.The spin-only magnetic moment calculated for each type from the number of unpaired electrons in different d^n ions is shown in Table 7.1.

Table 7.1: Calculated spin-only magnetic moment (BM) for octahedral complexes of d^4,d^5,d^6 and d^7 ions.

Configuration (High Spin)	Distribution t_{2g}	Distribution e_g	No. of unpaired electrons	μ (BM)
d^4	↑↑↑	↑	4	4.9
d^5	↑↑↑	↑↑	5	5.9
d^6	↑↓↑↑	↑↑	4	4.9
d^7	↑↓↑↓↑	↑↑	3	3.9
Configuration (low spin)	**Distribution t_{2g}**	**Distribution e_g**	**No. of unpaired electrons**	**μ (BM)**
d^4	↑↓↑↑		2	2.8
d^5	↑↓↑↓↑		1	1.7
d^6	↑↓↑↓↑↓		0	0
d^7	↑↓↑↓↑↓	↑	1	1.7

The experimental magnetic moments of complexes of d^1 to d^9 metal ions show good agreement with the spin-only value calculated on the basis of above distributions. The existence of two separate classes of complexes are distinctly shown by the following examples:

Configuration	Complex	Electronic configuration	$\mu_{calculated}$(BM)	$\mu_{experimental}$(BM)
High spin	$[CoF_6]^{3-}$	$t_{2g}^4 e_g^2$	4.9.	4.3
	$[FeF_6]^{3-}$	$t_{2g}^3 e_g^2$	5.9	5.9
Low spin	$[Co(NH_3)_6]^{3+}$	t_{2g}^6	0	0
	$[Fe(CN)_6]^{3-}$	t_{2g}^5	1.7	2.4

SAQ 5

What is the probable electron configuration of an octahedral complex of Co(+2) whose experimental magnetic moment is 4.0 BM?

Note: In this and many other cases, e.g., the $[Fe(CN)_6]^{3-}$ ion mentioned before, observed magnetic moments often deviate significantly from the spin-only value. This is mainly due to orbital contribution.

A paramagnetic substance is one that is attracted into a magnetic field. For a substance to be paramagnetic, it must contain unpaired electrons, the number of which determines the magnitude of its response to a magnetic field. This response can be measured by using a very accurate balance to determine the mass difference of a sample of the complex in the presence and absence of a magnetic field. This allows us to calculate the **magnetic moment (*μ*)** of the complex, and hence to determine the number of unpaired electrons it contains. The magnetic moment of a complex is measured in Bohr magnetons (**BM**) and is defined as:

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

Where *n* in the number of unpaired electrons in the complex. Therefore, a complex containing one unpaired electron should have $\mu = \sqrt{3} = 1.73$ BM while the value of *μ* for a complex containing three unpaired electrons would be $\mu = \sqrt{15} = 3.87\,\text{BM}$. Note that this equation applies only to complexes in which the orbital motion of the unpaired electrons between degenerate *d* orbitals is negligible. We will assume that this is the case in the examples presented.

Having introduced the concept of high-spin and low-spin electron configurations, we can now explain the unusual magnetic behavior of the $[Fe(OH_2)_6]^{2+}$ and $[Fe(CN_6)]^{4-}$ ions. Both complexes contain d^6 Fe(II) metal ions, but $[Fe(OH_2)_6]^{2+}$ is paramagnetic $(\mu \approx 4.9\,\text{BM})$. While $[Fe(CN)_6]^{4-}$ is diamagnetic $(\mu \approx 0\,\text{BM})$. We know from the spectrochemical series that H_2O induces a much smaller value of Δ_O than does CN^-, so that $[Fe(OH_2)_6]^{2+}$ is high-spin while $[Fe(CN)_6]^{4-}$ Is low-spin, as shown in Fig. 7.10.

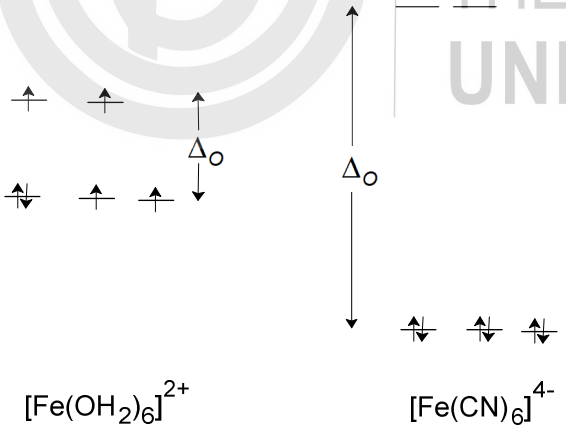


Fig. 7.10: The distribution of *d* electrons in $[Fe(OH_2)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ the magnitude of Δ_O for the cyanide complex is much larger than that for the complex containing water. This produces a maximum pairing of electrons in the t_{2g} orbitals in $[Fe(CN)_6]^{4-}$, and a corresponding low-spin configuration for this complex.

Therefore, $[Fe(OH_2)_6]^{2+}$ contain four unpaired electrons and is paramagnetic, while $[Fe(CN)_6]^{4-}$ has no unpaired electrons and is diamagnetic.

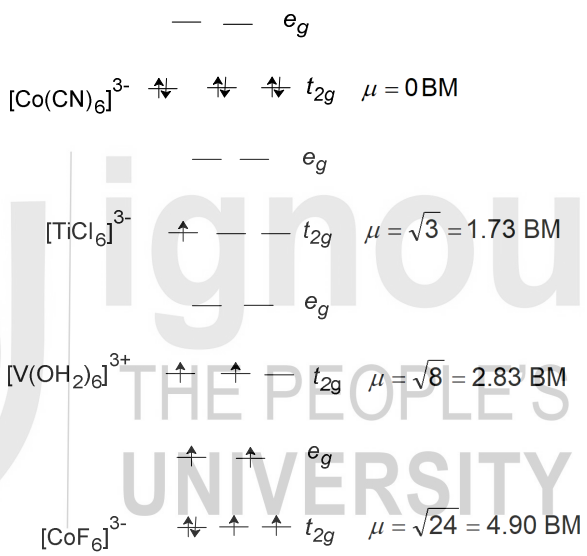
Magnetic measurements allow us to distinguish between high-spin and low-spin possibilities in transition metal complexes. For example, the magnetic moments of the d^4 $Cr(+2)$ d^4 complexes $[Cr(OH_2)_6]^{2+}$ and $[Cr(CN)_6]^{4-}$ are 4.9 BM and 2.8 BM, respectively. The value of 4.9 BM for $[Cr(OH_2)_6]^{2+}$ is

consistent with the presence of four unpaired electrons and, therefore, a high-spin $(t_{2g})^3(e_g)^1$ configuration. The value of 2.8 BM for $[Cr(CN)_6]^{4-}$ arises from two unpaired electrons, which suggests a low-spin $(t_{2g})^4(e_g)^0$ configuration.

Now with the help of the following examples understand the magnetic behaviour of octahedral transition metal complexes.

EXAMPLE 7.2: Out of the following octahedral transition metal complex ions find out which are paramagnetic or diamagnetic:
$[Co(CN)_6]^{3-}, [TiCl_6]^{3-}, [V(OH_2)_6]^{3+}, [CoF_6]^{3-}$. If they are paramagnetic, estimate their magnetic moments.

Hint: We can find out the *d* electron configurations of the complexes by first determining the oxidation states and then numbers of *d* electrons for each metal ion. Where high-spin and low-spin possibilities occur, we use the position of the ligand in the spectrochemical series to decide between the two configurations.



SOLUTION: The oxidation states are $Co(+3)$, $Ti(+3)$ $V(+3)$ and $Co(+3)$, which correspond to d^6, d^1, d^2 and d^6 configuration, respectively. High-spin and low-spin possibilities exist for both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$. We know that CN^- is a strong field ligand, while F^- is a weak-field ligand. We therefore predict that $[Co(CN)_6]^{3-}$ is d^6 low-spin and diamagnetic, while $[CoF_6]^{3-}$ high-spin, with four unpaired electrons, and paramagnetic. $[TiCl_6]^{3-}$ must be paramagnetic as it contains an odd number of *d* electrons, while $[V(OH_2)_6]^{3+}$ is also paramagnetic, as the two *d* electrons occupy two of the t_{2g} orbitals with parallel spins. Therefore, the electron configurations and magnetic moments are as shown on the right.

SAQ 6

Determine how many unpaired electrons are contained in the following octahedral complex ions: $[NiCl_6]^{2-}, [CuCl_6]^{4-}$. Estimate the magnetic moments of these complexes.

Next let us discuss the applications of coordination compounds in fields as divergent as biology, industry, agriculture and analytical chemistry. This makes it difficult to cite them all at one place. A few selected examples are given below to indicate their application of different fields. Let us first consider the role which the complexes play in gravimetric, volumetric, colorimetric analysis.

EDTA is an important reagent used in volumetric analysis. It can be used to determine the amount of various metal ions. It is also used to estimate the hardness of water, estimation of calcium in medicines and analysis of ores and alloys.

Fe(+3), Al(+3) or Cr (+3) are selectively precipitated as hydroxides with ammonia in presence of metal ions like Ag(+1), Cu(+2), Ni(+2), Co(+2), Mn(+2) and Zn(+2) which remain in solution as soluble ammine complexes.

From a mixture of Fe(+3), Cu(+2), Pb(+2), Bi(+3) and Ag(+1), only Ag(+1) ion can be precipitated as iodide, all other ions can be made to remain in solution by previous addition of EDTA (ethylenediaminetetraacetate ion) to the solution.

The EDTA complexes of some metal ions are stable even to hydrogen sulphide. For example, in the presence of EDTA, Pb(+2) is not precipitated as sulphide from weakly acidic solutions; Ni(+2), Mn(+2) and Zn(+2) which are normally precipitated as sulphides in ammoniacal solution would also not give any precipitate . Here EDTA is acting as a masking agent. Since the estimation of various cations using EDTA is largely pH dependent EDTA is also used as masking or demasking agent in titration of mixture of cations. Masking is the process in which a substance without the physical separation of it or its reaction products is so transformed that it does not participate in a reaction. In demasking the ability of the masked substance to participate in the reaction is recovered.

Yet another effective masking agent is the cyanide ion. It forms stable cyanido complexes with the zinc(+2), cadmium(+2), mercury(+2) nickel(+2), copper(+2) etc., but not with alkaline earths. Therefore, it is possible to estimate calcium(+2) and magnesium (+2) in the presence of above mentioned metal ions with an excess of cyanide ion.

Specific reagents like dimethylglyoxime are used to isolate red Ni(+2) complex and cupferron(bidentate, monoanionic) is used for the estimation of Fe(+3), Cu(+2), Zr(+4) etc.

Colorimetric analysis depends on the variation of the colour with the change in concentration of the compound. Usually, absorption of light is measured at different known concentrations of compound and a graph is plotted between the absorption and concentration. The absorption of an unknown concentration of the compound is then measured and its concentration evaluated from the graph. Thus, 1,10-phenanthroline or 2,2'-bipyridyl which forms coloured complexes with iron, are often used for its determination in fruits, wines, leather and other biological materials. There are many such reagents which are successfully employed for the quantitative determination of various metal ions.

Bioinorganic chemistry or the study of the role of metal ions in biological cycles is mainly the study of some typical metal complexes of biological importance. These complexes act as oxygen carriers, electron transfer agents, catalyst and as drugs. Out of all the first row transition elements, perhaps iron plays the most important role. The source of energy in human body comes from the oxidation of carbohydrates, proteins and fats. Transfer of electrons from these nutrients to the oxygen molecule is not direct but through a complex chain of molecules. One main electron transfer moleculein the chain is called cytochrome. Cytochromes are classified into four types –A, B, C, and D, on the basis of the kind of the heme that they possess as the prosthetic group, e.g. A-type cytochrome or cytochrome A has heme a as the prosthetic group. It consists of: an iron porphyrin complex heme (Fig. 7.11). The iron atom is also attached to a nitrogen atom of a histidine residue and a sulphur atom of a methionine residue. Porphyrin is a name given to a large number of compounds having the same central ring structure made up of four pyrrole rings linked together to give a large ring called porphine as shown in Fig. 7.12. Replacing the eight hydrogen atoms of porphine by substituents gives the naturally occurring porphyrins.

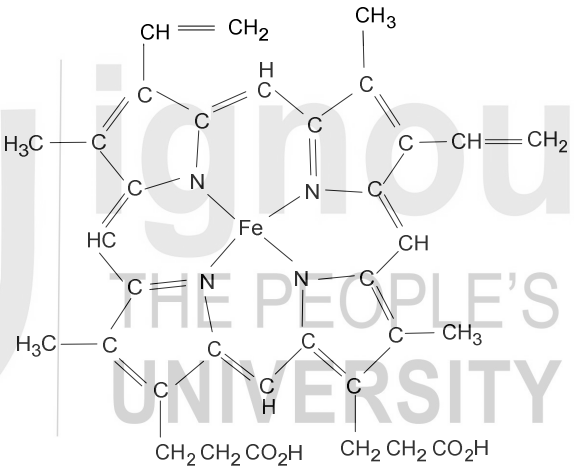


Fig. 7.11: Structure of heme.

A magnesium complex of porphyrin(with different substituents from that shown in Fig.7.11) is called chlorophyll, the green colouring material in plants and which is essential for photosynthesis.

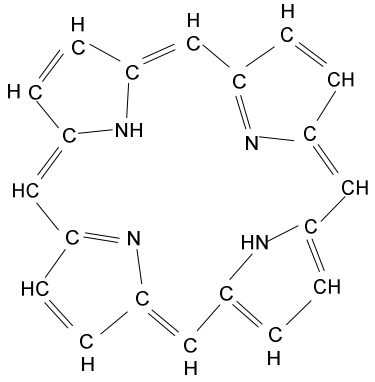


Fig. 7.12: The Structure of porphine.

Hemoglobin, plays the role of oxygen carrier in mammalian blood. In hemoglobin Fe^{2+} ion is not only surrounded by four nitrogens of porphyrin but

the fifth position is occupied by a nitrogen of the protein as shown in Fig. 7.13.

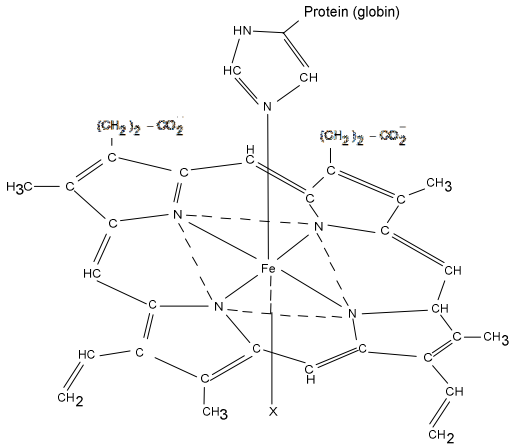


Fig. 7.13: Environment of the iron atom in hemoglobin.

The sixth position marked by X is either occupied by H_2O or O_2 molecule. The important thing to note is that Fe^{2+}in hemoglobin does not get oxidized to Fe^{3+}. On the other hand if gaseous O_2 is bubbled into an aqueous solution containing heme, the Fe^{2+} gets oxidised to Fe^{3+}. It is believed that the oxidation of Fe^{2+} to Fe^{3+} is prevented by the bulky protein (globin) in the hemoglobin. Each hemoglobin can bind four O_2 molecules to give a bright red complex which is characteristic of venous blood. Both CO and CN^- can form more stable complexes with Fe^{2+} ion than molecular oxygen. Thus they can destroy the normal functioning of blood as in oxygen carrier.

Catalytic activity of metalloenzymes depends on the complex forming ability of a particular metal ion. One specific example is carbonic anhydrase which is an important enzyme of respiration. It catalyses dehydration of carbonic acid and the release of CO_2.

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Carbonic anhydrase consists of a zinc ion which is tetrahedrally coordinated to three imidazole nitrogen atoms of histidine residues and a water molecule (Fig. 7.14). The active site of the enzyme is the one where molecule is attached to the zinc ion.

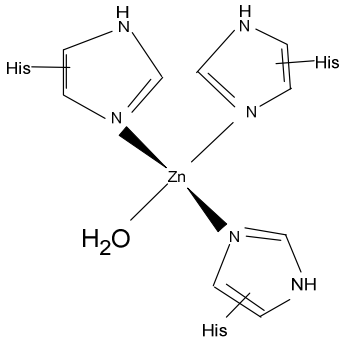


Fig. 7.14: Skeleton of carbonic anhydrase

Finally we shall consider a few examples of the application of complex formation in industrial processes. It is quite an arbitrary selection as there are innumerable examples.

Extraction of metals is very often done by complex formation. For example, the cyanide process for the extraction of silver and gold is well known. Purification of metals is often accomplished by solvent extraction of neutral complexes. Commonly encountered ligands for such purpose are 8-hydroxyquinoline, acetylacetone, dimethylglyoxime, salicylaldoxime or salicyldineimines. The role of complexes as catalysts in the production of organic chemicals is yet another field of importance. For example various complexes of copper, silver, mercury ruthenium, cobalt etc. are known to be good catalysts for hydrogenation process $[RhCl(PPh_3)_3]$, tris (triphenylphosphene) chloridorhodium (I) (Wilkinson's Catalyst) is one of the best known and thoroughly investigated compounds, Similarly, oxidation, polymerization, hydroformylation of olefins all involve the formation of complexes as intermediates. However, quite often they are not simple complexes rather they are organometallic compounds.

SAQ 7

Give some applications of complexes in the field of bioinorganic chemistry.

7.6 SUMMARY

This unit has dealt with crystal field splitting in tetrahedral complexes and thereafter a comparison of crystal field stabilization energy (CFSE) for octahedral and tetrahedral complexes was done. Next, crystal field splitting in square planar complexes which involved tetragonal distortion of octahedral geometry, also known as Jahn-Teller distortion were discussed. At the end square planar coordination was discussed in details along with some common applications of complexes.

7.7 TERMINAL QUESTIONS

1. Explain the following observations: The diamagnetic complex $[PdCl_2(PPH_3)_2]$ gives geometrical isomers whereas an analogous compound $[NiCl_2(PPh_3)_2]$ does not give any geometrical isomers and is found to be paramagnetic.

2. For the low-spin complex $[Fe(en)_3]Cl_3$ find:

   (a) the oxidation number and number of *d* electrons of the metal

   (b) the geometry of the complex

   (c) whether the complex is diamagnetic or paramagnetic

   (d) the number of unpaired electrons in the complex

   (e) the magnetic moment of the complex.

3. Ni(+2), Pd(+2) and Pt(+2) have the same number of *d* electrons. Four coordinated complexes of Pt(+2) and Pd(+2) are almost exclusively square planar while the same is not always noted for similar complexes of Ni(+2). Comment.

4. Both $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ ions appear almost colourless in dilute aqueous solution, though one is low-spin and the other is high-spin. Explain.

5. A metal ion M^{2+} forms complexes $[M(H_2O)_6]^{2+}$,$(MBr_6)^{4-}$ and $[(M(en)_3]^{2+}$ which are variously coloured like blue, green and red. What is the expected colour of each complex from the CFT?

6. (a) A metal forms two complexes in the same oxidation state. In one complex, the magnetic moment is 4.9 BM; in another it is 0.0 BM. Which of the following metal fit this description?

   Cr(+3), Mn(+2), Mn(+3), Fe(+2), Fe(+3), Co(+2).

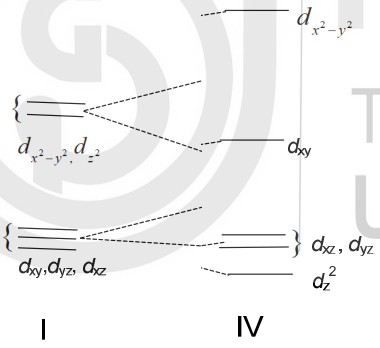
   (b) Which one of these metal ions will make complex compounds having magnetic moments 4.90 BM and 2.83 BM?

7.8 ANSWERS

Self-Assessment Questions

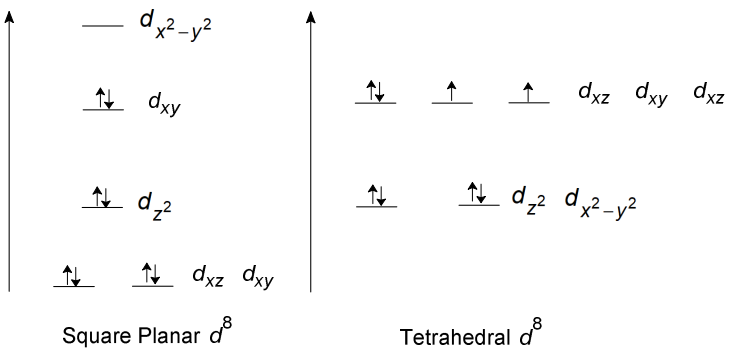
1. d^0, high spin d^5 and d^{10}. Distribution of electrons in t_{2g}, e_g or e, t_2 to be given.

2. d^9 configuration of $CuCl_2$ is $t_{2g}^6 e_g^3$. Fig. 7.6 should be given with the relevant explanation.



3. From Fig. 7.7 part I and IV we can find this is true and relevant explanation for the two cases must be given.

4. Since both the compounds given are tetra-coordinated, but show different magnetic properties, they must differ in their geometries. The two possible geometries for tetra-coordinate compounds are tetrahedral or square planar. According to crystal field theory, the *d* orbital splitting in the two cases can be shown as given below:

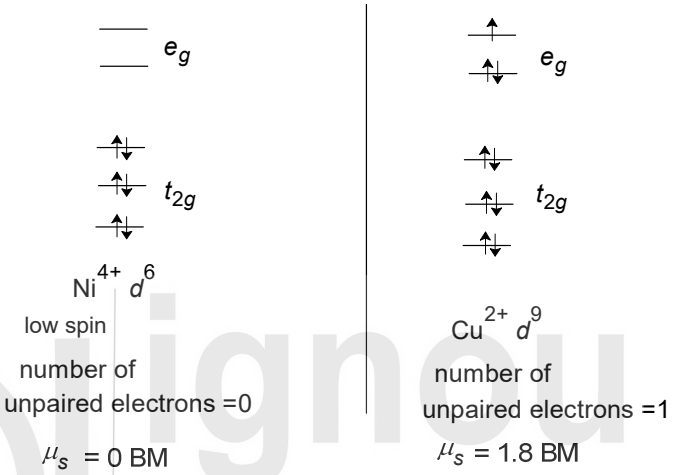


Electronic distribution in (a) tetrahedral field (b) square planar field.

As you can see, if the configuration is tetrahedral the compound would be paramagnetic and would have a magnetic moment corresponding to two unpaired electrons. However, if the geometry is square planar, all the eight electrons would pair up in low energy orbitals rather than any electron occupying $d_{x^2-y^2}$ orbital. Hence, the compound $[NiCl_4]^{2-}$ is tetrahedral and $[Ni(CN)_4]^{2-}$ is square planar.

5. Co(+2) is a d^7 species. The high-spin configuration $t_{2g}^5 e_g^2$ has three unpaired electrons with calculated spin-only magnetic moment 3.9 BM.

6. The number of unpaired electrons in the following octahedral complex ions $[NiCl_6]^{2-}$,$[CuCl_6]^{4-}$.



7. Bioinorganic chemistry or the study of the role of metal ions in biological cycles is mainly the study of some typical metal complexes of biological importance. These complexes act as oxygen carriers, electron transfer agents, catalyst and as drugs. Out of all the first row transition elements, perhaps iron plays the most important role. The source of energy in human body comes from the oxidation of carbohydrates, proteins and fats. Next, transfer of electrons from these nutrients to the oxygen molecule is not direct but through a complex chain of molecules. One main electron transfer molecules in the chain is called cytochrome. It consists of two parts: an iron complex heme and a porphyrin. Porphyrin is a name given to a large number of compounds having the same central ring structures but having different substituent groups. (relevant diagrams as given in unit may be given) Hemoglobin etc. may be given also.

Terminal Questions

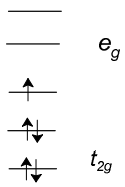
1. Since $[PdCl_2(PPh_3)_2]$ is a four coordinated complex and gives geometrical isomers, it must have square planar geometry. It will also be diamagnetic as explained in answer to SAQ 1. Though $[NiCl_2(PPh_3)_2]$ is also four coordinated and belongs to a d^8 system just like the first compound, yet is does not geometrical isomers. This indicates a tetrahedral geometry for the compound which will also be paramagnetic.

2. (a) the oxidation number +3, d^5

(b) octahedral

(c) diamagnetic

(d) number of unpaired electrons in the complex:



$[Fe(en)_3]Cl_3$

low spin

(e) 0 BM.

3. The 4*d* orbitals of Pd(2+) and Pt(2+) are more radially diffuse (it is bigger) and therefore form stronger overlap with the orbitals on Cl^-, as compared with 3*d* orbitals of Ni(2+). Hence, larger CFSE results. Also, since CFSE is larger in case of Pd(2+) and Pt(2+), the pairing energy *P* is smaller as it costs less energy to put the electrons in the same orbital.

4. The former absorbs in the UV region, the latter in the IR region. None absorb in the visible region.

5. Complementary colour is shown by complex absorbing in the visible region. So the lowest energy in the range which is the red region is the absorption region of the green complex. This is probably shown by the bromo complex as Br^- is the weakest among the given ligands.

6. (a) the metal has either four or no unpaired electron. This fits Fe(2+) which is a d^6 ion.

(b) the metal has either four or two unpaired electrons. This fits Mn(3+) which is a d^4 ion. (Also electron distributions according to CFT must be shown for both weak field and strong field for both a) and b).

Further Reading

1. James E Huheey, Ellen A Keiter, Richard L Keiter & Okhil K Medhi, Inorganic Chemistry (4th Edition) – PEARSON.
2. J.D. Lee, Concise Inorganic Chemistry, Wiley India.
3. Cotton, Wilkinson, Murillo & Bochmann, Advanced Inorganic Chemistry, Wiley India.
4. Ramaprasad Sarkar, General and Inorganic Chemistry, NCBA.
5. R. L. Dutta, Inorganic Chemistry - Part-II - Chemical Elements & Their Compounds, The New Book Stall.