



COMPLEX COMPOUNDS



- * Characteristics of Complexes
- * IUPAC Notations of Naming Complexes
- * Theories of Complexes
- * Isomerism in Complexes

CHARACTERISTICS OF COMPLEXES

6.1.1

Double and complex salts

Coordination compounds are a special class of compounds in which the central metal atom is surrounded by ions or molecules beyond its normal valency. These are also referred as complex compounds or simply complexes. These compounds are widely present in the minerals, plants and animals and play many important functions. Chlorophyll, haemoglobin and vitamin B₁₂ are coordination compounds of magnesium, iron and cobalt respectively. The transition elements form a large number of complex compounds. This is due to the comparatively small size of the metal ions, their high ionic charges and the availability of d-orbitals for bond formation.


*Double salts
lose their identity
when dissolved
in water*


When two or more salts combine either physically or chemically, molecular compounds or addition compounds are formed. Double salts are those molecular compounds which exist only in crystal lattice and lose their identity when dissolved in water. e.g: Carnallite, potash alum, Mohr's salt, etc. These are formed by physical union of stable compounds. Shape and size of the crystals of double salts are different from that of its component salts. But their solutions will show same physical and chemical properties as a mixture of solutions of their components. Thus, for example, aqueous solution of potash alum gives the test for K⁺, Al³⁺ and SO₄²⁻ ions.

Complex compounds are those molecular compounds which retain their identity even when dissolved in water. Properties of complexes are completely different from those of the constituents. Complexes are also called coordination compounds because they contain coordinate covalent bonds. e.g: Cuproammonium sulphate, potassium ferrocyanide, etc. These are formed by chemical union of stable compounds. The physical properties such as colour, conductivity etc., of these compounds are distinctly different from their constituents. Complex compounds are new chemical species different from their constituents. For example, potassium ferrocyanide aqueous solution can give test for ferrocyanide ion, [Fe(CN)₆]⁴⁻, but not Fe²⁺ and CN⁻ ions.



P.6.1 Solution

Which ions can be tested in a solution of Mohr's salt?
Composition of Mohr's salt is FeSO₄·(NH₄)₂SO₄·6H₂O. It is a double salt. It undergoes complete ionisation when dissolved in water.
Thus its aqueous solution gives test for Fe²⁺, NH₄⁺ and SO₄²⁻ ions.

6.1.2

Important terms

Central metal ion : The cation to which some neutral molecules or anions are attached by coordinate covalent bond is called central metal ion or centre of coordination. For example, in [Cu(NH₃)₄]SO₄, K₄[Fe(CN)₆] and K₃[Fe(CN)₆] central



metal ions are respectively Cu^{2+} , Fe^{2+} and Fe^{3+} . Some complex compounds possess, neutral central metal atoms. For example, in $[\text{Ni}(\text{CO})_4]$ and $[\text{Fe}(\text{CO})_5]$, centre of coordination are Ni and Fe, respectively.

Ligand : Any atom, ion or molecule which is capable of donating one or more electron pairs to the central metal atom or ion is called a ligand or a coordinating group. Further in a ligand, the atom which donates the electron pair is called donor atom. Thus a ligand is a donor of electrons and metal ion is an acceptor of electrons. However, the ligand may possess acceptor orbitals in addition to donor orbitals.

Ligands can be classified as mono, bi and polydentate ligands when they donate one, two and more than two electron pairs respectively. Number of ligating groups, (electrons donating groups) in the ligand is called denticity. Some examples for ligands are given in Table 6.1.

Table 6.1 Examples for mono, bi and polydentate ligands

Ligand type	Name of ligand	Formula	Donor atoms in ligand
Monodentate	Ammonia	$\ddot{\text{N}}\text{H}_3$	N
	Aqua or aquo	$\text{H}_2\ddot{\text{O}}$:	O
	Halo	X^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	X
Symmetrical bidentate	Ethylenediamine (en)	$\begin{array}{c} \text{CH}_2 - \ddot{\text{N}}\text{H}_2 \\ \\ \text{CH}_2 - \ddot{\text{N}}\text{H}_2 \end{array}$	two N
	Oxalate ion (ox)	$\text{-OOC} - \text{COO}^-$	two O
Unsymmetrical bidentate	Glycinate ion (gly)	$\text{-OOC} - \text{CH}_2 - \ddot{\text{N}}\text{H}_2$	N and O
Hexadentate	Ethylenediamine-tetraacetate ion (edta $^{4-}$)	$\begin{array}{c} \text{CH}_2\text{COO}^- \\ \\ \text{H}_2\text{C} - \ddot{\text{N}} - \text{CH}_2\text{COO}^- \\ \\ \text{H}_2\text{C} - \ddot{\text{N}} - \text{CH}_2\text{COO}^- \\ \\ \text{CH}_2\text{COO}^- \end{array}$	two N and four O

A bidentate ligand is called symmetrical bidentate ligand if two donor atoms in it are same and is called unsymmetrical if two donor atoms in it are different. Bi and polydentate ligands are called chelate ligands. Complex with chelate ligands is called chelate complex and is more stable.

A monodentate ligand containing more than one ligating group is called ambidentate ligand. eg: CN^- , NO_2^- and SCN^- . NO_2^- ion can coordinate through nitrogen or oxygen to a central metal ion. CN^- ion can coordinate through the carbon or nitrogen. SCN^- ion can coordinate through the sulphur or nitrogen atom.

Based on the charge, ligands can be classified as neutral ligands (NH_3 , H_2O , $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), negative ligands (Cl^- , NO_2^- , CN^- , $\text{C}_2\text{O}_4^{2-}$, $\text{H}_2\text{NCH}_2\text{COO}^-$) and positive ligands (NO^+). Ethylene can also act as ligand by donating π electrons.

Coordination number : Coordination number of central metal ion or atom in a complex compound is the number of coordinate covalent bonds formed by it or the maximum number of monodentate ligands that can be bound to it. For example in $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{CO})_4]$ and $[\text{Ag}(\text{NH}_3)_2]^+$, coordination numbers of Fe^{2+} , Ni and Ag^+ are respectively 6, 4 and 2.



Coordination number of in Co^{3+} $[\text{Co}(\text{en})_3]^{3+}$ and Fe^{3+} in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is 6, because of the use of bidentate ligands. Since in the complex formation the attraction between a metal ion and the dipolar molecule or anions around it is involved, the coordination number will tend to be as large as possible.

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

Coordination sphere : The central metal ion and the ligands attached to it are enclosed in square bracket and it is termed as the coordination sphere. For example, in the complex $\text{K}_4[\text{Fe}(\text{CN})_6]$, the coordination sphere is $[\text{Fe}(\text{CN})_6]$.

Complex ion: An electrically charged or a neutral species formed by the combination of a central metal atom or ion with more than one ligand is called complex ion. The charge carried by a complex ion is the algebraic sum of charges carried by the central metal ion and ligands coordinated to it. Charge of complex ion is balanced by some ionisable groups which are written outside the bracket and these are called counter ions. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Fe}(\text{CN})_6]^{4-}$ is complex ion and the counter ions are four K^+ ions.

Coordination polyhedron : The arrangement of coordinated ligands around the metal ion must be such that it minimises the electrostatic repulsion between the ligands. The spatial arrangement of ligands which are directly attached to the central metal ion defines a coordination polyhedron about the central atom. Shape of polyhedron can be known from coordination number. Coordination polyhedron for different coordination numbers are given in the Table 6.2.

Table 6.2 Coordination numbers and shapes of complex species

Coordination number	Shape of the complex species
Two	Linear
Three	Trigonal planar
Four	Tetrahedral
Four	Square planar
Five	Square pyramidal
Five	Trigonal bipyramidal
Six	Octahedral
Seven	Pentagonal bipyramidal

Homoleptic and heteroleptic complexes : Complexes in which the central metal is bound to only one kind of donor groups are called as homoleptic complexes. eg: $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{4-}$ etc. Complexes in which the central metal is bound to more than one kind of donor groups are known as heteroleptic complexes. eg: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.


Complexes
having one central atom are called mononuclear complexes


Mononuclear and polynuclear complexes : Complexes having only one central atom are called mononuclear complexes, eg: $K_4[Fe(CN)_6]$, $[(Co(NH_3)_6]Cl_3$, etc. Complexes having more than one central atom are called polynuclear complexes, eg: $[Co_2(NH_3)_6(OH)_3]Cl_3$, $[(Co)_3Fe(CO)_3Fe(CO)_3]$.

Cationic, anionic and neutral complexes : In the complex compound, if complex ion is cation, it is called cationic complex and if complex ion is anion, it is called anionic complex. Examples for cationic complexes are $[Co(NH_3)_6]Cl_3$, $[Cu(NH_3)_4]SO_4$, etc. and anionic complexes are $K_4[Fe(CN)_6]$, $Na_3[Ag(S_2O_3)_2]$, etc. Complexes in which only coordination sphere present without counter ions, are called neutral complexes, eg: $[Ni(CO)_4]$, $[Co(NH_3)_3Cl_3]$, etc.



P.6.2

Identify the ligands and central metal ion in $[Co(NH_3)_2(en)_2]^{3+}$. Calculate the oxidation number and coordination number of metal ion.

Solution

In $[Co(NH_3)_2(en)_2]^{3+}$, ligands are ammonia and ethylene diamine.

Oxidation number of cobalt = +3.

Central metal ion is Co^{3+} and it is surrounded by two monodentate ligands NH_3 and two bidentate ligands ethylene diamine. Thus coordination number of Co^{3+} is 6.



P.6.3

Which type of complex is cryolite?

Solution

Cryolite, $Na_3[AlF_6]$ is anionic complex. This is because the complex ion $[AlF_6]^{3-}$ is an anion.

EXERCISE - 6.1.1

- What are double salts? Write examples.
- How is a complex compound differentiated from its constituents?
- What are the distinguishing features of complex compounds?
- Discuss the shapes of complex ions with coordination numbers 4 and 6.
- What do you understand by the term ligand? Discuss neutral and ionic ligands.
- Give examples for ionic and neutral complexes.

IUPAC NOTATIONS

6.2.1

Formula


In the formula of complex, central atom is listed, followed by ligands in alphabetical order.


The following rules are applied while writing the formula of mononuclear complexes as per IUPAC recommendations of 2004.

- The central atom is listed first.
- The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge. For example, $[CoCl_2(NH_3)_4]Cl$ is wrong, $[Co(NH_3)_4Cl_2]Cl$ is correct.
- Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order. For example, $[CoBrCl(NH_3)_2(en)]Cl$ is wrong, $[Co(NH_3)_2BrCl(en)]Cl$ is correct.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, the formula of ligand is enclosed in parenthesis. Ligand abbreviations are also enclosed in parenthesis.
- There should be no space between the ligands and the metal within a coordination sphere.

6. When the formula of a charged coordination entity is to be written, without the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, etc.
7. The charge of the cation(s) is balanced by the charge of the anion(s).

6.2.2**Naming**


**Oxidation state
of the metal is
indicated by
Roman number
in parenthesis.**



**Names of the
positive ligands
end in 'ium'**


IUPAC has recommended the following rules for naming the mononuclear coordination compounds.

1. In ionic complexes, the cation, whether it is complex or not, must be named first as a single word and then the anion is named. Name of neutral complexes to be written as a single word.
2. In the name of complex ion, the ligands are named in alphabetical order before the name of the central metal atom or ion.
3. Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numerical in parenthesis.
4. Names of the anionic ligands end in 'o' but the names of positive ligands end in 'ium'. The 2004 IUPAC draft recommends that anionic ligands, particularly halides, will end with '-ido', so that chloro would become chlorido. Neutral ligands have their names either unchanged or have characteristic names. Names of anionic ligands are given in the Table 6.3. The names of cationic and neutral ligands are given in the Table 6.4.

Table 6.3 Names of anionic ligands

Ligand	Name	Ligand	Name
F^-	Fluorido	SCN^-	Thiocyanato
Cl^-	Chlorido	NCS^-	Iothiocyanato
Br^-	Bromido	CN^-	Cyano
I^-	Iodido	CO_3^{2-}	Carbonato
H^-	Hydrido	NO_3^-	Nitrato
N^{3-}	Nitrido	$\text{S}_2\text{O}_3^{2-}$	Thiosulphato
N_3^-	Azido	CH_3COO^-	Acetato
NH_2^-	Amido	$\text{C}_2\text{O}_4^{2-}$	Oxalato
NH^{2-}	Imido	SO_4^{2-}	Sulphato
NO_2^-	Nitrito-N	O^{2-}	Oxo
ONO^-	Nitrito-O	O_2^{2-}	Peroxo
$\text{H}_2\text{NCH}_2\text{COO}^-$	Glycinato	OH^-	Hydroxo

Table 6.4 Names of cationic and neutral ligands

Cationic ligand	Name	Neutral ligand	Name
NO^+	Nitrosonium	H_2O	Aqua
NO_2^+	Nitronium	NH_3	Ammine
NH_2NH_3^+	Hydrazinium	CO	Carbonyl
		$\text{C}_5\text{H}_5\text{N}$	Pyridine
		$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	Ethane-1,2-diammine
		NH_2CH_3	Methylamine


**Aqua for H_2O ,
amine for NH_3
and carbonyl
for CO liquids**


5. Prefixes di, tri, tetra, penta, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms bis, tris and tetrakis are used for two, three and four ligands respectively and the name of ligand is placed in parenthesis. For example, the complex $[\text{NiCl}_2(\text{PPh}_3)_2]$ is named as dichlorobis(triphenylphosphine)nickel(II).

6. If the complex ion is a cation, the metal is named same as the element. For example, Fe in a complex cation is called iron and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix '-ate'. For example, Co in a complex anion is called cobaltate. For some metals, the Latin names are used in the complex anions. eg: Ferrate, cuprate, hydrargyrate and argentate are used for Fe, Cu, Hg and Ag respectively.

7. There is no need to indicate the number of counter ions with a number prefix, in the name of ionic complexes.

8. The neutral complex molecule is named similar to that of the cationic complex.

Illustrative examples:

*Number prefix
is not used to
denote number
of counter loss*

$\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$
is named as tetra-
amminebiaqua-
chromium(III)

1. $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$ is named as tetraamminediaquachromium(III) chloride. In this compound cation is complex ion and Cl^- ions are counter ions. Ammine ligands are named before the aqua ligands according to alphabetical order.

Four ammine ligands and two aqua ligands are present. Thus the number prefix tetra used for ammine and di for aqua. After writing names of ligands, name of the metal chromium written without ending with -ate, since it is cationic complex. Oxidation state of chromium is indicated in Roman number in parenthesis. The name of anion, chloride is written as a separate word. There is no need to indicate the number of counter ions.

2. $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ is named as tris(ethane-1,2-diammine)cobalt(III) sulphate. The sulphate is the counter anion in this molecule. Since it takes three sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further ethane-1,2-diammine is a neutral ligand, so the oxidation number of cobalt in the complex ion must be +3. Since the number prefix is already present in the name of ligand, we use tris instead of tri for three ligands.



P.6.4 List out the wrong among the following according to IUPAC and write the correct formula:
(a) $[\text{Zn}(\text{OH})_4]\text{K}_2$, (b) $[\text{CoCl}(\text{NH}_3)_4(\text{H}_2\text{O})]\text{Cl}_2$, (c) $[\text{Ag}(\text{CN})_2][\text{Ag}(\text{NH}_3)_2]$ and (d) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$.

Solution Formula (a), (b) and (c) are wrong and only (d) is the correct formula.

To correct (a) and (c) formula of cation is to be written first. After correction, the correct formula for (a) and (c) are $\text{K}_2[\text{Zn}(\text{OH})_4]$ and $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$. To correct (b), ligands are to be in alphabetical order irrespective of charge. After correction, the correct formula of (b) is $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$.



P.6.5 Write the IUPAC names of the following coordination compounds:

a) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$, b) $[\text{Ni}(\text{CO})_4]$, c) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$ and d) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

Solution a) Dichloridobis(ethane-1,2-diammine)cobalt(III) chloride,
b) Tetracarbonylnickel(0)
c) Diamminechloridonitrito-N-platinum(II) and
d) Hexaamminechromium(III) hexacyanocobaltate(III)



P.6.6 Write the formula of the following coordination compounds:

- Amminebromidochloridonitrito-O-platinum(II) ion
- Dichloridobis(ethane-1,2-diammine)platinum(IV) nitrate
- Diaquatetrahydroxoaluminate(III) ion and
- Mercury(I) tetrathiocyanatocobaltate(III).

Solution a) $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{ONO})]^-$, b) $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$, c) $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$ and d) $\text{Hg}[\text{Co}(\text{SCN})_4]$.

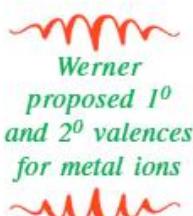
EXERCISE - 6.1.2

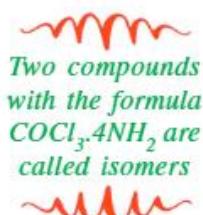
- Write the structures of following compounds:
 - Tetraamminecopper(II) sulphate, ii) Trichlorotriammine cobalt(III)
 - Tetracarbonylnickel(0) iv) Dichlorodiammineplatinum(II) and
 - v) Trinitrotriamminecobalt(III)
- Write the IUPAC names of the following complexes
 - $\text{K}_3[\text{Fe}(\text{CN})_6]$
 - $[\text{Pt}(\text{NH}_3)_6](\text{SO}_4)_2$
 - $\text{K Fe}^{\text{III}} [\text{Fe}(\text{CN})_6]$
 - $\text{Cs}_2[\text{Co}^{\text{II}}\text{Cl}_4]$
 - $[\text{Co F}_6]^{3-}$

THEORIES OF COMPLEXES

6.3.1

Werner's theory


Werner proposed 1^o and 2^o valences for metal ions


Two compounds with the formula $\text{COCl}_3 \cdot 4\text{NH}_3$ are called isomers

Alfred Werner was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques.

Werner proposed the concept of primary and secondary valence for a metal ion. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as silver chloride on adding excess silver nitrate solution but some chlorides remained unprecipitated.

One mole $\text{CoCl}_3 \cdot 6\text{NH}_3$ (yellow) gave three mole AgCl , one mole $\text{CoCl}_3 \cdot 5\text{NH}_3$ (purple) gave two mole AgCl , one mole $\text{CoCl}_3 \cdot 4\text{NH}_3$ (green) gave one mole AgCl . These observations, together with the results of conductivity measurements in solution can be explained if six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction. Werner proposed the term secondary valence for the number of groups bound directly to the metal ion. Two compounds in Table 6.5, have identical empirical formula, $\text{CoCl}_3 \cdot 4\text{NH}_3$, but distinct properties. Such compounds are termed as isomers.

Table 6.5 Formulation of cobalt(III)chloride-ammonia complexes

Colour	Formula	Composition	Solution conductivity corresponds to
Yellow	$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	1:3 electrolyte
Purple	$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{CoCl}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	1:2 electrolyte
Green	$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1 electrolyte
Violet	$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1 electrolyte

*Primary valence
is ionisable and
secondary
valence is non-
ionisable*

Postulates in Werner's theory

1. In coordination compounds metals show two types of valences primary and secondary valence.
2. The primary valences are normally ionisable and are satisfied by negative ions. Primary valence is numerically equal to the oxidation number of central metal ion.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number.
4. The groups bounded by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
5. Werner further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoCl}_2(\text{NH}_3)_4]^+$ are octahedral entities, while $[\text{Ni}(\text{CO})_4]$ is tetrahedral and $[\text{PtCl}_4]^{2-}$ is square planar.

Primary valencies are non directional and are represented by discontinuous lines (----). Secondary valencies are directional and are represented by a continuous line (—) in the structure. Werner's structures of some complex compounds are given in Fig 6.1.

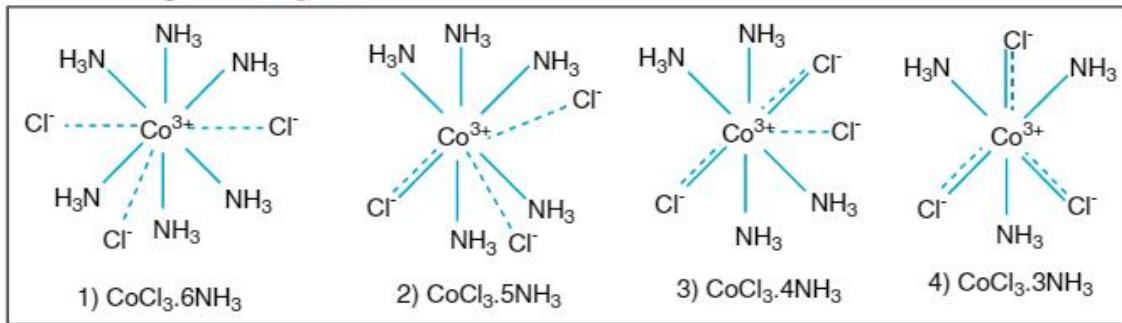


Fig 6.1 Werner's structures of cobalt amine complexes

In $\text{CoCl}_3 \cdot 6\text{NH}_3$ complex, primary valence of cobalt is satisfied by three Cl^- ions and the secondary valence is satisfied by six NH_3 molecules. This complex can be written as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. One mole of this complex can give three moles chloride ions and one mole complex ions $[\text{Co}(\text{NH}_3)_6]^{3+}$ when dissolved in water.

In $\text{CoCl}_3 \cdot 5\text{NH}_3$ complex, primary valence of cobalt is satisfied by three Cl^- ions and the secondary valence is satisfied by five NH_3 and one Cl^- ion. One chloride ion satisfies both primary and secondary valences. This complex can be written as $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Species satisfying both primary and secondary valence are also not ionisable. One mole of this complex gives two moles of chloride ions and one mole complex ions $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ when dissolved in water.

In $\text{CoCl}_3 \cdot 4\text{NH}_3$ complex, primary valence is satisfied by three Cl^- ions. The secondary valence is satisfied by four NH_3 molecules and two Cl^- ions. Two chloride ions satisfy both primary and secondary valences and this complex can be written as $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$. One mole of this complex gives one mole of chloride ions and one mole of complex ions, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ when dissolved in water.

In $\text{CoCl}_3 \cdot 3\text{NH}_3$ complex, three Cl^- ions satisfy primary valence. Three NH_3 molecules and three Cl^- ions satisfy secondary valence and complex can be written as $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$. It cannot give any ions when dissolved in water and is neutral complex.

*$\text{CoCl}_3 \cdot 3\text{NH}_3$ is a
neutral complex
and does not give
any ions in water*

*Werner's theory
does not explain
directional,
magnetic and
optical properties*

All the cobaltamine complexes prepared by Werner are hexacoordinated. All these complexes have octahedral geometry.

Werner's theory failed to answer some basic questions like,

1. Why only certain elements possess the reasonable property of forming coordination compounds?
2. Why the bonds in coordination compound have directional properties?
3. Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been introduced to explain the nature of bonding in coordination compounds. They are valence bond theory (VBT), crystal field theory (CFT), ligand field theory (LFT) and molecular orbital theory (MOT). We shall focus our attention on elementary treatment of the application of VBT and CFT to coordination compounds.



- P.6.7** Arrange the complexes $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$ and $\text{CoCl}_3 \cdot 3\text{NH}_3$ in the descending order of conductivity of their aqueous solutions.

Solution Aqueous solutions containing one mole of $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$ and $\text{CoCl}_3 \cdot 3\text{NH}_3$ gives respectively 4, 3, 2 and zero moles of ions.

Thus the conductivity order is $\text{CoCl}_3 \cdot 6\text{NH}_3 > \text{CoCl}_3 \cdot 5\text{NH}_3 > \text{CoCl}_3 \cdot 4\text{NH}_3 > \text{CoCl}_3 \cdot 3\text{NH}_3$.

Aqueous solution of $\text{CoCl}_3 \cdot 3\text{NH}_3$ does not possess any ions and it is non conductor of electricity. $\text{CoCl}_3 \cdot 3\text{NH}_3$ is a non electrolyte.



- P.6.8** When excess ammonia gas is passed through aq CrCl_3 solution, complexes A and B are formed. Complex A gives 2 particles and complex B gives 4 charges. Write the formula of complexes.

Solution Complex A gives two ions, in which one is complex ion and other is chloride.

Formula of the complex, A is $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Complex B gives cation with two charges and anions with total of two charges.

Formula of the complex B is $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$



- P.6.9** When excess of silver nitrate solution is added to the aqueous solution containing 0.1 mole of $\text{CoCl}_3 \cdot x\text{NH}_3$, if 28.7g of silver chloride precipitated, what is the value of x?

Solution Number of moles of AgCl precipitated = $\frac{28.7}{143.5} = 0.2$ mole.

0.1 mole of $\text{CoCl}_3 \cdot x\text{NH}_3$ gives 0.2 mole AgCl . One mole of $\text{CoCl}_3 \cdot x\text{NH}_3$ gives 2 moles of AgCl . Thus in the complex $\text{CoCl}_3 \cdot x\text{NH}_3$, two chloride ions satisfy only primary valence. One chloride ion satisfies both secondary valence and primary valence.

Since the secondary valence of Co^{3+} is six and one Cl^- is in coordination sphere, complex possesses five NH_3 . Thus 'x' value is five.



- P.6.10** The secondary valence of Pt^{4+} is six. Calculate the number of moles of AgCl participated, when excess of AgNO_3 solution is added to 2L of 0.1M $\text{PtCl}_4 \cdot 4\text{NH}_3$ solution.

Solution Secondary valence of Pt^{4+} is six and it will be satisfied by four NH_3 and two Cl^- ions. The remaining two Cl^- ions satisfy only primary valence. $\text{PtCl}_4 \cdot 4\text{NH}_3$ can be written as $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$.

One mole of this complex gives 2 moles of chloride ions in the aqueous solution.

Number of moles of complex present in 2L of 0.1M $\text{PtCl}_4 \cdot 4\text{NH}_3$ = $M \times V = 0.1 \times 2 = 0.2$.

Number of moles of chloride ions present in 2L of 0.1M $\text{PtCl}_4 \cdot 4\text{NH}_3$ solution = $2 \times 0.2 = 0.4$.

Number of moles of AgCl precipitated from 2L of 0.1 M $\text{PtCl}_4 \cdot 4\text{NH}_3$ is 0.4.

6.3.2

Sidgwick theory

According to Sidgwick, primary valence of metal regarded as formed by electron transfer. The secondary valence corresponds to the coordinate covalent bonds.

The ligands possess pairs of electrons which are donated to fill the vacant orbitals of the metal and form coordinate covalent bonds.

Sidgwick also suggested that the metal ion will continue accepting electron pairs from ligands until the total number of electrons on the metal in the complex is equal to that of the next inert gas. The total number of electrons at the central metal in a complex after coordination is known as effective atomic number (EAN) of the metal in that complex.

The EAN of a metal in a complex is obtained by subtracting the number of electrons lost by the metal in its ion formation from the atomic number (Z) and then adding the number of electrons gained through coordination. The number of electrons lost by the metal is equal to its oxidation state in the complex and the number of electrons gained by the metal is equal to twice of its coordination number.

$$\text{EAN} = \text{Number of electrons in metal ion} + (2 \times \text{coordination number}).$$

In many complexes, EAN of a metal in a complex corresponds to atomic number of the next heavier inert gas. But as it is seen from the Table 6.6, there are some exceptions to the Sidgwick rule.

Table 6.6 EAN values of metals in some complex compounds

Complex	Central metal	Atomic number of metal (Z)	Oxidation number (x)	Coordination number (y)	EAN = Z-x+2y	Z of next inert gas
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Fe	26	2	6	$26-2+12=36$	36(Kr)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Fe	26	3	6	$26-3+12=35$	36(Kr)
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	Cu	29	2	4	$29-2+8=35$	36(Kr)
$[\text{Ni}(\text{CO})_4]$	Ni	28	0	4	$28-0+8=36$	36(Kr)
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Cr	24	3	6	$24-3+12=33$	36(Kr)
$[\text{CoCl}_2(\text{en})_2]^+$	Co	27	3	6	$27-3+12=36$	36(Kr)
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Ag	47	1	2	$47-1+4=50$	54(Xe)
$[\text{PdCl}_4]^{2-}$	Pd	46	2	4	$46-2+8=52$	54(Xe)
$[\text{Pt}(\text{NH}_3)_4]^{2+}$	Pt	78	2	4	$78-2+8=84$	86(Rn)



P.6.11 If $[\text{PtCl}_6]^{x-}$ follows the Sidgwick rule of stability, what is the oxidation state of Pt and complex?

Solution $[\text{PtCl}_6]^{x-}$ following Sidgwick rule of stability, thus EAN of Pt is to be equal to the atomic number of nearest inert gas 86(Rn).

Let the oxidation state of platinum in $[\text{PtCl}_6]^{x-}$ complex ion is y

$$y + 6(-1) = -x \text{ (or)} \quad y = 6 - x$$

$$86 = 78 - (6-x) + 2 \times 6 = 78 - 6 + x + 12; x = 2$$

Oxidation state of platinum forming the complex = $6-x = 6-2 = +4$

Oxidation state of the complex = -2.



P.6.12 If $[\text{Fe}(\text{CO})_x]$ follows the Sidgwick rule of stability, what is the value of 'x'?

Solution $[\text{Fe}(\text{CO})_x]$ following the Sidgwick rule of stability, EAN of Fe is to be equal to the atomic number of nearest inert gas, 36(Kr).

$$36 = 26 - 0 + 2 \times x \Rightarrow x = 5$$

Hence the value of x is 5 and this is the coordination number

6.3.3

Valence bond theory

Valence bond theory is the oldest theory of complex compounds proposed by Linus Pauling. Pauling explained formation of complex between a metal and ligand and structures of complex compounds. Important postulates of this theory are given below:

1. The central metal first loses requisite number of electrons to form the ion and necessary number of vacant orbitals are created.
2. The number of electrons lost is numerically equal to the oxidation state of the metal.
3. The vacant orbitals of the metal ion undergo suitable hybridization so that the desired shape is obtained by the complex. The type of hybridization and the shape of complex species are given in the Table 6.7.

Table 6.7 Hybridization and shapes of the complexes of 3d-metals

S.No.	Orbitals involved in hybridization	Hybridization	Coordination number	Shape of the complex
1	one 4s, three 4p	sp^3	4	tetrahedral
2	one 3d, one 4s, two 4p	dsp^2	4	square planar
3	two 3d, one 4s, three 4p	d^2sp^3	6	octahedral
4	one 4s, three 4p, two 4d	sp^3d^2	6	octahedral

4. In octahedral complexes, if $(n-1)d$ orbitals are used for hybridization along with ns and np orbitals, then it is d^2sp^3 hybridization. Such complexes are called inner orbital or low spin or spin paired or strong field or covalent complexes.
5. In octahedral complexes, if nd orbitals are used for hybridization along with ns and np orbitals, then it is sp^3d^2 hybridization. Such complexes are called outer orbital or high spin or spin free or weak field or ionic complexes.
6. In the formation of some complexes, the electrons in the metal orbital may undergo pairing against to Hund's rule to get required number of empty $(n-1)d$ orbitals.
7. Completely filled orbitals of ligand overlap the vacant metal orbitals to form a strong coordinate covalent bond to the extent possible.
8. The metal acquires the next inert gas configuration or comes nearest to the inert gas configuration.
9. The electrons in an incompletely filled orbitals give rise to the resultant magnetic moment.

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of valence bond theory. In the diamagnetic complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$, cobalt is in +3 oxidation state and has the electronic configuration 3d^6 . Since $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic, four unpaired electrons in free Co^{3+} paired up to generate two empty 3d orbitals. Co^{3+} undergoes d^2sp^3 hybridization by using two empty 3d-orbitals, one empty 4s-orbital and three empty 4p-orbitals.

Electrons of metal may undergo pairing against to Hund's rule in $(n-1)d$ orbital

*Co³⁺ ion in
Co(NH₃)₆³⁺ is
d²sp³ hybridised*

*Co³⁺ ion in
CoF₆³⁻ is sp³d²
hybridised*

*Ni in Ni(CO)₄ and
Ni²⁺ in NiCl₄²⁻ are
sp³ hybridised*

Six pairs of electrons, one from each NH₃ molecule, occupy the six empty hybrid orbitals. Thus [Co(NH₃)₆]³⁺ is inner orbital complex and has octahedral structure. The hybridization scheme in Co³⁺ of the complex [Co(NH₃)₆]³⁺ is as shown in Fig 6.2.

Orbitals of Co ³⁺ ion	3d	4s	4p
	↑↓ ↑↑↑↑↑		
Hybridised orbitals of Co ³⁺	3d	d ² sp ³ hybrid orbitals	
	↑↓↑↓↑↓	6 pairs from NH ₃ ligands	
Inner orbital [Co(NH ₃) ₆] ³⁺ complex	3d		
	↑↓↑↓↑↓		

Fig 6.2 Scheme of hybridisation of Co³⁺ in [Co(NH₃)₆]³⁺

The paramagnetic octahedral complex, [CoF₆]³⁻ uses the outer 4d orbitals in hybridization (sp³d²). It is thus called outer orbital complex. The hybridization scheme in Co³⁺ of this complex is as shown in Fig 6.3.

Orbitals of Co ³⁺ ion	3d	4s	4p	4d
	↑↓ ↑↑↑↑↑			
Hybridised orbitals of Co ³⁺	3d	sp ³ d ² hybrid orbitals		4d
	↑↓↑↑↑↑			
Outer orbital [CoF ₆] ³⁻ complex	3d	6 pairs from F ⁻ ligands		4d
	↑↓↑↑↑↑			

Fig 6.3 Scheme of hybridisation of Co³⁺ in [CoF₆]³⁻

In complexes with the coordination number four, square planar structure dsp² hybridization possible if one (n-1)d empty orbital is available along with one empty ns orbital and two empty np orbitals. If empty (n-1)d orbitals are not available then tetrahedral structure with sp³ hybridization is possible.

In paramagnetic complex, [NiCl₄]²⁻, nickel is in +2 oxidation state and the ion has the electronic configuration 3d⁸. Since the complex is paramagnetic, two half filled 3d orbital of Ni²⁺ remains as it is. Now Ni²⁺ undergo sp³ hybridization and the complex, [NiCl₄]²⁻, has tetrahedral structure. Similarly, [Ni(CO)₄] has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electrons. The hybridization scheme of in Ni²⁺ of the complex [NiCl₄]²⁻ is given in Fig 6.4.

Orbitals of Ni ²⁺ ion	3d	4s	4p
	↑↓↑↓↑↓↑↑↑↑		
Hybridised orbitals of Ni ²⁺	3d	sp ³ hybrid orbitals	
	↑↓↑↓↑↓↑↑↑↑		
High spin [NiCl ₄] ²⁻ complex	3d	4 pairs from Cl ⁻ ligands	
	↑↓↑↓↑↓↑↑↑↑		

Fig 6.4 Scheme of hybridisation of Ni²⁺ in [NiCl₄]²⁻

*Ni²⁺ ion in
 $\text{Ni}(\text{CN})_4^{2-}$ is $d\text{sp}^2$
 hybridised*

In diamagnetic complex, $[\text{Ni}(\text{CN})_4]^{2-}$, nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. Since the complex is diamagnetic, electrons in two half filled 3d-orbitals of Ni^{2+} paired up to generate one empty 3d-orbital. Ni^{2+} undergoes $d\text{sp}^2$ hybridization and the complex has square planar structure. The hybridization scheme of Ni^{2+} is as shown in Fig 6.5. Hybridization and structures of some more complexes given in the Table 6.8. It is important to note that the hybrid orbitals do not actually exist. In fact, hybridization is a mathematical manipulation of wave equation for the atomic orbitals involved.

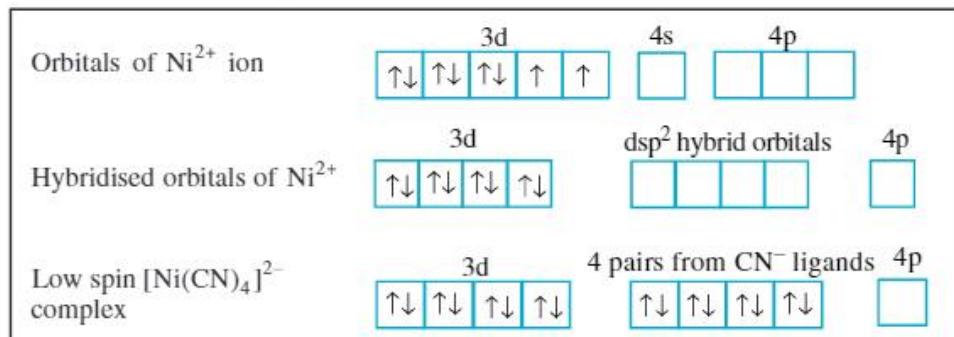
Fig 6.5 Scheme of hybridisation of Ni^{2+} in $[\text{Ni}(\text{CN})_4]^{2-}$

Table 6.8 Hybridisation of metal ion and structures of some complexes

Formula of complex	Electronic configuration	Oxidation state	Type of hybridisation	Geometry of complex	No.of unpaired e ⁻	Magnetic nature
$[\text{Mn}(\text{CN})_6]^{4-}$	$\uparrow\downarrow \uparrow\downarrow \uparrow \square \square \square \square \square \square$	+ 2	$d^2\text{sp}^3$	Octahedral (Inner)	1	Para-magnetic
$[\text{MnCl}_4]^{2-}$	$\uparrow\uparrow \uparrow\uparrow \uparrow\uparrow \uparrow \square \square \square \square$	+ 2	sp^3	Tetrahedral	5	Para-magnetic
$[\text{CuCl}_4]^{2-}$	$\uparrow\downarrow \uparrow\uparrow \uparrow\uparrow \uparrow \square \square \square \square$	+ 2	sp^3	Tetrahedral	1	Para-magnetic
$[\text{PdBr}_4]^{2-}$	$\uparrow\downarrow \uparrow\uparrow \uparrow\downarrow \uparrow \square \square \square \square$	+ 2	$d\text{sp}^2$	Square planar	0	Diamagnetic
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$\uparrow\uparrow \uparrow \square \square \square \square \square \square$	+ 3	$d^2\text{sp}^3$	Octahedral (Inner)	3	Para-magnetic
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$\uparrow\uparrow \uparrow \square \square \square \square \square \square$	+ 3	$d^2\text{sp}^3$	Octahedral (Inner)	3	Para-magnetic
$[\text{Fe}(\text{CN})_6]^{4-}$	$\uparrow\downarrow \uparrow\uparrow \uparrow\downarrow \square \square \square \square \square \square$	+ 2	$d^2\text{sp}^3$	Octahedral (Inner)	0	Diamagnetic
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$\uparrow\downarrow \uparrow\uparrow \uparrow\uparrow \uparrow \square \square \square \square \square \square$	+ 2	sp^3d^2	Octahedral (Outer)	4	Para-magnetic
$[\text{Fe}(\text{CN})_6]^{3-}$	$\uparrow\downarrow \uparrow\uparrow \uparrow \square \square \square \square \square \square$	+ 3	$d^2\text{sp}^3$	Octahedral (Inner)	1	Para-magnetic
$[\text{Fe}(\text{CO})_5]$	$\uparrow\downarrow \uparrow\uparrow \uparrow\downarrow \uparrow \square \square \square \square \square$	0	$d\text{sp}^3$	Trigonal bipyramidal (Inner)	0	Diamagnetic


Complexes with unpaired electrons are paramagnetic



[Co(C₂O₄)₃]³⁻ is a diamagnetic with d²sp³ hybridisation of Co³⁺


Magnetic properties : The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the structures adopted by metal complexes. For metal ions with up to three electrons in the d-orbitals, like (d¹) Ti³⁺; (d²) V³⁺ and (d³) Cr³⁺, two vacant 3d-orbitals are available for octahedral hybridisation along with 4s and 4p orbitals. The magnetic behaviour of these free ions and their coordination entities are similar. When more than three 3d electrons are present, the required pair of vacant 3d orbitals for octahedral hybridisation is not directly available. Thus, for d⁴ (Cr²⁺, Mn³⁺); d⁵(Mn²⁺, Fe³⁺) and d⁶ (Fe²⁺, Co³⁺) cases, a vacant pair of d- orbitals results only by pairing 3d electrons which leaves two, one and zero unpaired electrons respectively.

In many cases the magnetic data of complexes agree with partial spin pairing for metal ions with d⁴ configuration and maximum spin pairing for metal ions with d⁵ and d⁶ configuration. [Mn(CN)₆]³⁻ has magnetic moment of two unpaired electrons, while [MnCl₆]³⁻ has a paramagnetic moment of four unpaired electrons. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. [Mn(CN)₆]³⁻, [Fe(CN)₆]³⁻ and [Co(C₂O₄)₃]³⁻ are inner orbital complexes involving d²sp³ hybridization. The former two complexes are paramagnetic and the latter diamagnetic. On the other hand, [MnCl₆]³⁻, [FeF₆]³⁻ and [CoF₆]³⁻ are outer orbital complexes involving sp³d² hybridisation. These are paramagnetic corresponding to four, five and four unpaired electrons.

Limitations : While the VB theory explains the formation, structures and magnetic behaviour of coordination compounds to a larger extent, it suffers from the following short comings. Applying VB theory, [Cu(NH₃)₄]²⁺ complex is expected to be tetrahedral with sp³ hybridisation of metal ion. Experimentally, the complex was observed to be square planar.

VB theory involves a number of assumptions, does not give quantitative interpretation of magnetic data and colour exhibited. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds. It does not explain field strength of the ligands.



P.6.13

The spin only magnetic moment of [MnBr₄]²⁻ is 5.9BM. Predict the geometry of the complex ion.

Solution

Since the coordination number of Mn²⁺ ion in the complex ion is 4, the geometry may be either tetrahedral (sp³) or square planar (dsp²).

But the fact that the magnetic moment of the complex ion is 5.9BM, it should be tetrahedral in shape but not square planar. This is because of the presence of 5 unpaired electrons in the d-orbitals.

6.3.4

Crystal field theory


Degeneracy of five d orbitals is maintained in a symmetrical field of ligands


The crystal field theory considers metal ligand bond as ionic which is arising purely from electrostatic interaction between the metal ion and ligand.

In crystal field theory, ligands are treated as point charges in case of anionic ligands or dipoles in case of neutral ligands. The five d orbitals in an isolated gaseous metal ion are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the ion. However, when this negative field is due to ligands in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d-orbitals. The pattern of splitting depends upon the nature of the crystal field.

In octahedral field, t_{2g} is lower energy set of 3 orbitals and e_g is higher energy set of 2 orbitals

Crystal field splitting in octahedral complexes : In an octahedral coordination entity with six ligands surrounding the metal ion, there will be repulsion between the electrons in metal d-orbitals and the electrons (or negative charges) of ligand. Such a repulsion is more when the metal d-orbital is directed towards ligand, than when it is away from the ligand.

In $d_{x^2-y^2}$ and d_{z^2} orbitals lobes are orientated towards axes but in d_{xy} , d_{yz} and d_{xz} orbitals lobes are oriented in between the axes. Since the ligands approach the metal ion along the axes, $d_{x^2-y^2}$ and d_{z^2} orbitals experience more repulsion and the energy of orbitals is raised. The energy of d_{xy} , d_{yz} and d_{xz} orbitals is lowered relative to average energy of d-orbitals in the spherical crystal field. The three lower energy orbitals set is called t_{2g} and two higher energy orbitals set is called e_g . This splitting of degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o as shown in Fig 6.6.

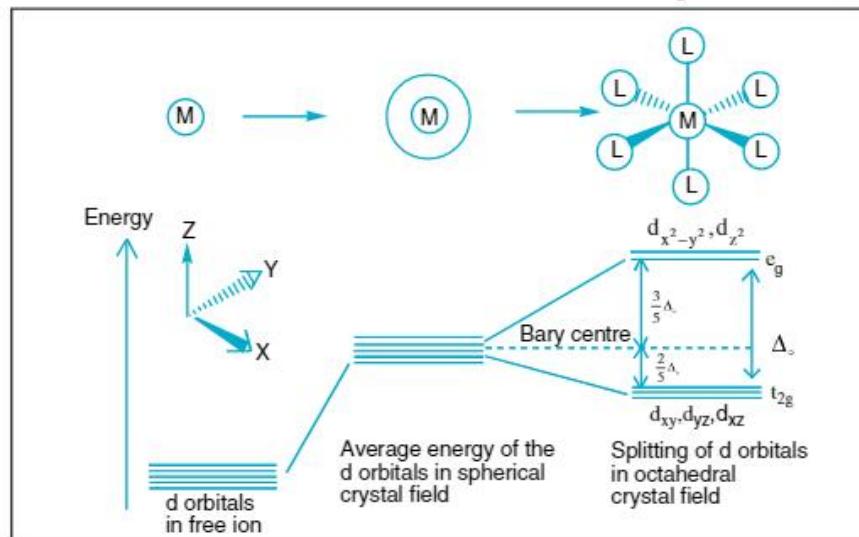
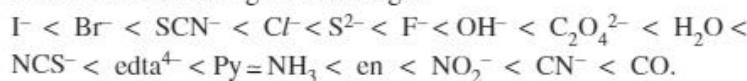


Fig 6.6 Splitting of d-orbitals in an octahedral crystal field

The energy of e_g orbitals is increased by $(3/5)\Delta_o$ and the energy of t_{2g} orbitals is lowered by $(2/5)\Delta_o$. Each electron entering the t_{2g} orbital stabilises the complex by $0.4\Delta_o$ units and each electron entering e_g destabilises the complex by $0.6\Delta_o$ units.

The crystal field splitting energy, Δ_o , depends upon the field produced by the ligand and charge on the metal ion. In general, ligands can be arranged in a series in the order of increasing field strength.



This series is called spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

In d^1 , d^2 and d^3 coordination entities, the d-electrons occupy t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions two ways of electron distributions are possible. In one way the fourth electron enters t_{2g} level and pairs with an existing electron. In the second way the fourth electron enters e_g level without pairing in t_{2g} level. The way of electron distribution depends on the magnitude of crystal field splitting energy, Δ_o and the pairing energy, P . Pairing energy is the energy required for electron pairing in a single orbital.

Series of ligands with increasing field strength is called spectrochemical series

If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes or outer orbital complexes.

Strong field ligands form low spin complex compounds

If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes or inner orbital complexes.

Filling up of d-orbitals and crystal field stabilization energies are given in the Table 6.9. Crystal field stabilisation energy calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

Table 6.9 Crystal field stabilisation energies in the presence of strong and weak field ligands

Configuration	Distribution in strong field		Stabilisation energy	No. of unpaired electrons	Distribution in weak field		Stabilisation energy	No. of unpaired electrons
	t_{2g} orbitals	e_g orbitals			t_{2g} orbitals	e_g orbitals		
d^1	↑		0.4 Δ_o	1	↑		0.4 Δ_o	1
d^2	↑	↑	0.8 Δ_o	2	↑	↑	0.8 Δ_o	2
d^3	↑	↑	1.2 Δ_o	3	↑	↑	1.2 Δ_o	3
d^4	↑↓	↑	1.6 Δ_o	2	↑	↑	0.6 Δ_o	4
d^5	↑↓	↑↓	2.0 Δ_o	1	↑	↑	0.0 Δ_o	5
d^6	↑↓	↑↓	2.4 Δ_o	0	↑↓	↑	0.4 Δ_o	4
d^7	↑↓	↑↓	1.8 Δ_o	1	↑↓	↑↓	0.8 Δ_o	3
d^8	↑↓	↑↓	1.2 Δ_o	2	↑↓	↑↓	1.2 Δ_o	2
d^9	↑↓	↑↓	0.6 Δ_o	1	↑↓	↑↓	0.6 Δ_o	1
d^{10}	↑↓	↑↓	0.0 Δ_o	0	↑↓	↑↓	0.0 Δ_o	0

Crystal field splitting in tetrahedral coordination entities: In the formation of tetrahedral coordination entity, the d-orbital splitting is inverted and is smaller as compared to the octahedral field splitting. Splitting of d-orbitals in a tetrahedral crystal field is given in the Fig 6.7.

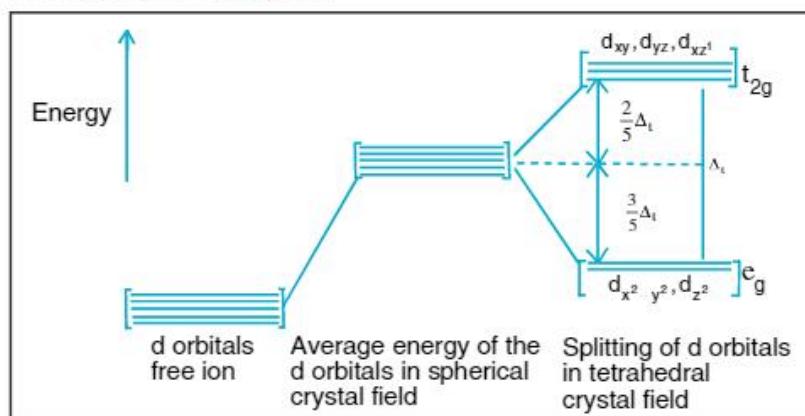


Fig 6.7 Splitting of d-orbitals in a tetrahedral crystal field


For same metal,
splitting energies

$$\Delta_t = (4/9)\Delta_o$$



Colours of
complexes is due
to d-d transitions




CFT explains
structures, colour
and magnetic
properties of
complexes

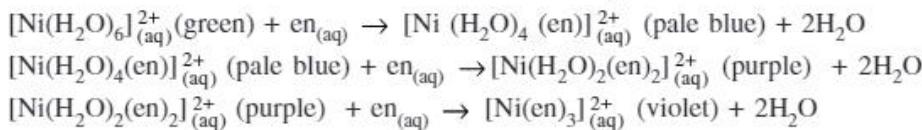


For the same metal, same ligands and metal - ligand distance, the relation between tetrahedral splitting energy, Δ_t and octahedral splitting energy, Δ_o , is $\Delta_t = (4/9)\Delta_o$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

Colour in coordination compounds: Crystal field theory can also explain the colour of complexes in same way of colour of hydrated transition metal ions which was already discussed in previous unit. For example, in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, Ti^{3+} has one d-electron in t_{2g} level. If light corresponding to the energy of yellow - green region is absorbed by the complex, it would excite the electron from t_{2g} level to e_g level. Consequently, the complex appears red-violet in colour, which is the complementary colour of absorbed light. The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, anhydrous Ti^{3+} is colourless. Similarly, anhydrous CuSO_4 is white, but $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour. The influence of the ligand on the colour of a complex may be illustrated by considering the complex $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

If the bidentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratio of metal and ligand, 1:1, 1:2 and 1:3, the following series of reactions occur. Reactions can be observed with the colour changes.



Limitations : The crystal field theory successfully explains the formation, structures, colour and magnetic properties of coordination compounds to a larger extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect than neutral ligands. But actually anionic ligands like halides exerting very less splitting effect. Further, it does not take into account the covalent character of bonding between the ligand and central metal ion.

The relationship between absorbed wavelength and the observed colour of some complexes is given in Table 6.10.

Table 6.10 Formulation of cobalt(III)chloride-ammonia complexes

Coordination complex	Absorbed wavelength	Absorbed colour	Complementary colour observed
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498 nm	Blue green	Violet
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	535 nm	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$	500 nm	Blue green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475 nm	Blue	Yellow Orange
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600 nm	Red	Blue
$[\text{Co}(\text{CN})_6]^{3-}$	310 nm	U.V	Pale Yellow

All these weaknesses of CFT are latter explained by ligand field theory and molecular orbital theory which are beyond the scope of this book.



P.6.14 How the gem stones ruby exhibits red colour and emerald exhibits green colour ?

Solution Ruby is aluminium oxide (Al_2O_3) containing about 0.5–1% Cr^{3+} ion (d^3). This chromium (III) is an octahedral complex incorporated into the alumina lattice. The d-d transitions in Cr^{3+} give the red colour to ruby. Emerald is the beryl mineral ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) having some Cr^{3+} ions at octahedral sites. The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to reflect green colour.



P.6.15 Anhydrous copper sulphate is colourless, but hydrated copper sulphate is blue. Explain ?

Solution In anhydrous copper sulphate, the splitting is very less. It absorbs energy in infrared region. It is colourless.

In hydrated copper sulphate, water molecules are present in the coordination sphere. The splitting of d-orbitals is reasonably increased. If it absorbs energy in visible region of light. Hence it is exhibit colour.



P.6.16 Why hexaquamanganese(II)ion contains five unpaired electrons, while the hexacyno manganese (II)ion contains only one unpaired electron ?

Solution $\text{Mn}^{2+} \rightarrow$

$3d^5$	$4s^0$	$4p^0$	$4d^0$
$\uparrow \uparrow \uparrow \uparrow \uparrow$			

H_2O is a weak field ligand and CN^- is a strong field ligand. Thus in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, pairing of unpaired electrons is not possible and it possesses five unpaired electrons.

In $[\text{Mn}(\text{CN})_6]^{4-}$ pairing of four unpaired electrons takes place and it possesses one unpaired electron.



P.6.17 How many unpaired electrons present in the square planar $[\text{Pt}(\text{CN})_4]^{2-}$ ion ?

Solution $\text{Pt}^{2+} \rightarrow$

$4d^8$	$5s^0$	$5p^0$
$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow$		

 Square planar $[\text{Pt}(\text{CN})_4]^{2-}$

$4d^8$	$5s^0$	$5p^0$
$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$

 In $[\text{Pt}(\text{CN})_6]^{2-}$, no unpaired electrons are present and it is diamagnetic.



P.6.18 Why $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex where as $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex?

Solution In these complexes central metal ions are Co^{3+} and Ni^{2+} .

$\text{Co}^{3+} \rightarrow$

$3d^6$	$4s^0$	$4p^0$	$4d^0$
$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$			

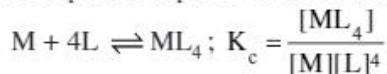
 $\text{Ni}^{2+} \rightarrow$

$3d^8$	$4s^0$	$4p^0$	$4d^0$
$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$			

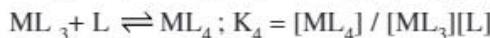
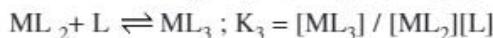
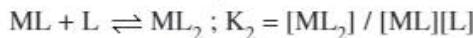
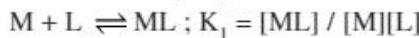
NH_3 is a strong field ligand. It can cause pairing of unpaired electrons. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, if electron spins of Co^{3+} are paired up two empty 3d orbitals will be created. Thus Co^{3+} undergoes $d^2\text{sp}^3$ hybridisation by using two empty 3d orbitals. The complex is inner orbital complex.

In $[\text{Ni}(\text{NH}_3)_6]^{2+}$, if electron spins of Ni^{2+} are paired up only one empty 3d orbital will be created. Thus Ni^{2+} undergoes sp^3d^2 hybridization by using two empty 4d-orbitals. The complex is an outer orbital complex.

Stability of complex compounds : The equilibrium constant for the formation of a complex compound is the stability constant.



Here equilibrium constant, K_c , can be taken as stability constant. Larger the stability constant, the higher the proportion of ML_4 that exists in solution. Thus greater the stability constant, greater the stability of complex compound. The complex, ML_4 , can be considered as it is formed from metal M, and ligand, L, in four steps, with K_1 , K_2 , etc., are referred to as stepwise stability constants.



Generally successive stability constant decreases. The overall stability constant is the product of stepwise stability constants.

$$K_c = K_1 \times K_2 \times K_3 \times K_4$$

The instability constant or dissociation constant of coordination compound is defined as the reciprocal of the stability constant. Lesser the instability constant, greater the stability of complex compound.



P.6.19 $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $K_1 = 3.5 \times 10^{-3}$; $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 = 1.7 \times 10^{-3}$. Calculate the formation constant of $[Ag(NH_3)_2]^+$? What is the instability constant?

Solution

Overall formation constant is the product of successive formation constants, $K_c = K_1 \times K_2$. Formation constant of $[Ag(NH_3)_2]^+ = 3.5 \times 10^{-3} \times 1.7 \times 10^{-3} = 5.95 \times 10^{-6}$.

Instability constant is the inverse of the stability constant, $\frac{1}{K_c} = \frac{1}{5.95 \times 10^{-6}} = 1.7 \times 10^7$.

6.3.5

Organometallic compounds

Compounds with metal carbon bonds are called organometallics

Compounds having one or more metal carbon bonds are called organometallic compounds. For example, CH_3MgBr is an organometallic compound whereas C_2H_5ONa is not organo-metallic compound since the metal atom is attached to oxygen.

Organometallic compounds have wide application in synthetic organic chemistry. These compounds can be broadly classified into three types : a) σ bonded organometallics, b) π bonded organometallics and c) metal carbonyls.

σ Bonded organometallics : These compounds contain metal carbon covalent sigma bond. Some examples for this type of compounds are Grignard reagent, diethyl zinc, trimethyl aluminium, tetramethyl tin, etc.

π Bonded organometallics : These are organometallic compounds which involve the use of π bonds present in the organic compounds. Zeise's salt, $K[PtCl_3(C_2H_4)]$, ferrocene $[Fe(C_5H_5)_2]$ and dibenzene chromium are organometallic compounds of this type. In all these compounds π electrons of the organic compound interact with metal ion and thus occupy one of the coordination sites.

Metal carbonyls : These are the homoleptic complexes of metal and neutral ligands, carbon monoxide. Metal carbonyls have well defined structures. Tetracarbonyl nickel(0) is tetrahedral, pentacarbonyliron(0) is trigonal bipyramidal,

Metal–carbon bond in carbonyl complexes has both σ and π character

while hexa-carbonyl chromium(0) is octahedral. Decacarbonyldimanganese(0) is made up of two square pyramidal $\text{Mn}(\text{CO})_5$ units joined by a Mn–Mn bond. Octacarbonyldicobalt(0) is made up of two trigonal pyramidal $\text{Co}(\text{CO})_4$ units joined by a Co–Co bond.

The metal–carbon bond in metal carbonyls possesses both σ and π character. The σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide as indicated in Fig 6.8. The metal to ligand bonding creates a synergic effect which strengthens the bond between carbon monoxide and the metal. The total bonding is thus $\text{M} = \text{C} = \text{O}$.

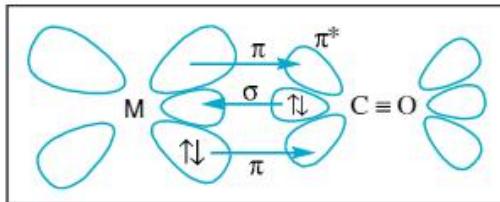


Fig 6.8 Synergic bonding in a carbonyl complex

The π bond between metal and carbonyl carbon reduces the bond order of C–O bond from triple bond in CO towards to a double bond. This is shown by increase in C–O bond length from 1.128\AA in CO to about 1.15\AA in many carbonyls.

Ziegler–Natta catalyst is a mixture of TiCl_4 and R_3Al

Organometallic compounds have good number of applications. In Mond process for refining of nickel, impure nickel first converted into volatile compound, $[\text{Ni}(\text{CO})_4]$ and then decomposed to get pure nickel. A mixture of TiCl_4 and trialkyl aluminium is called Ziegler–Natta catalyst and is used for polymerisation of alkenes. Alkyl lithium, dialkyl zinc, dialkyl cadmium and Grignard reagent are used in many organic synthesis. Ethyl mercury chloride ($\text{C}_2\text{H}_5\text{HgCl}$) is used as a fungicide.

EXERCISE - 6.1.3

- Explain Werner's theory of complex compounds. Give the Werner's structures of $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$ and $\text{CoCl}_3 \cdot 3\text{NH}_3$.
- Identify the primary valency of the central metal in the tetra coordinated CuSO_4 and hexa coordinated $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.
- A linear complex $\text{AgCl} \cdot 2\text{NH}_3$ undergoes complete ionization. What are the ions formed?
- Write the postulates of valence bond theory of complex compounds.
- Explain the formation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ on the basis of VBT.
- Write the CFT splitting of octahedral and tetrahedral complexes.

ISOMERISM IN COMPLEXES

Two or more compounds that have the same chemical formula but a different arrangement of atoms are called isomers and the phenomenon is known as isomerism. Isomerism in complexes may be broadly divided into two types structural isomerism and stereo isomerism.

6.4.1 Structural isomerism


Complexes with same formula but gives different ions are called ionisation isomers


Complexes with different number of H_2O molecules as ligands and in hydration are called hydrate isomers


Compound with cation and anion entities exhibit coordination isomerism

Structural isomerism arises due to different kinds of bonds between the metal and the ligands. This can be subdivided into ionisation, solvate, linkage and coordination and isomerism.

Ionisation isomerism : The compounds which have same molecular formula but give different ions in solution are called ionisation isomers. This type of isomerism is possible when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. Generally anionic complexes can not exhibit ionisation isomerism.

Ionisation isomers will be produced when ligands inside and counter ions outside the coordination sphere are interchanged. For example, violet $[Co(NH_3)_5Br]SO_4$ and red $[Co(NH_3)_5(SO_4)]Br$ are together ionisation isomers. Aqueous solution of first compound gives white precipitate with $BaCl_2$ solution showing the presence of SO_4^{2-} ion and gives no precipitate with aqueous solution of $AgNO_3$ showing the absence of Br^- ion. Aqueous solution of second compound gives pale yellow precipitate with $AgNO_3$ solution showing the presence of Br^- ion and gives no precipitate with $BaCl_2$ solution showing the absence of SO_4^{2-} ion. Other examples are: $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4 Br_2]Cl_2$; $[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4 Cl(NO_2)]Cl_2$.

Solvate isomerism : The compounds which have same molecular formula but differ in the number of solvent molecules present as ligands or as molecules of solvation are called solvent isomers. It is similar to ionisation isomerism, in which water molecules may occur inside and outside the coordination sphere. It is also called hydrate isomerism.

$CrCl_3 \cdot 6H_2O$ molecular formula represents three possible isomers. They are $[Cr(H_2O)_6]Cl_3$ (violet), $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (light green) and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (dark green). $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ may also be possible. With excess of aqueous $AgNO_3$ solution, one mole of violet coloured $CrCl_3 \cdot 6H_2O$ gives three moles of $AgCl$ precipitate, one mole of light green $CrCl_3 \cdot 6H_2O$ gives two moles of $AgCl$ precipitate and one mole of dark green $CrCl_3 \cdot 6H_2O$ gives one mole of $AgCl$ precipitate. Other examples for hydrate isomers are : $[Co(en)_2(H_2O)Cl]Cl_2$ and $[Co(en)_2Cl_2]Cl \cdot H_2O$

Linkage isomerism : Linkage isomerism arises in complexes having at least one ambidentate ligand. Compounds having the same molecular formula but differ in the mode of attachment of a ligand to the metal ion are called linkage isomers. Jorgensen discovered linkage isomer in the complex $[Co(NH_3)_5NO_2]Cl_2$ as shown in Fig 6.9.

Complex in which the nitrite ligand is bound through oxygen ($-ONO$) is red and the complex in which the nitrite ligand is bound through nitrogen ($-NO_2$) is yellow.

Coordination isomerism : In ionic complexes, if the cation and anion are complex entities, then coordination of isomerism may arise. Mutual exchange of ligands completely or partially between the cation and anion results this isomerism.

For example, $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are coordination isomers.

In the first complex, NH_3 ligands are bound to Co^{3+} and CN^- ligands to Cr^{3+} , but in the second complex, NH_3 ligands are bound to Cr^{3+} and CN^- ligands to Co^{3+} . $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Cu}(\text{NH}_3)_3\text{Cl}] [\text{Pt}(\text{NH}_3)\text{Cl}_3]$ are coordination isomers formed by partial exchange of ligands.

$[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$ are coordination isomers formed by complete exchange of ligands.

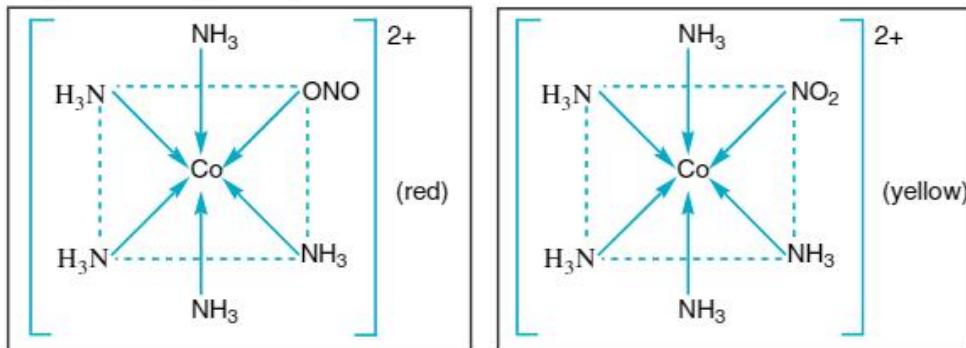


Fig 6.9 Linkage isomers of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$

6.4.2

Stereoisomerism

Stereoisomers have the same chemical formula and chemical bonds but have different spatial arrangement. Stereoisomerism is mainly two types: geometrical isomerism and optical isomerism.

Geometrical isomerism : This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

In the cis isomer similar ligands are adjacent to each other, but in the trans isomer, similar ligands are opposite to each other. Geometrical isomerism of compounds with coordination members 4 and 6 is most important.

The complexes having coordination number four adopt tetrahedral or square planar geometry. Tetrahedral complexes do not exhibit geometrical isomerism because the relative positions of the ligands attached to the central metal are the same with respect to each other. However, square planar complexes show geometrical isomerism.

Square planar complexes of the type MA_2X_2 and MA_2XY (A, X and Y are monodentate ligands) can exhibit geometrical isomerism. Square planar complex of the type MABXY shows 3 isomers, 2 cis and 1 trans. Geometrical isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ are given in Fig 6.10.

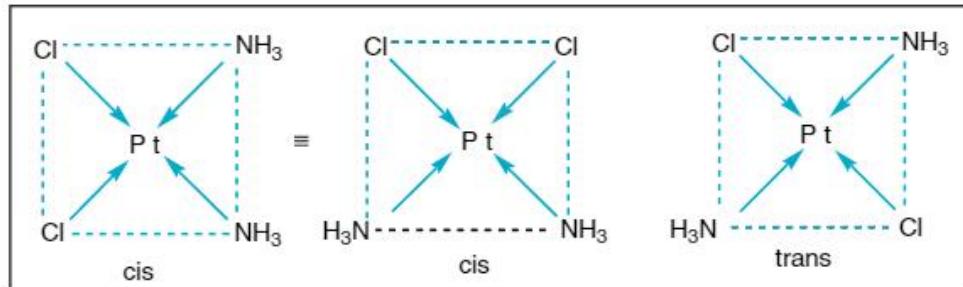


Fig 6.10 Geometrical isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

*[MA₄X₂] and
[M(AA)₂X₂] type
complexes exhibit
cis-trans isomers*

The octahedral complexes of the type [MA₄X₂], [M(AA)₂X₂], etc., exhibit geometrical isomerism. Here A, X are monodentate ligands and (AA) is symmetrical bidentate ligand. Geometrical isomers of [Co(NH₃)₄Cl₂]⁺ are given in the Fig 6.11 and of [Co(en)₂Cl₂]⁺ are given in the Fig 6.12.

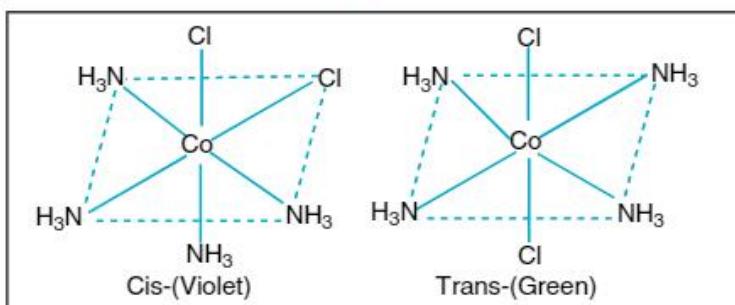


Fig 6.11 Geometrical isomers of [Co(NH₃)₄Cl₂]⁺

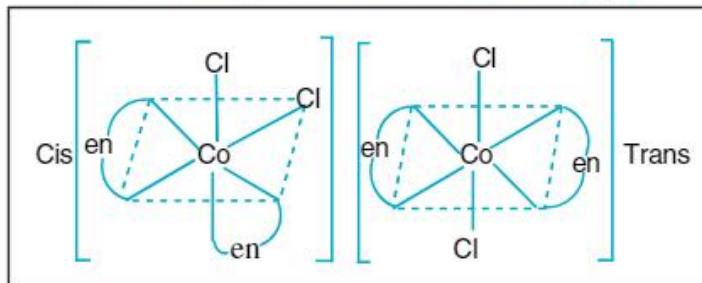


Fig 6.12 Geometrical isomers of [Co(en)₂Cl₂]⁺

Another type of geometrical isomerism occurs in octahedral complexes of the type Ma₃b₃. If three donor atoms of the same ligand occupy adjacent positions at the corners of octahedral face, it is called facial or fac isomer. When the position of atoms of the same ligand occupy meridian of octahedron, it is called meridional or mer isomer. These isomers are shown in Fig 6.13.

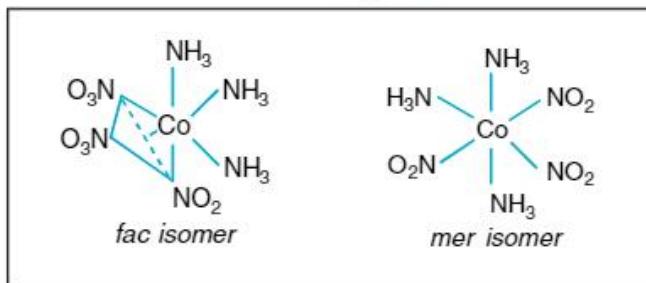


Fig 6.13 The 'fac' and 'mer' isomers of [Co(NH₃)₃(NO₂)₃]

*The d- and l-
isomers are mirror
images
and cannot be
superimposed*

Optical isomerism : Compounds which can rotate plane polarised light are optically active substances. These substances are called optical isomers.

The isomer which rotates the plane of polarised light to the right and to the left are called dextro rotatory (d) and laevo rotatory (l) respectively. The d- and l- isomers of a compound are mirror images that cannot be superimposed on the other. These are called as enantiomers. Optical isomerism is exhibited by assymmetric compounds.


Octahedral complexes may exhibit optical isomerism



A 1:1 mixture of d- and l-isomers is called racemic mixture


Optical isomerism is common in octahedral complexes involving bidentate ligands. Octahedral complexes of the type $[M(AA)_3]$, $[M(AA)_2X_2]$, $[M(AA)_2XY]$, cis $[M(AA)_2X_2]$ and cis $[M(AA)_2Y_2]$ can exhibit optical isomerism, where (AA) is symmetrical bidentate ligand, X and Y are monodentate ligands.

Trans form of $[M(AA)_2X_2]$ can not exhibit optical isomerism due to the presence of plane of symmetry. Examples for optical isomers are $[Co(en)_3]^{3+}$, cis $[Co(en)_2Cl_2]^+$ and $[Co(en)(NH_3)_2Cl_2]^+$. Optical isomers of cis $[Co(en)_2Cl_2]^+$ are given in Fig 6.14.

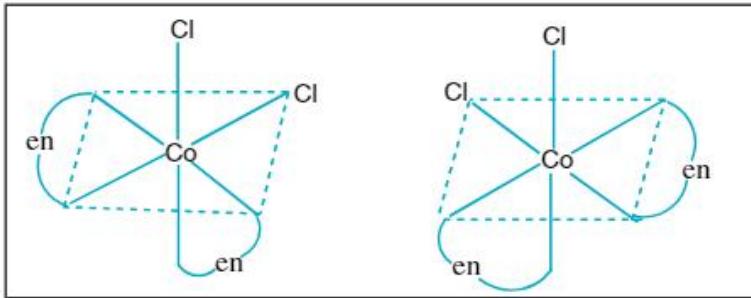


Fig 6.14 Enantiomers of cis $[Co(en)_2Cl_2]^+$

Octahedral complexes containing hexadentate ligands such as ethylenediamine tetraacetate also show optical isomerism. For example, $[Co(edta)]^-$ ion or $[Co(en)_3]^{3+}$ is optically active. A 1:1 mixture of d- and l-isomers of a complex is called racemic mixture. Racemic mixture is optically inactive, due to external compensation.



P.6.20 $CoCl_3 \cdot xNH_3$ exhibits geometrical isomerism. What is the value of x?

Solution The value of x may be 3 and 4. $CoCl_3 \cdot 3NH_3$ exhibits facial-meridional isomerism. $[Co(NH_3)_4Cl_2]Cl$ exhibits cis-trans geometrical isomerism.



P.6.21 Which type of isomerisms are possible with the molecular formula $Co(NO_2)_3 \cdot 2H_2NCH_2CH_2NH_2$.
Solution Linkage, geometrical and optical isomerisms are possible.

Due to the presence of ambidentate ligand, NO_2 , it exhibits linkage isomerism. $[Co(en)_2(NO_2)_2]NO_2$ can exhibit geometrical isomerism and its cis isomer is optically active.

EXERCISE - 6.1.4

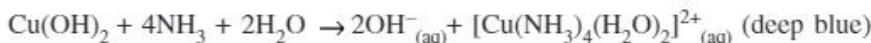
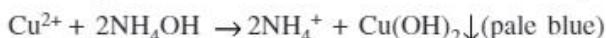
- Explain structural isomerism with examples.
- Explain geometrical isomerism in complexes with coordination number 4 and 6 with examples.
- Explain the optical isomerism in octahedral complexes.
- Define the following and give examples for Enantiomers and Diastereomers
- What kind of isomerism is shown by the pairs of following complex compounds?
 - $[Pt(H_2O)_4Cl_2]Cl_2 \cdot 2H_2O$ and $[Pt(H_2O)_5Cl]Cl_3 \cdot H_2O$,
 - $[Cu(NH_3)_4][Ni(CN)_4]$ and $[Ni(NH_3)_4][Cu(CN)_4]$.

APPLICATIONS OF COMPLEXES

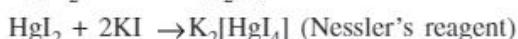
The coordination compounds are widely present in the mineral, plant and animal worlds. They play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below.

6.5.1**Qualitative and quantitative analysis**

Cupric salt gives pale blue precipitate with aqueous ammonia solution. It dissolves in excess of ammonia solution due to the formation of deep blue water soluble complex. This is the identification test for cupric ion.

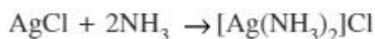


Mercuric chloride (HgCl_2) gives a scarlet red precipitate of mercuric iodide with small amount of KI. On adding excess of KI, the precipitate formed again dissolves forming a complex, $\text{K}_2[\text{HgI}_4]$ which is a colourless substance. Solution of this complex taken in excess of caustic potash solution is known as Nessler's reagent. The reagent is used to detect ammonia and hence ammonium salts.



The most common complexes are simple hydrates. All the transition metals form hydrated ions. These simple ions have characteristic colours in aqueous solutions. For example, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is pale green and $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ is blue.

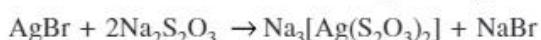
In the Lassaigne's test for nitrogen, Prussian blue coloured compound formed ferric ferrocyanide, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ is a complex compound. Silver chloride white precipitate is soluble in excess of ammonia due to the formation of the complex.



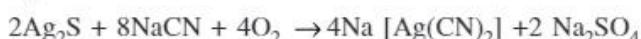
Hardness of water is estimated by simple titration with edta. The Ca^{2+} and Mg^{2+} ions form stable complexes with edta. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.

6.5.2**Photography**

In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex, $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$

**6.5.3****Metallurgy**

Silver is found in the free state and also as silver sulphide. Native gold is also known. Both silver and gold are extracted from the mineral with aqueous sodium or potassium cyanide as a complex $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$. The silver and gold metals present in solutions are displaced from the complex in the solution by adding zinc.



Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$, than from a solution of simple metal ions.

Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. Impure nickel is converted to $\text{Ni}(\text{CO})_4$, which is decomposed to yield pure nickel in Mond's process.

6.5.4**Medicine**

There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in animal systems. Thus, excess of copper and iron are removed by using the chelating ligands D-penicillamine and desferrioxime B, via the formation of coordination compounds.

Ethylenediamine tetraacetate is used in the treatment of lead poisoning. A platinum complex cis $[\text{PtCl}_2(\text{NH}_3)_2]$ known as cis platin is used in cancer chemotherapy.

6.5.5**Catalysis and bio systems**

Coordination compounds act as catalysts in different reactions. Wilkinson catalyst, $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, is used in hydrogenation of alkenes.

The green pigment responsible for photosynthesis, chlorophyll, is a coordination compound of Mg^{2+} . It is called magnesium phorphyrine. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of Fe^{2+} . Vitamin B_{12} , cyano-cobalamin, is a coordination compound of Co^{3+} . Some enzymes like, carboxypeptidase A and carbonic anhydrase are also coordinated metal ions.



P.6.22 How is the theory of complexes used to separate Fe_2O_3 and Al_2O_3 ?

Solution Al_2O_3 is separated from Fe_2O_3 using aqueous caustic soda. Al_2O_3 acts as acid to NaOH and forms a soluble complex. Fe_2O_3 acts as a base and is insoluble, which is separated by filtration.

**EXERCISE - 6.1.5**

1. Give an example of a complex that is formed in qualitative analysis.
2. How is silver halide used in photography? What is the complex formed?
3. How is concept of complexes used in metallurgy?
4. Mention a complex that is present in biological systems and in medicine.



1. Addition compounds which exist in solid state but loses their identity when dissolved in water are called double salts. eg: carnalite, potash alum, Mohr's salt, etc.
2. Addition compounds which retain their identity when dissolved in water are called complex compounds. eg: $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, etc.
3. In complex compounds, ligand is electron pair donor and central metal ion is electron pair acceptor.
4. As per latest IUPAC rules of naming complex compounds, ligands are to be written in their alphabetical order irrespective of their charge.
5. Primary valences are ionisable but secondary valences are non ionisable.

CHEMISTRY IIC

6. EAN of metal in the complex is the sum of electrons in metal ion and twice the coordination number.
7. According to Sidgwick, if the effective atomic number (EAN) of central metal atom or ion is equal to the atomic number of nearest inert gas, then the complex is stable.
8. With the coordination number four, sp^3 hybridisation gives tetrahedral structure and dsp^2 hybridisation gives square planar structure.
9. Complexes with coordination number six are octahedral, with sp^3d^2 or d^2sp^3 hybridisation.
10. In $[NiCl_4]^{2-}$, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ hybridisation of Ni is sp^3 , sp^3 and dsp^2 respectively. The complexes are paramagnetic, diamagnetic and diamagnetic respectively.
11. Complexes with d^2sp^3 hybridization are called inner orbital and with sp^3d^2 hybridisation are outer orbital complexes.
12. CO, CN^- , NO_2^- , en and NH_3 are examples for strong field ligands. F^- , Cl^- , Br^- , I^- and H_2O are examples for weak field ligands.
13. According to VBT, metal ligand bond is dative but according to CFT, metal ligand bond is ionic.
14. For the same metal, same ligands and metal-ligand distance, $\Delta_t = (4/9)\Delta_o$.
15. In metal carbonyls, the metal–carbon bond possesses both σ and π character.
16. Ionisation isomerism is possible in the complexes, in which the counter ion is capable of acting as ligand. Complex having at least one ambidentate ligand can exhibit linkage isomerism.
17. Square planar complex with the general formula $[MA_2X_2]$, $[MA_2XY]$ and $[MABXY]$ can exhibit geometrical isomerism.
18. Octahedral complexes of $[MA_4BX_2]$ and $[(M)(AA)_2X_2]$ type exhibit cis-trans isomerism.
19. Octahedral asymmetric complexes of bidentate ligands exhibit optical isomerism.

EXERCISE - 6.2

1. Write the central metal ion or atom, ligands, counter ion, complex ion and the coordination number in the complexes: $K_3[Cr(ox)_3]$; $Na_3[Ag(S_2O_3)_2]$; $H_2[PtCl_6]$ and $[Ni(gly)_2]$
2. Write the IUPAC names of Lithium aluminium hydride, Cryolite, Prussian blue and Brown ring.
3. Calculate the number of moles of ions given by one mole each of Potassium hexacyanoferrate(III), Hexaammineplatinum(IV) sulphate and Iron(III) hexacyanoferrate(II)
4. If $CoCl_3 \cdot xNH_3$ is neutral complex, what is the value of x? Why? (Ans : 3)
5. Calculate the EAN of central metal in the following complexes:
 - a) $[Co(NH_3)_6]^{3+}$, b) $[Cr(ox)_3]^{3-}$, c) $[Pd(NH_3)_6]^{4+}$ and d) $[Pt(NH_3)_2Cl_2]$.

6. A solution containing 1.332 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is passed through a cation exchange. The chloride ions in solution was precipitated with excess AgNO_3 to give 1.43 g of residue. How many water molecules are in the coordination sphere ? (Ans : 5)
7. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is paramagnetic and square planar complex. Justify.
8. Ferricyanide is paramagnetic, but ferrocyanide is diamagnetic. Explain.
9. One mole of each $\text{PdCl}_2 \cdot 4\text{NH}_3$, $\text{PtCl}_2 \cdot 2\text{NH}_3$, $\text{PtCl}_4 \cdot 2\text{HCl}$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$ gave 2, 0, 0 and 1 mole of AgCl , respectively when excess of AgNO_3 solution is added. Assign the secondary valences to the metals in these complexes. (Ans: 4, 4, 6 and 6)
10. What is the volume of 0.1M AgNO_3 required to precipitate Cl^- in 100mL of 0.2M $\text{CoCl}_3 \cdot 5\text{NH}_3$. (Ans : 400mL)
11. Ruby is alumina containing 1% chromic salt. Discuss the type of complex involved in the colour. (Ans : Octahedral complex with d^3 configuration of Cr^{3+})
12. The complex, $\text{Cr}(\text{CO})_x$ has EAN value 36. What is x? (Ans : 6)
13. $[\text{Al}(\text{NH}_3)_6]^{3+}$ does not exist in aqueous solution. Why?
14. How many unpaired electrons in the square planar $[\text{Pt}(\text{CN})_4]^{2-}$ ion? (Ans : zero)
15. $[\text{Cu}(\text{CN})_4]^{2-}$ is a colourless complex. Explain.
16. Deduce the structures of $\text{Ni}(\text{CN})_4^{2-}$ and NiCl_4^{2-} . Write their magnetic moments? (Ans : 0; 2.83 BM)
17. CoF_6^{3-} is an example of high spin complex. Why?
18. Calculate crystal field stabilization energy for $[\text{Fe}(\text{CN})_6]^{3-}$. (Ans : $2.0\Delta_o$)
19. Calculate the spin only magnetic moment of $\text{Hg}^{2+} [\text{Co}(\text{SCN})_4]^{2-}$. (Ans : $\sqrt{15}$ BM)
20. $\text{Fe}^{3+} \xrightarrow{\text{SCN}^- \text{ excess}} \text{A(blood red)} \xrightarrow{\text{F}^- \text{ excess}} \text{B(colourless)}$. Write the IUPAC name of A and B. Calculate the spin only magnetic moment of B. (Ans : 5.92BM)
21. One gram of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ was passed through cationic exchanger and the HCl produced is diluted to 1 L. Find the molarity of acid. (Ans : 0.0112 M)
22. Square planar complexes may exhibit geometrical isomerism, but not tetrahedral complexes. Why?
23. Wave lengths of the light absorbed by $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$ are respectively λ_1 and λ_2 . What is the relation between λ_1 and λ_2 . (Ans : $\lambda_1 > \lambda_2$)
24. How are the isomers $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ distinguished?
25. Which types of isomerism are possible with the molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.
26. Report the number of geometrical isomers and enantiomeric pairs of the complex $[\text{PtCl}_2(\text{NH}_3)_2(\text{Py})_2]^{2+}$. (Ans : 6 and 1)
27. In carbon monoxide carbon, oxygen bond length is 1.128A° . What is the carbon, oxygen bond length in $[\text{Fe}(\text{CO})_5]$? Why? (Ans : 1.15A°)

