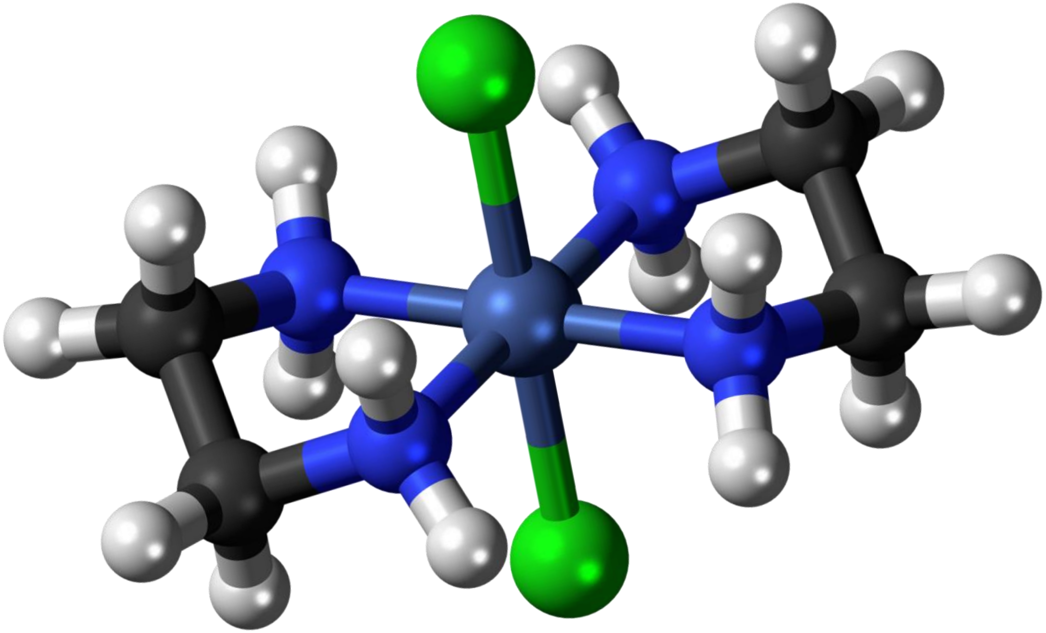
Fundamentals of Chemistry-I

Unit-2 Coordination chemistry



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Objectives

To understand the basic concepts related to coordination compounds through the oxidation number, ligands, chelates, stability of complexes and applications through the theories of coordination complexes

Outcome

At the end of the course, the student has acquired knowledge on

- Coordiantion compounds and its properties
- Characteristics of coordination compounds
- Metal complexes
- Various theories of coordination.

Prerequisites:

Electronic configuration

Valency of elements

Octet rule

Coordination compound

- Complex compounds is a special class of compounds in which the metal atoms (or) ions are bound to a number of anions (or) neutral molecules.
- In modern terminology, these compounds are called coordination compounds.
- Coordination compounds (or) complex compounds are a type of addition compounds.

Coordination compounds

Complex compounds is the study of a class of compounds formed by metals.

For example, when an excess of aqueous potassium cyanide is added to aqueous ferrous sulphate, a yellow solution is formed, this reaction is denoted by the equation

$$Fe^{2+} + 6CN^{-} \longrightarrow [Fe(CN)_6]^{4-}$$

- The product $[Fe(CN)_6]^{4-}$ is called *a metal complex ion*, it can isolated as its potassium Salt $K_4[Fe(CN)_6]$. This product is called a coordination compounds.
- The formation of a coordination compound form a metal is called *complexation.*
- The part $[Fe(CN)_6]^{4-}$ in $K_4[Fe(CN)_6]$ is called the *complex species or complex entity.*
- The formula of the complex species is written within bracket [ ].

Characteristics of Coordination compounds

1. A coordination compound is a compound of a metal with a certain number of species called ligands.
   In $[Fe(CN)_6]^{4-}$, the six CN^- groups are called the *ligands.*
   Ligands bind metals.

   Many of the ligands are anions-Example CN^-, Cl^-, SCN^-, etc.
   Neutral molecules -Example H_2O, CO, NH_3, etc.

   Normally positive ion cannot function as a ligand, as the availability of an electron pair on the ligand for binding with the positive metal is the prime requirement for complex formation.

A ligand is nucleophilic.

Characteristics of Coordination compounds

2. Complex species are of different types: cationic, neutral and anionic.

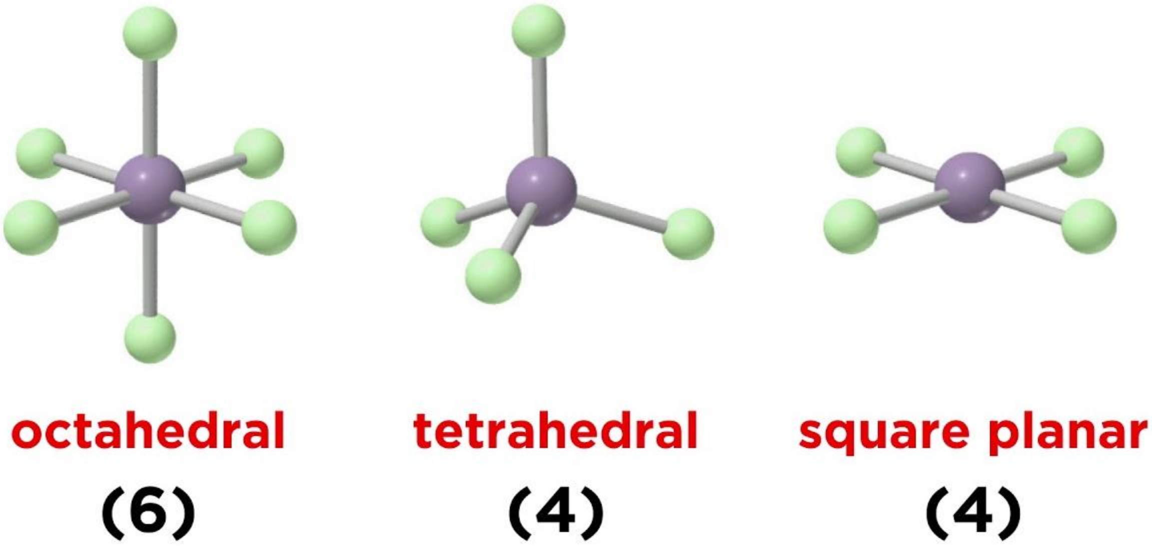
$[Pt\ (NH_3)_4]^{2+}$	**cationic**
$[Pt\ (NH_3)_2\ Cl_2\ ]$	**neutral**
$[Pt\ (Cl)_4]^{2-}$	**anionic**

3. Complexation of a metal ion usually ***increases stability*** of the metallic species, thus the complex of a metal ion is more stable than the metal ion itself. However, *different complexes of a metal have different stability.*

4. Complex formation is often accompanied by ***striking changes in colour***. For example, the complexation of the light yellow, aqueous Fe (III) with SCN^- produces a blood-red color.

Characteristics of Coordination compounds

5. The molecules (or ions) of complexes have characteristic shapes such as *tetrahedral, square–planer, octahedral, etc* depending on the number of ligands bonded to the central metal.



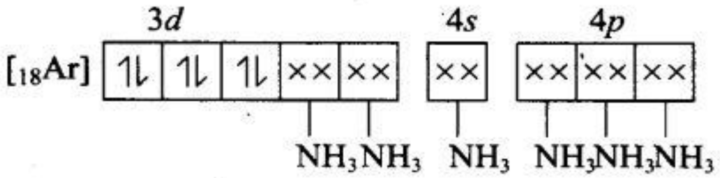
Characteristics of Coordination compounds

6. A complex may be **diamagnetic or paramagnetic** depending on the type of bonding in it.

Many transition metal complexes have **unpaired** electrons and hence are **paramagnetic**.

Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain **no unpaired electrons are diamagnetic.** Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

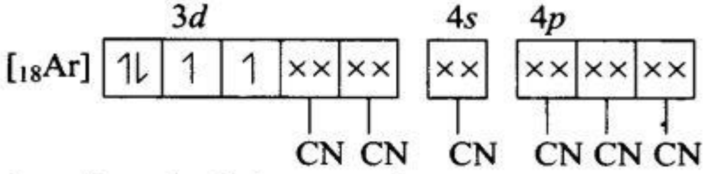
(a) Molecular orbital electronic configuration of Co^{3+} in $[Co(NH_3)_6]^{3+}$ is



Number of unpaired electron = 0

Magnetic property = Diamagnetic

(b) Molecular orbital electronic configuration of Mn^{3+} in $[Mn(CN)_6]^{3-}$



Number of unpaired electron = 2

Magnetic property = Paramagnetic

Characteristics of Coordination compounds

7. A metal complex differs from an ordinary salt in some respects. When a simple salt such as $FeSO_4$ is dissolved in water, it produces its constituent simple ions, Fe^{2+} and SO_4^{2-}, but when a complex compound is dissolved in a solvent, it produces complex ions. For example, the complex $K_4[Fe(CN)_6]$ produces $[Fe(CN)_6]^{4-}$ on its dissolution in water.

The ligand (CN-) attached to the central metal ion are not easily ionized away from the metal ion.

The species $[Fe(CN)_6]^{4-,}$ though containing a metal, migrates to the positive electrode (anode) when its solution is electrolysed.

Characteristics of Coordination compounds

8. Some of the metal complexes are soluble in water whereas the others are insoluble.

For example, $[Ag(NH_3)_2]+$ is soluble whereas the complex of Ni(II) with dimethylglyoxime is insoluble in water.

Some complexes are soluble in organic solvents.

For example bis(acetylacetonato) copper (II) is insoluble in water but soluble in organic solvents.

Double salts

When ***two or more simple salt solutions are mixed*** in requisite proposition and allowed to crystaline together, addition or molecular compounds are formed. These compounds are either double salt or coordination compound.

Double salt or lattice compound exist only in the crystalline state and ionise into water or any other solvent.

Example

Carnallite – $KCl.MgCl_2.6H_2O$

Potash alum - $K_2SO_4.Al_2(SO_4)_3.24H_2O$

these compound are stable in solid state and decompose or ionise in water or any solvent

complex salts

A complex salt is a salt which contains a complex ion or complex neutral molecule in which there is a central metal ion surrounded by a number of neutral molecules or negative ions.

Examples:

potassium ferrocyanide ($K4\ [Fe(CN)_6]$),

potassium argento cyanide ($K\ [Ag(CN)_2]$) ,

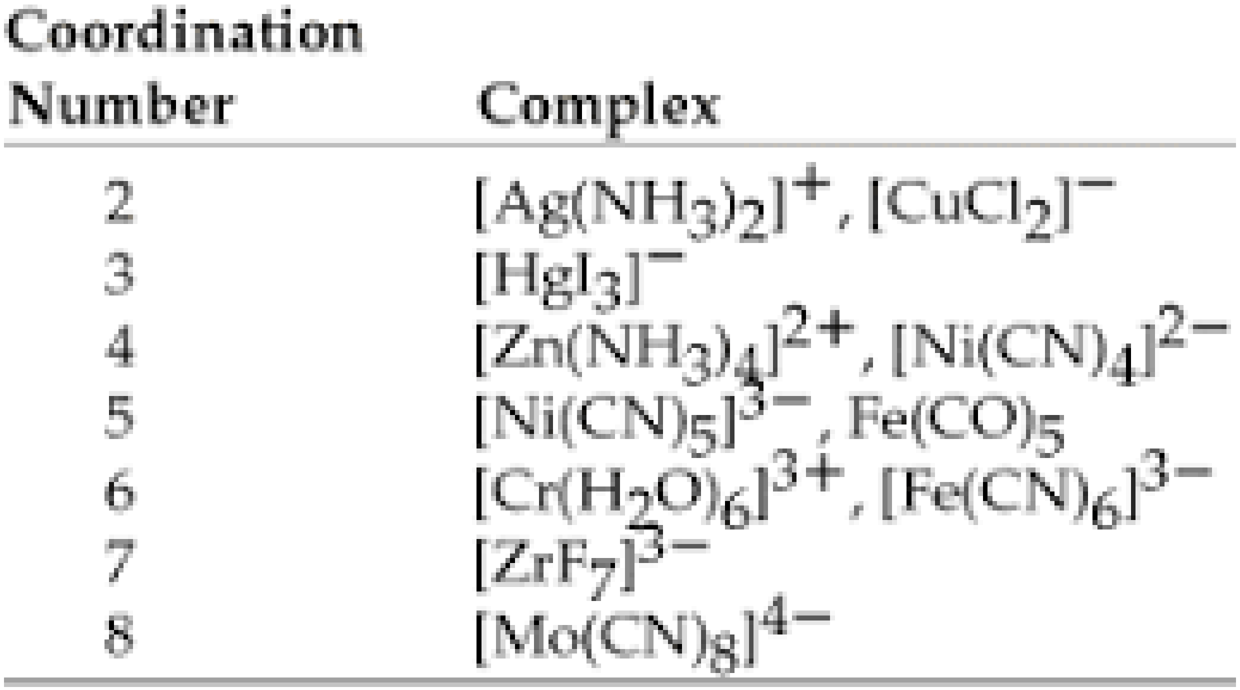
tetra amino cupric sulphate ($[Cu(NH_3)_4]SO_4$) etc

DOUBLE SALT VERSUS COMPLEX SALT

DOUBLE SALT	COMPLEX SALT
A double salt is a compound prepared by the combination of two different salt compounds	A complex salt is a compound composed of a central metal atom having coordination bonds with ligands around it
Completely dissociate into its ions in water	Do not completely dissociate into its ions in water
Give simple ions when added to water	Do not give simple ions
Can easily be analyzed by determining the ions present in the aqueous solution	Cannot be easily analyzed by determining the ions in the aqueous solution

Coordination number

The total number of ligands attached to the central metal in a complex is called the Coordination number.



Coordination Number	Complex
2	$[Ag(NH_3)_2]^+$, $[CuCl_2]^-$
3	$[HgI_3]^-$
4	$[Zn(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$
5	$[Ni(CN)_5]^{3-}$, $Fe(CO)_5$
6	$[Cr(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
7	$[ZrF_7]^{3-}$
8	$[Mo(CN)_8]^{4-}$

Oxidation number

This number denotes the charge, the central metal atom would have if all the ligands in the complex were removed along with their electron pairs that were shared with the central atom.

It is represented by a Roman numeral

$$\left[\mathrm{Co}\ (\mathrm{NH_3})_4\ (\mathrm{H_2O})\ \mathrm{Cl}\right]^{2+}$$

$$x + [4 \times (0)] + [1 \times 0] + (-1) = +2$$

$$\text{i.e.}\quad x - 1 = +2\ ;\qquad x = +3$$

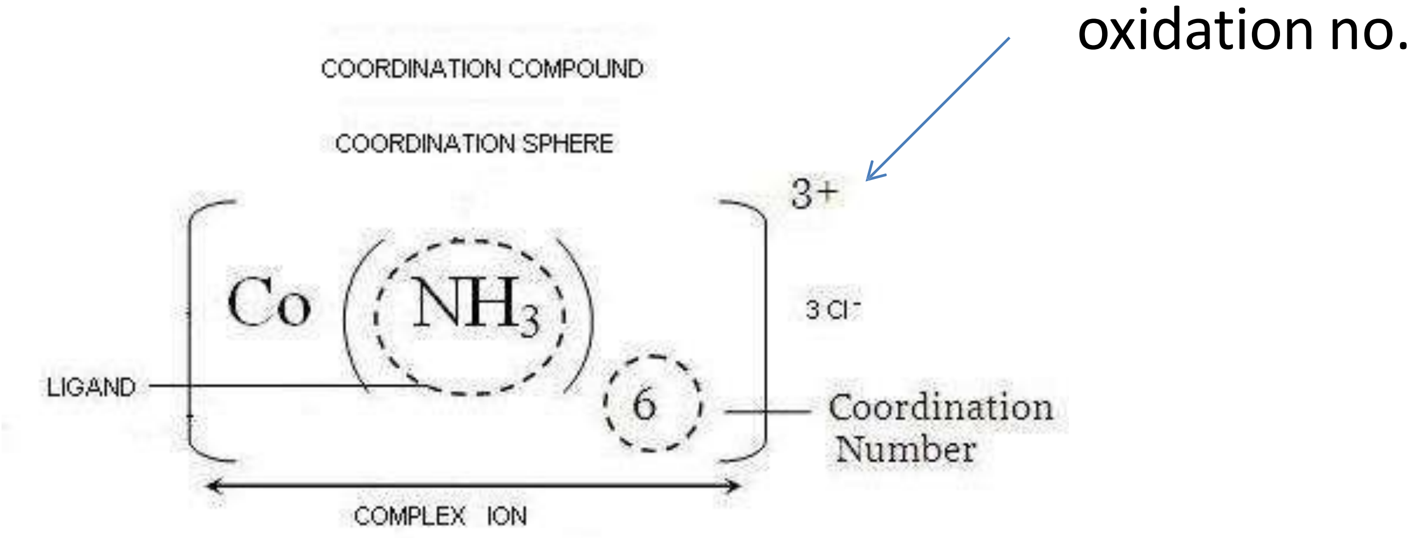
Coordination sphere

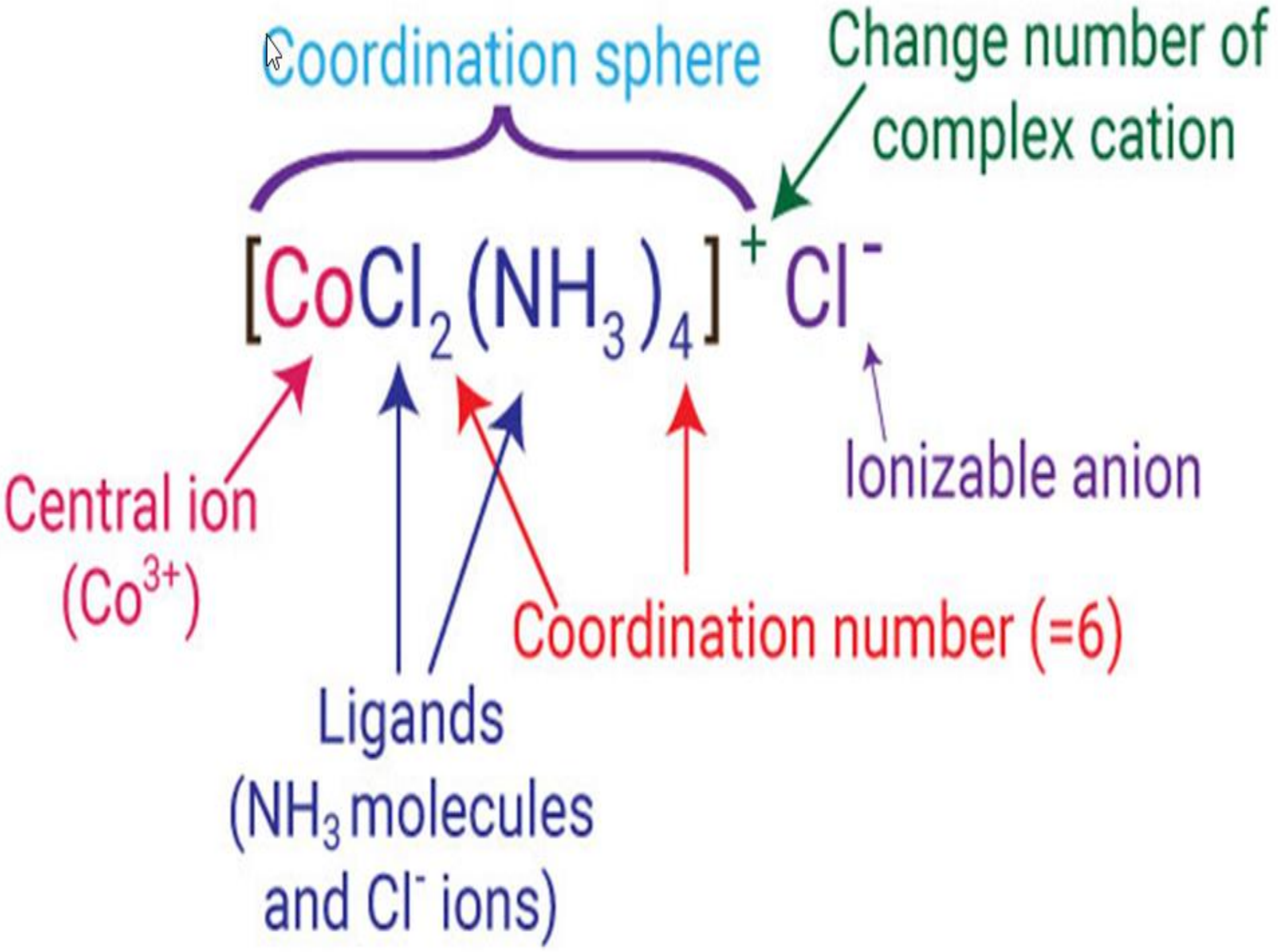
The non-ionizable part of a complex compound which consists of central transition metal ion surrounded by neighbouring atoms or groups enclosed in square bracket.

The coordination centre, the ligands attached to the coordination centre, and the net charge of the chemical compound as a whole, form the **coordination sphere** when written together.

This coordination sphere is usually accompanied by a counter ion (the ionizable groups that attach to charged coordination complexes).

Example: $[Co(NH_3)_6]C/3$ – coordination sphere




Coordination sphere
Change number of complex cation
$[CoCl_2(NH_3)_4]^+ Cl^-$
Central ion (Co^{3+})
Ligands (NH_3 molecules and Cl^- ions)
Coordination number (=6)
Ionizable anion

Types of Ligands

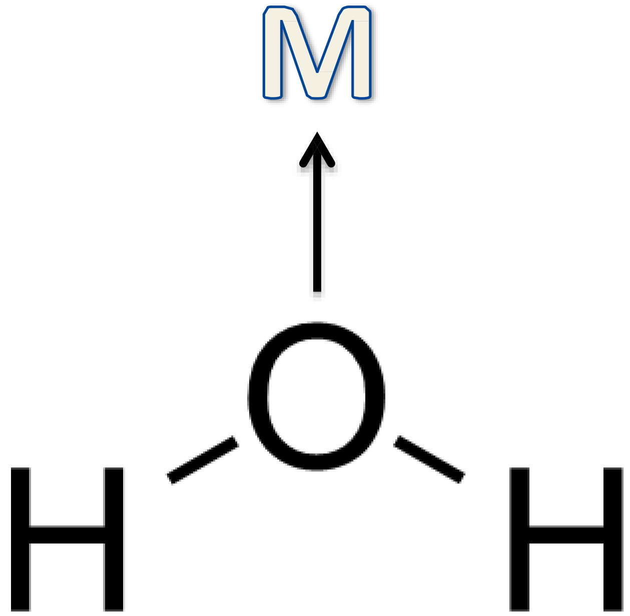
1. Mono or Unidentate ligand
2. Poly or multidentate ligand
3. A bridging ligand
4. An ambidentate ligand
5. A flexidentate ligand

Types of Ligands

1. Mono or Unidentate ligands

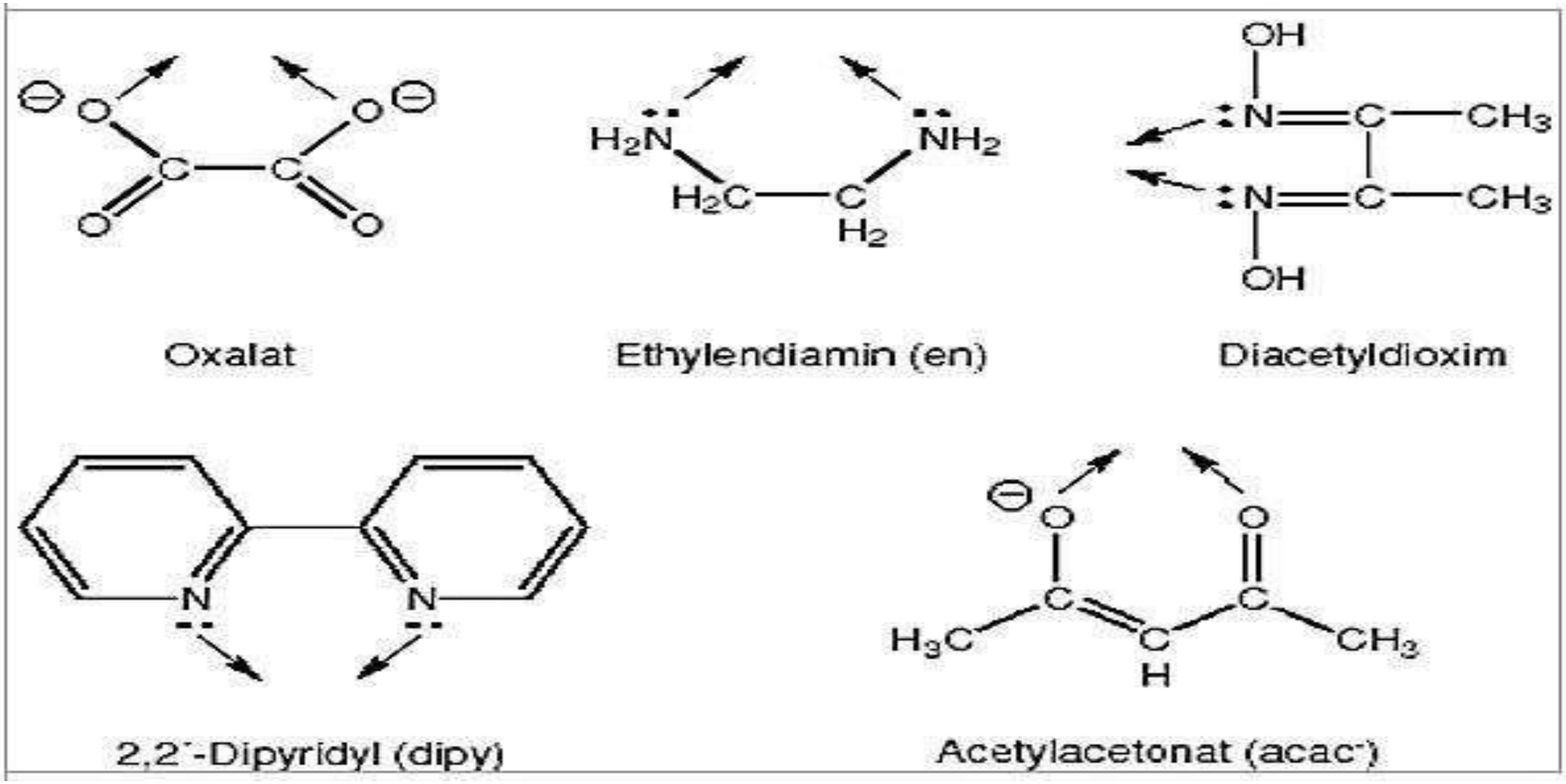
one donor atom or one point of attachment and can coordinate with the metal ion at only one site in a complex.

Eg. Cl^-, NH_3,H_2O etc.



2. Poly or mutlidentate ligand

Two or more donor atom or points of attachements. Polydentate ligands are further classified as bi, tri,…..hexa dentate.



Oxalat

Ethylendiamin (en)

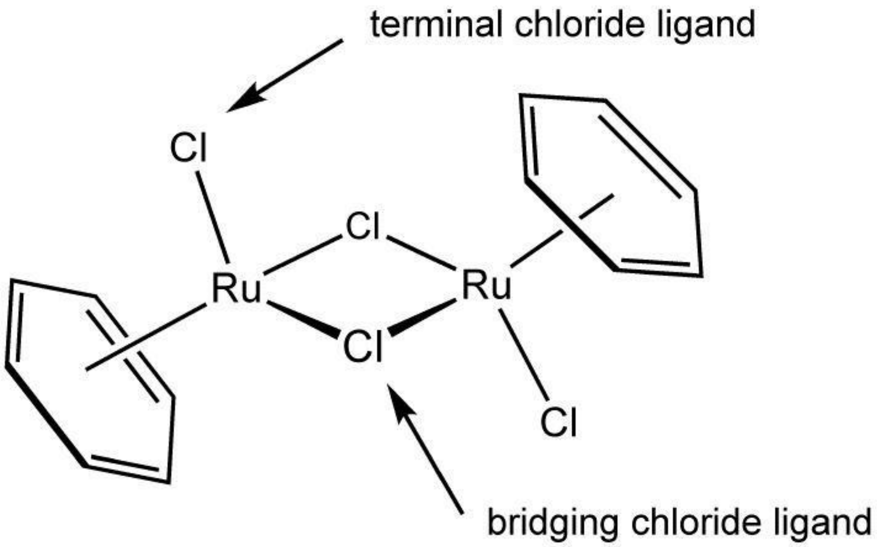
Diacetyldioxim

2,2´-Dipyridyl (dipy)

Acetylacetonat (acac⁻)

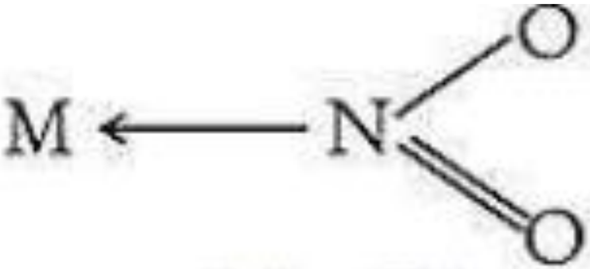
3. A bridging ligand

A bridging ligand is a ligand which simultaneously binds two metals, it forms a bridge between the two metals, acting as a ligand to both metals.

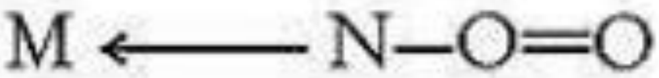


4. An ambidentate ligand

If a ligand has 2 or more donar atoms, complex is formed only 1 donor atom is attached to the metal.



nitrito-N
(In yellow complex)
I

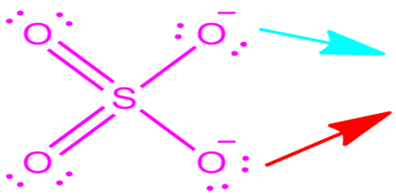


nitrito-O
(In red complex)
II

5. A flexidentate ligand

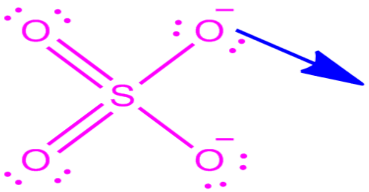
A flexidentate ligand is a polydentate ligand which can bind to a metal with different numbers of its ligand sites.

Sulfate ion



Behave as bidentate ligand .

Sulfate ion



Behave as mono dentate ligand .

$[\overset{III}{Co}(NH_3)_4CO_3]Br$

Carbonate ion behave as bidentate ligand .

$[\overset{III}{Co}(NH_3)_5CO_3]Br$

Carbonate ion behave as monodentate ligand

Nomenclature of metal complexes

- The cation is named before the anion
- When naming a complex:
  - Ligands are named first
    - alphabetical order
  - Metal atom/ion is named last
    - oxidation state given in Roman numerals follows in parentheses
  - Use no spaces in complex name

Nomenclature of metal complexes

- The names of anionic ligands end with the suffix -o
  - -ide suffix changed to -o
  - -ite suffix changed to -ito
  - -ate suffix changed to -ato

Ligand	Name
bromide, Br^-	bromo
chloride, Cl^-	chloro
cyanide, CN^-	cyano
hydroxide, OH^-	hydroxo
oxide, O^{2-}	oxo
fluoride, F^-	fluoro

Ligand	Name
carbonate, CO_3^{2-}	carbonato
oxalate, $C_2O_4^{2-}$	oxalato
sulfate, SO_4^{2-}	sulfato
thiocyanate, SCN^-	thiocyanato
thiosulfate, $S_2O_3^{2-}$	thiosulfato
Sulfite, SO_3^{2-}	sulfito

Nomenclature of metal complexes

- Neutral ligands are referred to by the usual name for the molecule
  - Example
    - ethylenediamine
  - Exceptions
    - water, H_2O = aqua
    - ammonia, NH_3 = ammine
    - carbon monoxide, CO = carbonyl

Nomenclature of metal complexes

- Greek prefixes are used to indicate the number of each type of ligand when more than one is present in the complex
  - di-, 2; tri-, 3; tetra-, 4; penta-, 5; hexa-, 6
- If the ligand name already contains a Greek prefix, use alternate prefixes:
  - bis-, 2; tris-, 3; tetrakis-,4; pentakis-, 5; hexakis-, 6
  - The name of the ligand is placed in parentheses

Nomenclature of metal complexes

- If a complex is an anion, its name ends with the -ate –appended to name of the metal

Transition Metal	Name if in Cationic Complex	Name if in Anionic Complex
Sc	Scandium	Scandate
Ti	titanium	titanate
V	vanadium	vanadate
Cr	chromium	chromate
Mn	manganese	manganate
Fe	iron	ferrate
Co	cobalt	cobaltate
Ni	nickel	nickelate
Cu	Copper	cuprate
Zn	Zinc	zincate

Nomenclature of metal complexes

$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) trichloride
$[Co(NH_3)_6]^{3+}$	hexaamminecobalt(3+)
$[CoCl(NH_3)_5]Cl_2$	pentaamminechlorocobalt(III) trichloride
$[CoCl(NH_3)_5]^{2+}$	pentaamminechlorocobalt(2+)
$[CoCl(NO_2)(NH_3)_4]Cl$	tetraamminechloronitritocobalt(III) chloride
$[CoCl(NO_2)(NH_3)_4]^+$	tetraamminechloronitritocobalt(1+)
$[PtCl(NH_2CH_3)(NH_3)_2]Cl$	bisamminechloromethylamineplatinum(II) chloride
$[PtCl(NH_2CH_3)(NH_3)_2]^+$	diamminechloromethylamineplatinum(+)
$[CuCl_2\{O{=}C(NH_2)_2\}_2]$	dichlorobis(urea)copper(II)
$K_2[PdCl_4]$	potassium tetrachloropalladate(II)
$K_2[OsCl_5N]$	potassium pentachloronitrodoosmate(VI)
$[Co(H_2O)_2(NH_3)_4]Cl$	tetraamminediaquacobalt(III) chloride

Sidgwick’s electronic theory

- ❑ Sidgwick’s in his theory used the Lewis concept of the covalent bond between two atoms in a molecule.

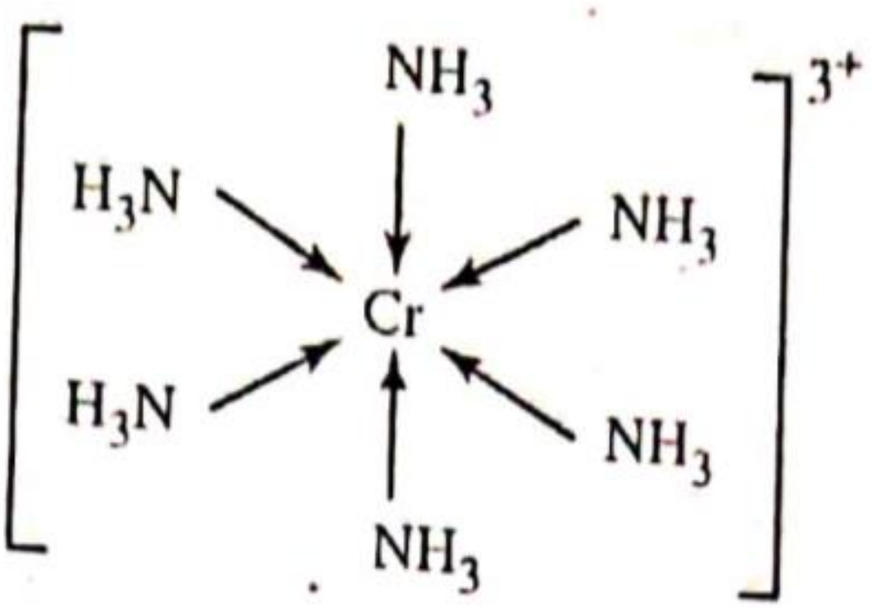
- ❑ He introduced a new concept of coordinate bond, also called *dative bond or semi-polar bond*.

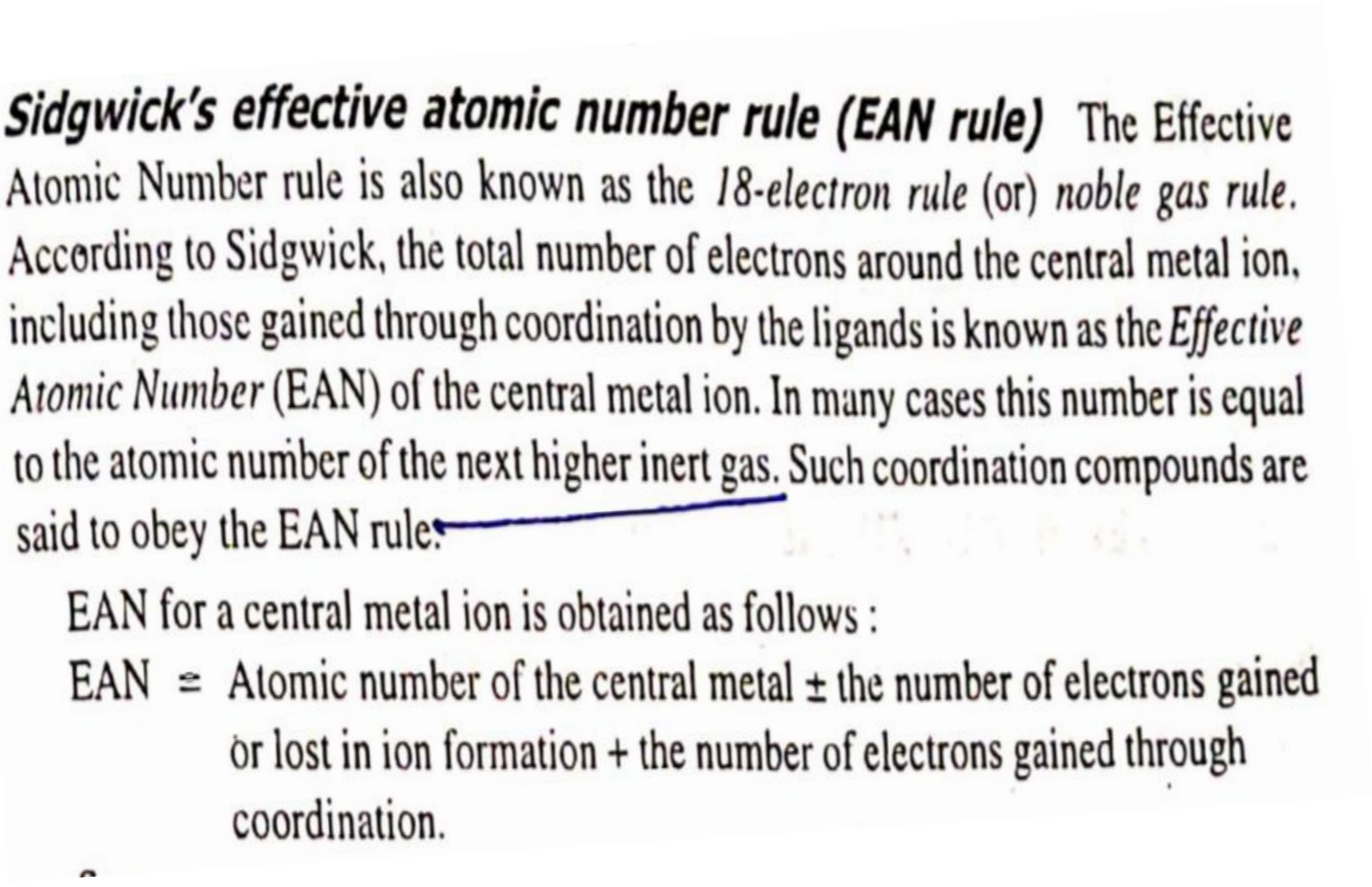
- ❑ According to him, the ligands donate electron pairs to the central metal ion to form coordination compounds. These ligands are known as the *donors* and the central metal ions are known as the *acceptors.*

- ❑ The bonds formed between the donors and acceptors are called *coordinate or dative or semipolar bonds*, which are not very different from a covalent bond.

- ☐ The coordinate bond formed is generally represented by an ***arrow*** staring from the donor pointing towards the acceptor as L-> M, where *M is the acceptor and L is the donor of electrons*.

For example, the complex ion,





Sidgwick's effective atomic number rule (EAN rule) The Effective Atomic Number rule is also known as the *18-electron rule* (or) *noble gas rule*. According to Sidgwick, the total number of electrons around the central metal ion, including those gained through coordination by the ligands is known as the *Effective Atomic Number* (EAN) of the central metal ion. In many cases this number is equal to the atomic number of the next higher inert gas. Such coordination compounds are said to obey the EAN rule.

EAN for a central metal ion is obtained as follows :

EAN = Atomic number of the central metal ± the number of electrons gained or lost in ion formation + the number of electrons gained through coordination.

1. K4[Fe(CN)$_6$]

Number of electrons in Fe^{2+} = 24

Number of electrons by Six CN = 2×6 = 12

Total number of electrons possessed by Fe^{2+} = 24 + 12

Therefore, the effective atomic number = 36.

2. [Co(NH$_3$)6]Cl$_3$

Number of electrons in Co^{3+} = 24

Number of electrons by Six NH_3 = 2×6 = 12

Total number of electrons possessed by Co^{3+} = 24 + 12

Therefore, the effective atomic number = 36.

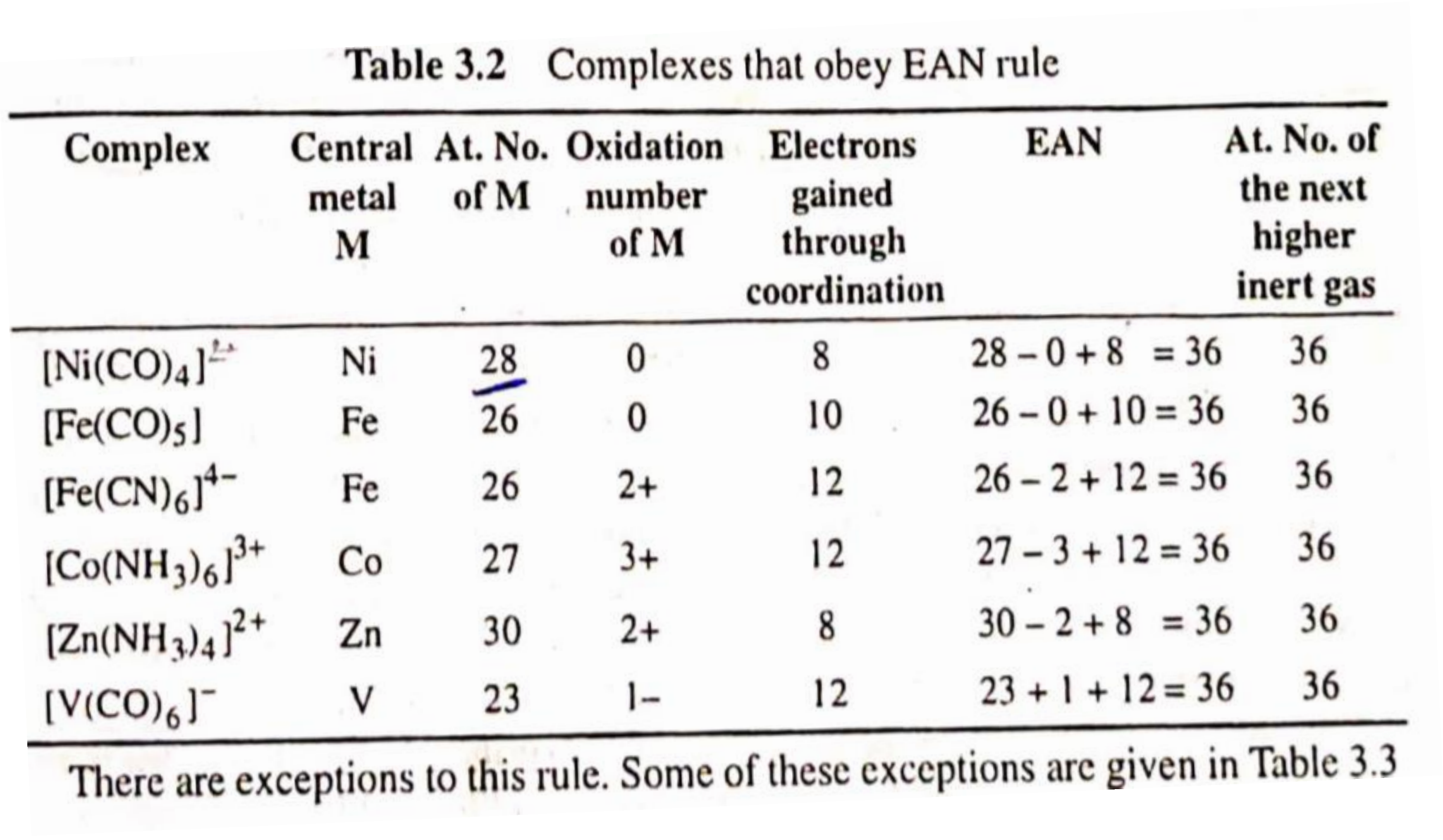


Table 3.2 Complexes that obey EAN rule

Complex	Central metal M	At. No. of M	Oxidation number of M	Electrons gained through coordination	EAN	At. No. of the next higher inert gas
$[Ni(CO)_4]$	Ni	28	0	8	$28 - 0 + 8 = 36$	36
$[Fe(CO)_5]$	Fe	26	0	10	$26 - 0 + 10 = 36$	36
$[Fe(CN)_6]^{4-}$	Fe	26	2+	12	$26 - 2 + 12 = 36$	36
$[Co(NH_3)_6]^{3+}$	Co	27	3+	12	$27 - 3 + 12 = 36$	36
$[Zn(NH_3)_4]^{2+}$	Zn	30	2+	8	$30 - 2 + 8 = 36$	36
$[V(CO)_6]^-$	V	23	1–	12	$23 + 1 + 12 = 36$	36

There are exceptions to this rule. Some of these exceptions are given in Table 3.3

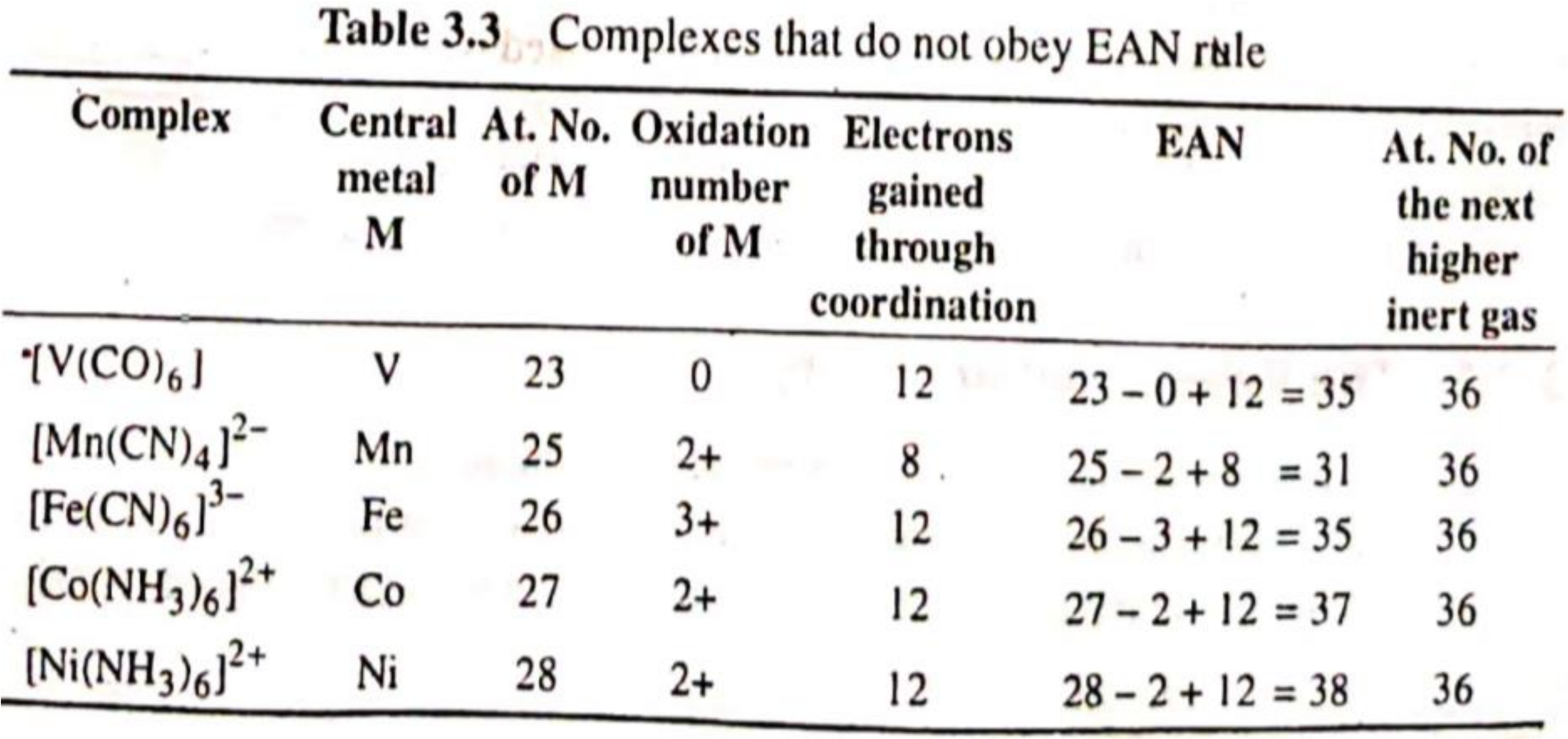


Table 3.3 Complexes that do not obey EAN rule

Complex	Central metal M	At. No. of M	Oxidation number of M	Electrons gained through coordination	EAN	At. No. of the next higher inert gas
$[V(CO)_6]$	V	23	0	12	23 – 0 + 12 = 35	36
$[Mn(CN)_4]^{2-}$	Mn	25	2+	8	25 – 2 + 8 = 31	36
$[Fe(CN)_6]^{3-}$	Fe	26	3+	12	26 – 3 + 12 = 35	36
$[Co(NH_3)_6]^{2+}$	Co	27	2+	12	27 – 2 + 12 = 37	36
$[Ni(NH_3)_6]^{2+}$	Ni	28	2+	12	28 – 2 + 12 = 38	36

Defects of Sidgwick's theory Sidgwick's electronic theory is also not free from defects. Some of the defects of this theory are listed below:

(1) The donation of electrons by the ligands to the central metal ion would cause an accumulation of unfavourable negative charge over the electropositive central metal. This will reduce the stability of the complex.

(2) The electron pair donated by H_2O, NH_3 etc. to the central metal ion is $2s^2$ pair of electrons. This $2s^2$ pair has no bonding characteristics. In order to make them useful for bonding purpose, these electrons should be promoted to higher energy level. This requires more energy than what is usually available in the bond formation.

(3) According to Sidgwick, coordination compounds must be covalent. But there are complexes which are predominantly ionic in nature. Hence, the forces acting between the central metal ion and the ligands may be regarded as essentially electrostatic.

Theories of Bonding in Coordination Compounds

There are mainly three theories which are used to describe the nature the nature of metal-ligand bonding in coordination compounds.

1. Valence Bond Theory (VBT) or Pauling's Theory of Complexes:
VBT was developed by Linus Pauling and Others in 1930.

This theory is primarily concerned with the shapes and magnetic behavior of metal complexes.

2. Crystal Field Theory (CFT):
CFT was proposed by Hans Bethe in 1929.

This theory is useful in describing metal-Ligand interaction and is especially helpful in explaining the visible absorption spectra of metal complexes.

3. Ligand Field Theory (LFT) or Molecular Orbital Theory (MOT):
Developed by J.H.Van Vleck in 1935.

Valence Bond Theory (VBT) or Pauling’s Theory of Complexes

VBT was the first theory used to explain the geometry and magnetic property of many to coordination compounds. The basic idea of the theory is that the formation of a complex is a reaction between a Lewis base (ligand; electron donor) and a Lewis acid (metal or metal ion; electron acceptor) with the formation of a coordinate-covalent bond (dative bond) between the ligand and the metal.

Postulates:

1. The central metal atom or ion provides number of vacant s,p & d orbitals equal to its coordination number to form coordinate bond with the ligand orbitals.

2. A covalent bond is formed by the head-on overlap of a vacant metal orbital and a filled ligand orbital:

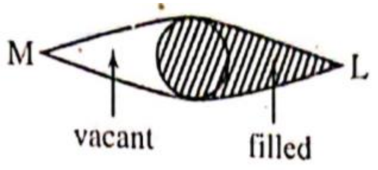


Fig. 3.4 M – L σ bond formation

*This head-on overlap leads to the formation of M-L, **sigma bond***

3. In addition to the sigma bond, there is the possibility of a pi bond formation due to the side-ways overlapping of a filled metal orbital with a suitable vacant ligand orbital.

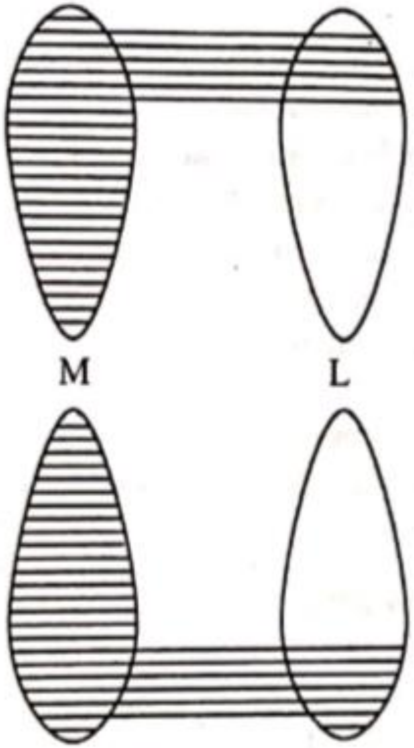


Fig. 3.5 M-L, π bond formation

4. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called hybridisation.

A hybridised orbital has better directional characteristics than an unhybridised one.

Numerous combination of s,p and d orbitals are possible for hybridization giving rise to different spatial geometries. But in practice only a few are encountered in metal complexes.

Table gives the coordination number, orbital hybridisation, spatial geometry and examples for some of the more important geometries.

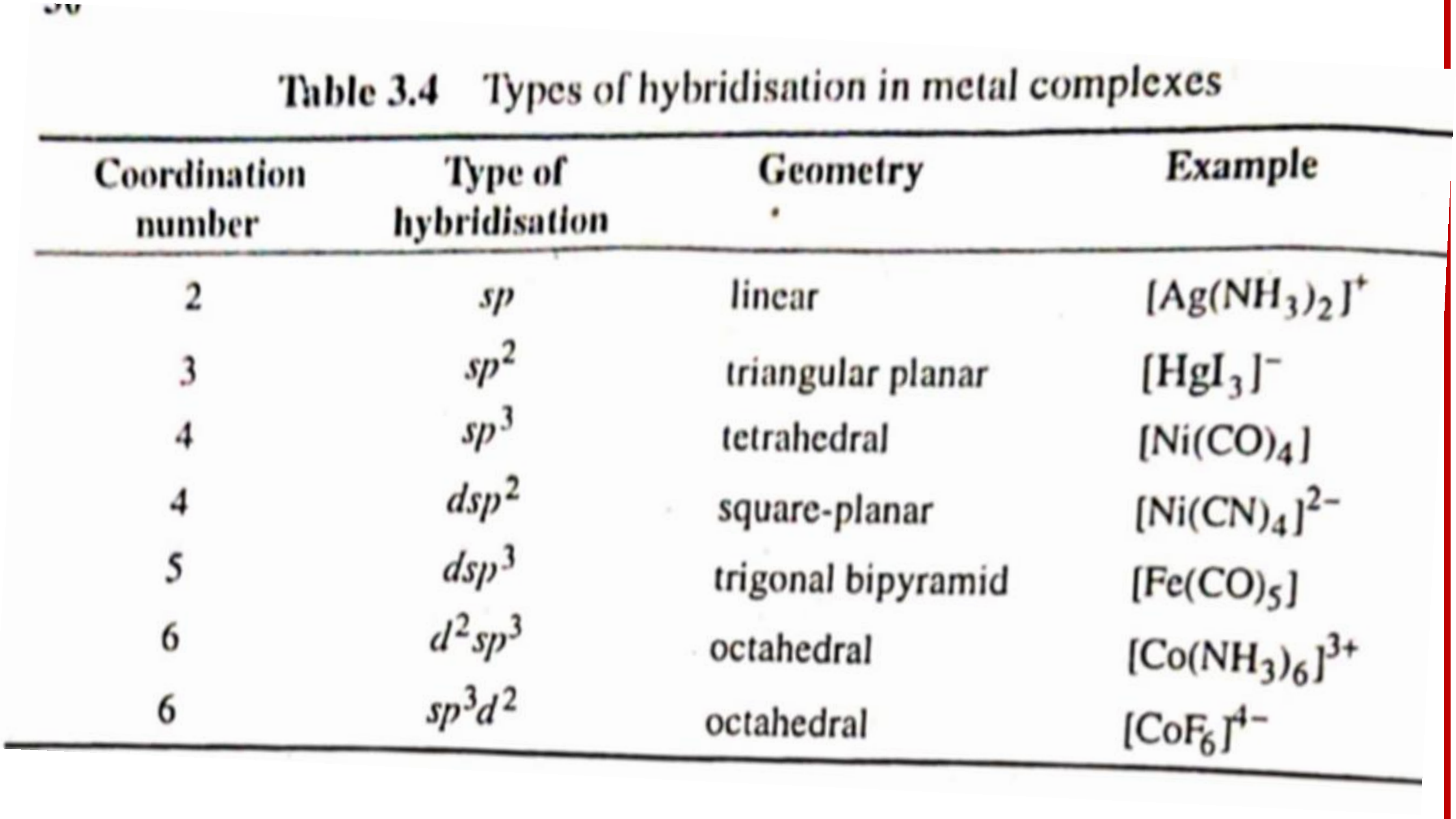
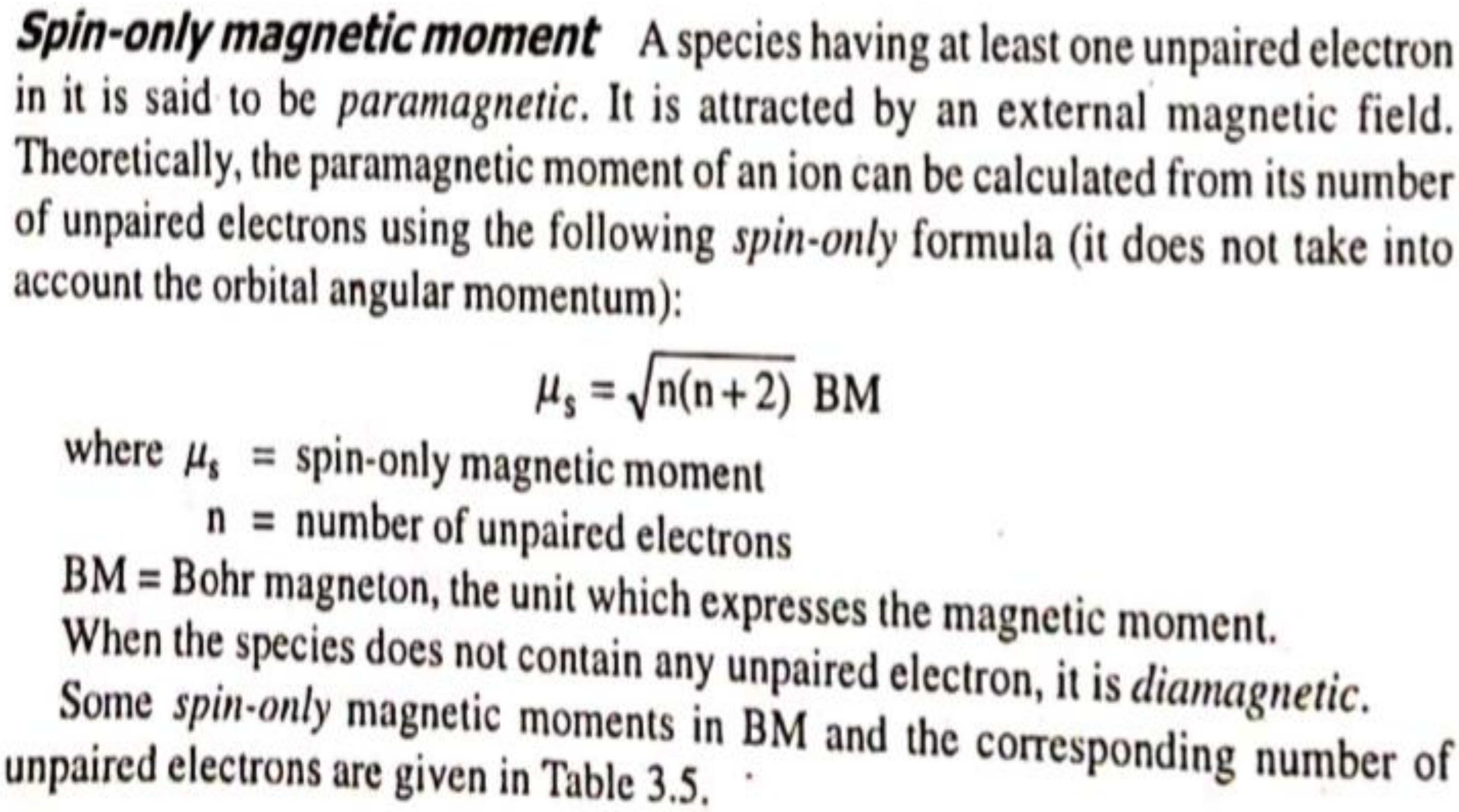


Table 3.4 Types of hybridisation in metal complexes

Coordination number	Type of hybridisation	Geometry	Example
2	*sp*	linear	$[Ag(NH_3)_2]^+$
3	*sp*^{2}	triangular planar	$[HgI_3]^-$
4	*sp*^{3}	tetrahedral	$[Ni(CO)_4]$
4	*dsp*^{2}	square-planar	$[Ni(CN)_4]^{2-}$
5	*dsp*^{3}	trigonal bipyramid	$[Fe(CO)_5]$
6	*d*^{2}*sp*^{3}	octahedral	$[Co(NH_3)_6]^{3+}$
6	*sp*^{3}*d*^{2}	octahedral	$[CoF_6]^{4-}$



Spin-only magnetic moment A species having at least one unpaired electron in it is said to be *paramagnetic*. It is attracted by an external magnetic field. Theoretically, the paramagnetic moment of an ion can be calculated from its number of unpaired electrons using the following *spin-only* formula (it does not take into account the orbital angular momentum):

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

where μ_s = spin-only magnetic moment
n = number of unpaired electrons

BM = Bohr magneton, the unit which expresses the magnetic moment.

When the species does not contain any unpaired electron, it is *diamagnetic*.

Some *spin-only* magnetic moments in BM and the corresponding number of unpaired electrons are given in Table 3.5.

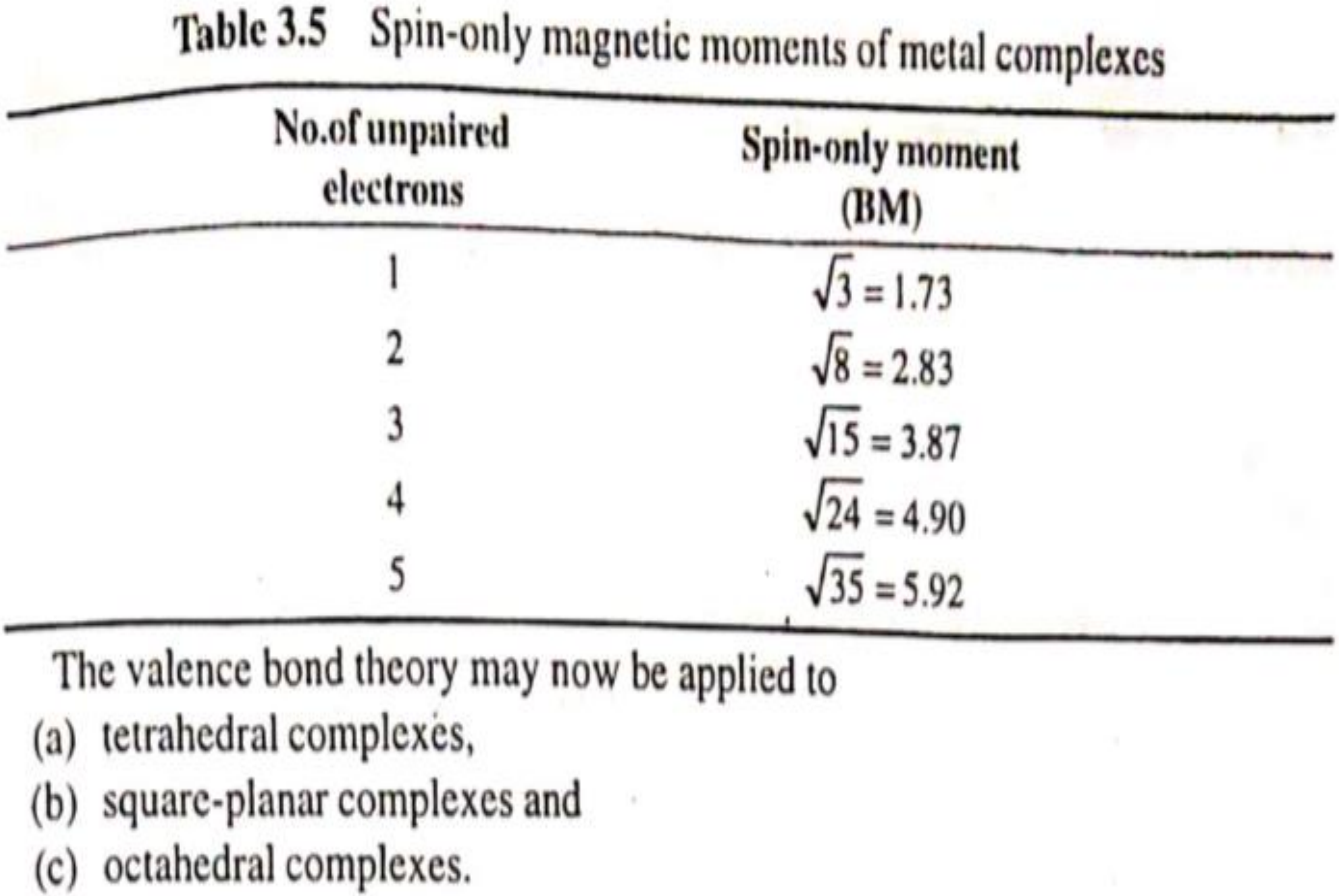


Table 3.5 Spin-only magnetic moments of metal complexes

No.of unpaired electrons	Spin-only moment (BM)
1	$\sqrt{3} = 1.73$
2	$\sqrt{8} = 2.83$
3	$\sqrt{15} = 3.87$
4	$\sqrt{24} = 4.90$
5	$\sqrt{35} = 5.92$

The valence bond theory may now be applied to

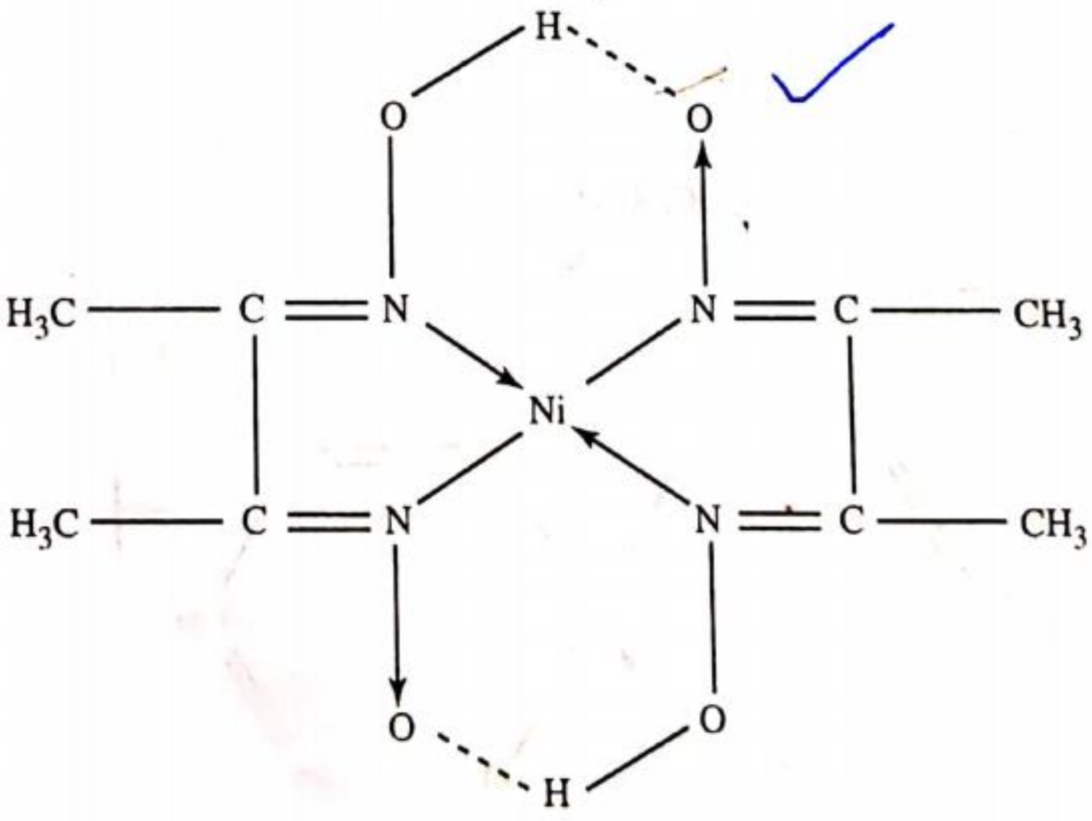
(a) tetrahedral complexes,
(b) square-planar complexes and
(c) octahedral complexes.

Chelates

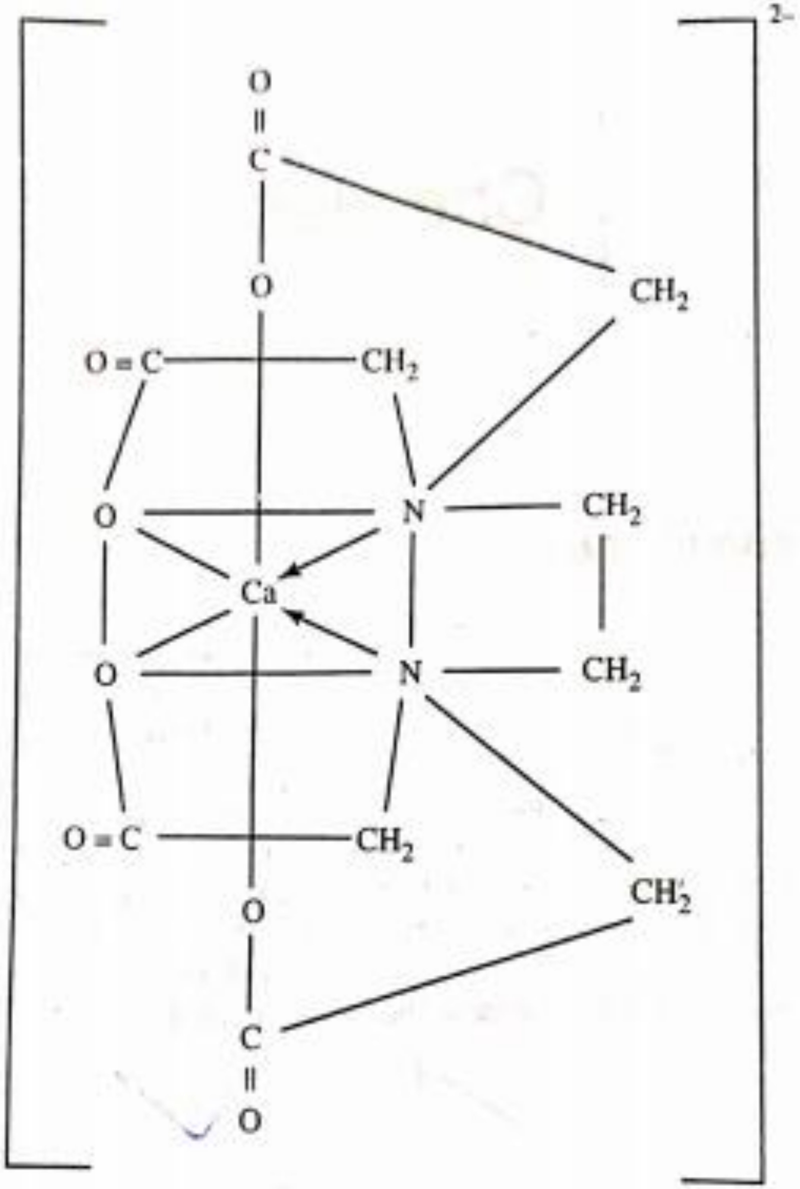
A ligand having more than one point of attachment to the central metal ion in a complex is called *a polydentate ligand*.
Examples of such polydentate ligands are
ethylenediamine (en),
diethylenetriamine (dien),
Dimethylglyoxime (DMG),
Ethylleneidaminetetraacetate (EDTA),
Acetylacetonate (acac), etc

These polydentate ligands coordinate through their points of attachment to the same central metal ion to form complexes with ring structures. Such ring-structured metal complexes with the metal forming a part of the ring system are called the ***chelates.***

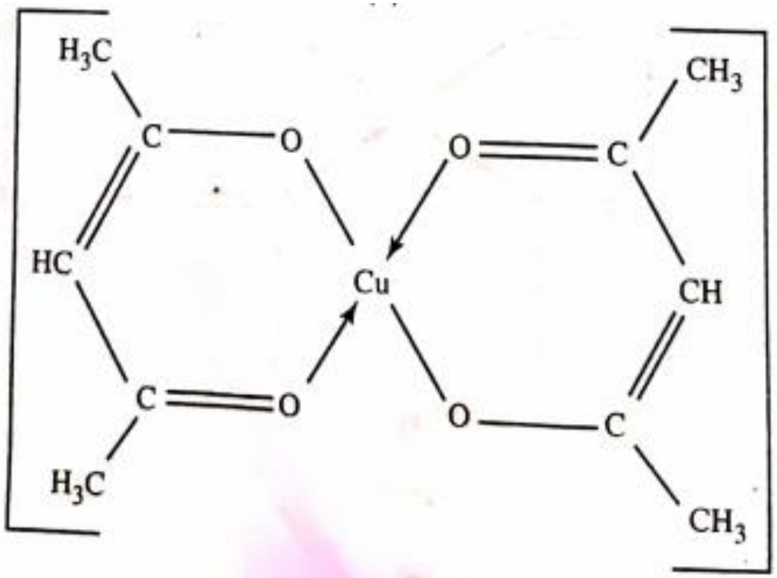
Some examples of metal chelates are



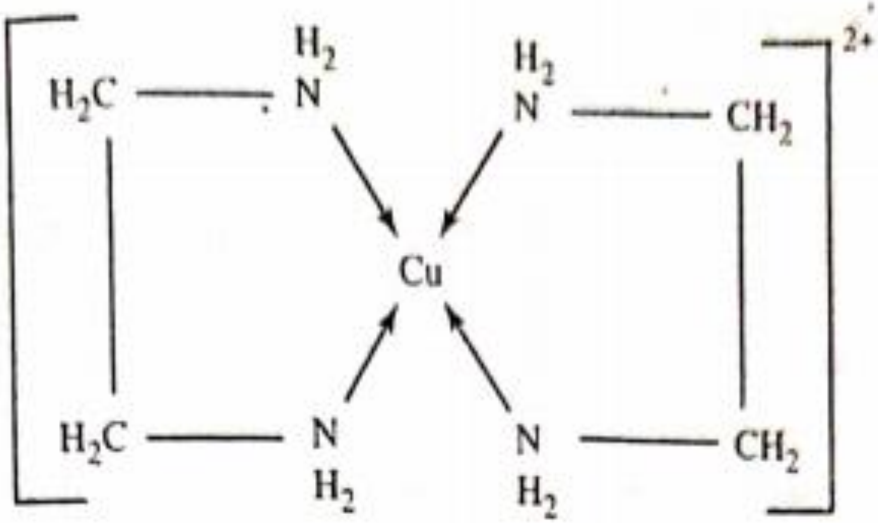
$[Ni(DMG)_2]$



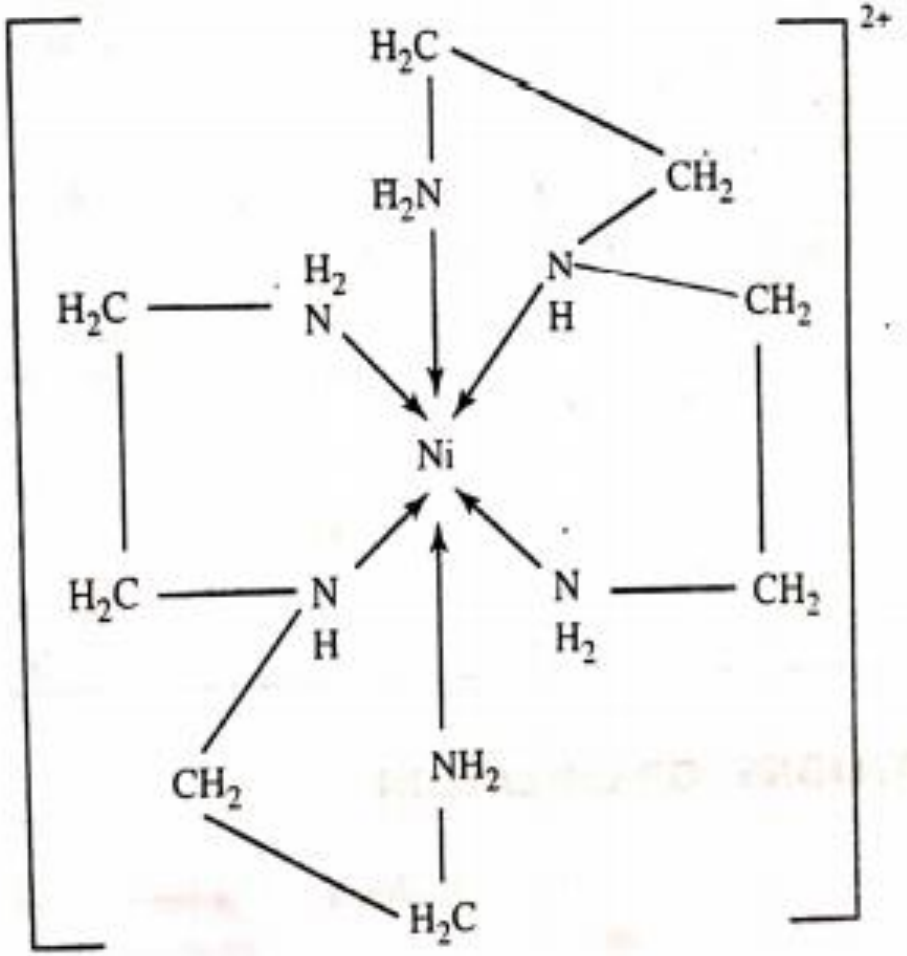
$[Ca\text{-}EDTA]^{2-}$



$[Cu(acac)_2]$



$[Cu(en)_2]^{2+}$



$[Ni(dien)_2]^{2+}$

The polydentate ligands that form the chelates are called ***the chelating agents*****.**

The process of chelate formation is known as ***chelation***. Due to chelation the stability of the complex is enhanced. This extra stability conferred on a complex due to chelation is called ***the chelate effect***.

CHELATE EFFECT

Thermodynamically, the chelate effect can be related to the entropy change of the reaction.
When a solvated metal ion in solution reacts with a chelating agent, the solvent molecules in the coordination sphere of the metal ion are replaced by the chelating agent.
For example,

$$[\mathrm{Ni(H_2O)_6}]^{2+} + 3\,\mathrm{en} \longrightarrow [\mathrm{Ni(en)_3}]^{2+} + 6\mathrm{H_2O}$$

$$1 + 3 \text{ particles} \longrightarrow 1 + 6 \text{ particles}$$

This chelation process results in an increase of three particles (7-4=3). The replacement of the monodentate ligands by chelating agents always has this effect. This increase in the number of particles results in an increase in randomness of the system.

This in turn, results in a positive ΔS^0 which adds on to the already negative ΔH^0 to give more negative

$$\Delta G^\circ \; (\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ)$$

$$\text{As, } -\Delta G^\circ = RT\ln K,$$

The more negative is ΔG^0, the larger the formation constant or stability constant. Thus an increase in the degree of randomness of the system causes greater complex stability.

As a general rule, stability of a chelate complex is higher than that of a non-chelate complex of the same metal ion.

Table gives the overall stability constants for a number of metal ammines (non-chelates) and the corresponding ethylenediamine chelates.

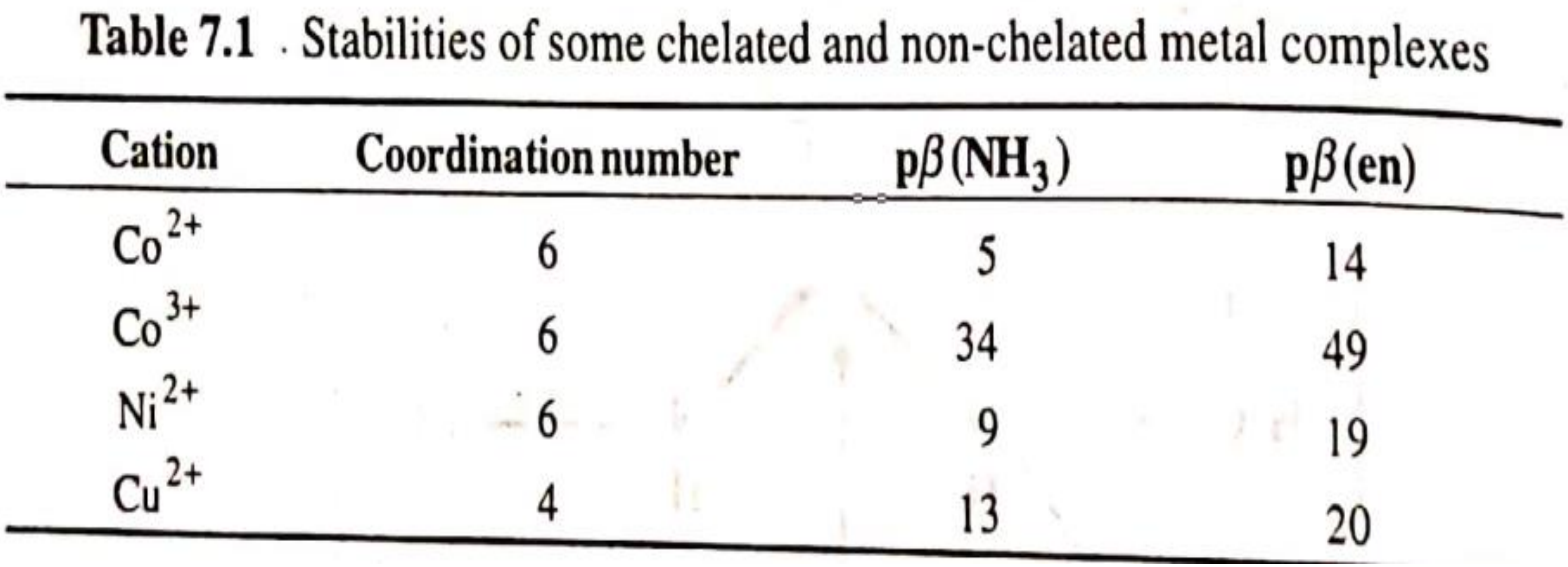


Table 7.1 . Stabilities of some chelated and non-chelated metal complexes

Cation	Coordination number	$p\beta(NH_3)$	$p\beta(en)$
Co^{2+}	6	5	14
Co^{3+}	6	34	49
Ni^{2+}	6	9	19
Cu^{2+}	4	13	20

Conditions for chelation

The chelating agents must possess at least two donor groups per molecule. ie. The ligand should be polydentate.

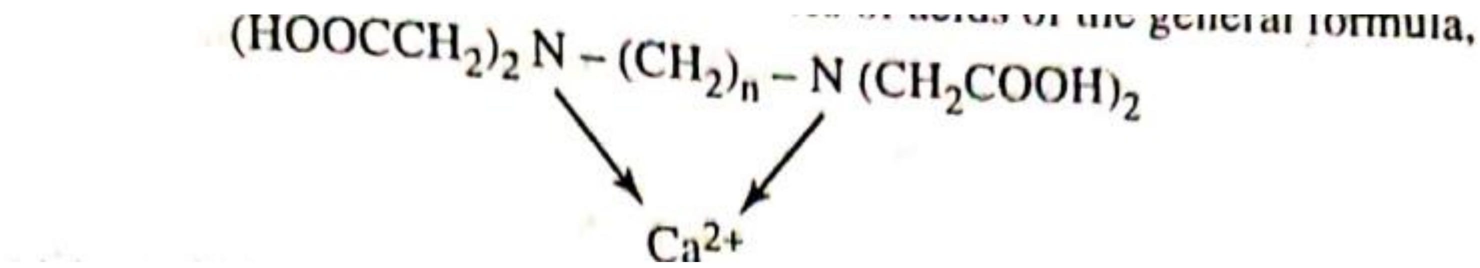
These donor groups must be so situated in the molecule in such a way that they permit the formation of a ring with the metal atom without any strain.

The donor atoms should be sterically capable of coordinating to the same metal to form a chelate. Hydrazine ($H_2N\text{-}NH_2$), even though a polydentate ligand, does not form a stable chelate, because it does not satisfy the second condition pertaining to steric condition.

Factors affecting stability of chelates

1. A factor of great importance in chelation is the size of the chelate ring produced. If there is no double bond in the chelate ring, then a 5-membered ring is most stable. Chelate rings having more or less than 5-members are generally less stable.

The stability constant with ring size of the calcium complexes with a series of acids of the general formula,



$$(HOOCCH_2)_2N-(CH_2)_n-N(CH_2COOH)_2 \rightarrow Ca^{2+}$$

Which are bidentate ligands. When n=2, a 5-membered ring is formed between the two nitrogen atoms and the metal; when n=3, a 6-membered ring is formed and so on. The greatest stability for th chelate is found when n=2.

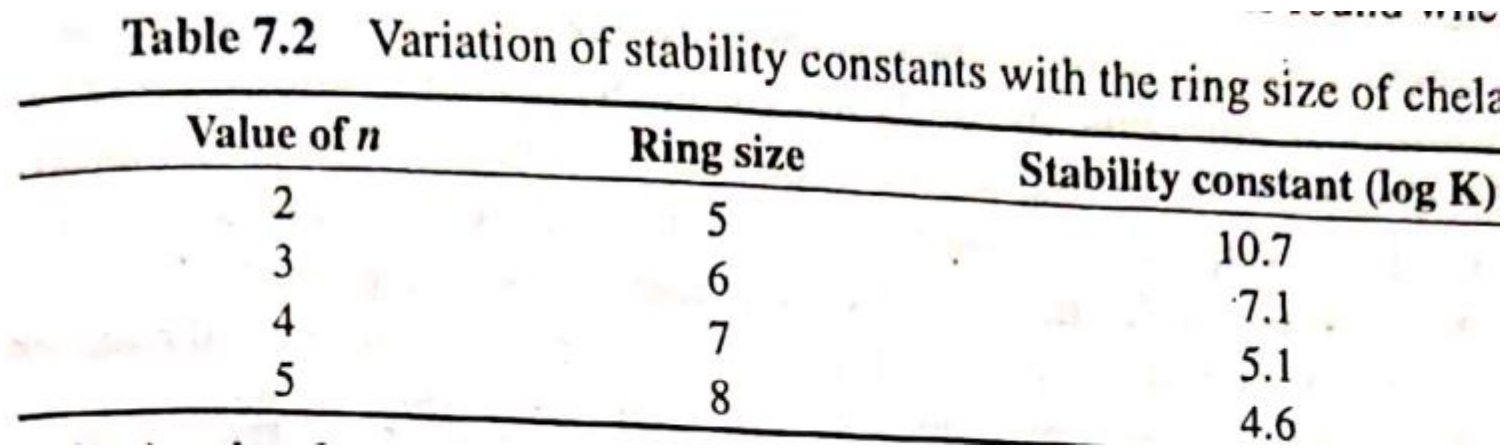


Table 7.2 Variation of stability constants with the ring size of chela

Value of *n*	Ring size	Stability constant (log K)
2	5	10.7
3	6	7.1
4	7	5.1
5	8	4.6

2. Another factor which determines chelate stablity is the influence of the number of chelate rings in a chelate molecule.

Greater the number of chelate rings greater will be the stability of the complex.

As the number of donor atoms in a chelating agent increases, the stability increases.

This is attributed to the increase in the number of chelate rings formed by such ligands.

Table shows the increase in the stability constants of Ni2+ complexes with some polydentate ligands which give rise to different numbers of chelate rings.

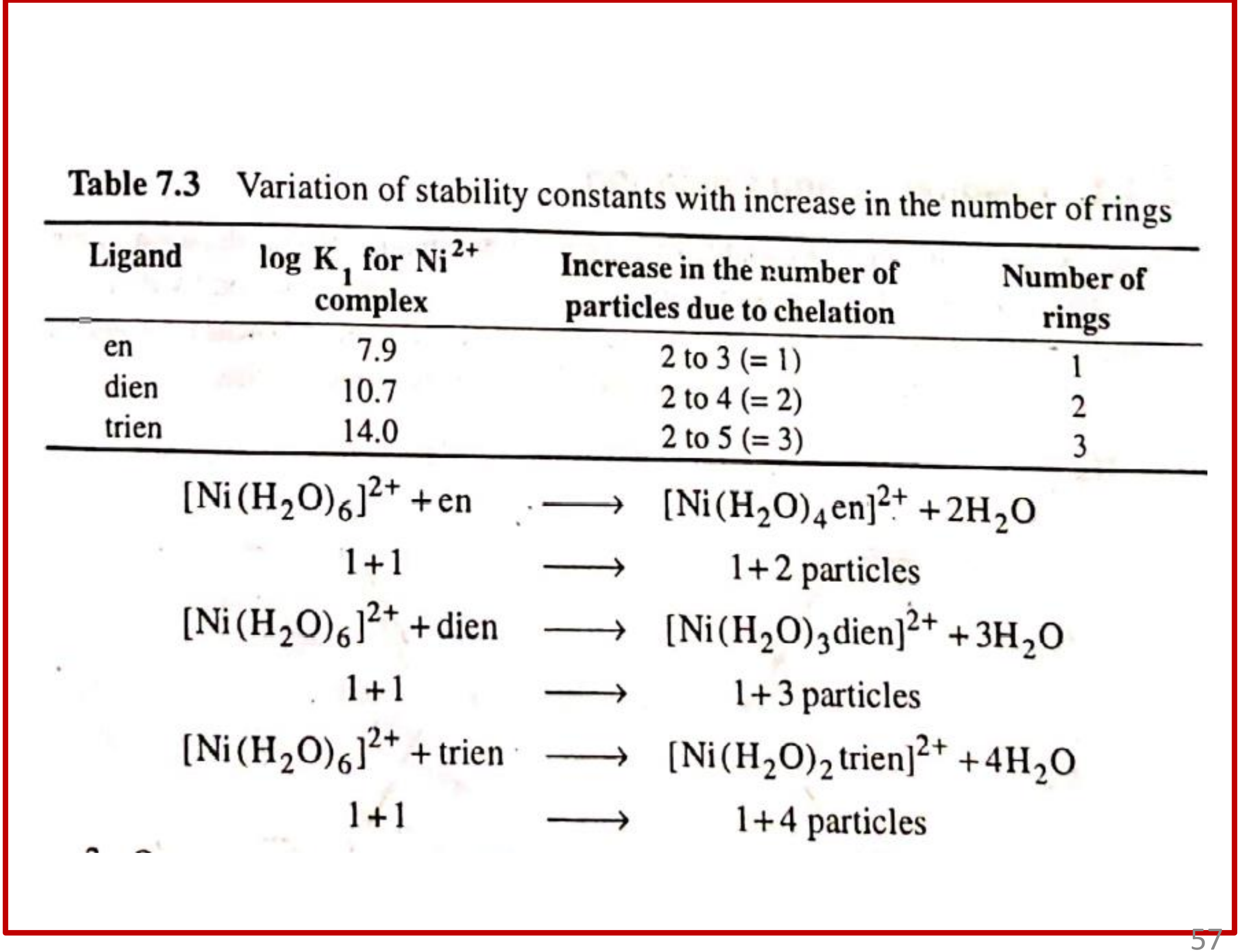


Table 7.3 Variation of stability constants with increase in the number of rings

Ligand	log K_1 for Ni^{2+} complex	Increase in the number of particles due to chelation	Number of rings
en	7.9	2 to 3 (= 1)	1
dien	10.7	2 to 4 (= 2)	2
trien	14.0	2 to 5 (= 3)	3

$$[Ni(H_2O)_6]^{2+} + en \longrightarrow [Ni(H_2O)_4en]^{2+} + 2H_2O$$

$$1+1 \longrightarrow 1+2 \text{ particles}$$

$$[Ni(H_2O)_6]^{2+} + dien \longrightarrow [Ni(H_2O)_3dien]^{2+} + 3H_2O$$

$$1+1 \longrightarrow 1+3 \text{ particles}$$

$$[Ni(H_2O)_6]^{2+} + trien \longrightarrow [Ni(H_2O)_2trien]^{2+} + 4H_2O$$

$$1+1 \longrightarrow 1+4 \text{ particles}$$

3. One more factor of significance in chelation is the **steric factor.**

This arises due to the presence of a bulky group either attached to or near to a donor atom to cause mutual repulsion between the ligands and thereby weakening the metal-ligand bond.

This leads to lesser stability. This is well illustrated by the stabilities of three complexes formed by Ni2+ with three different chelating agents such as 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline and 4-methyl-8-hydroxyquinoline.

The second stage formation constants for these complexes are given in the Table.

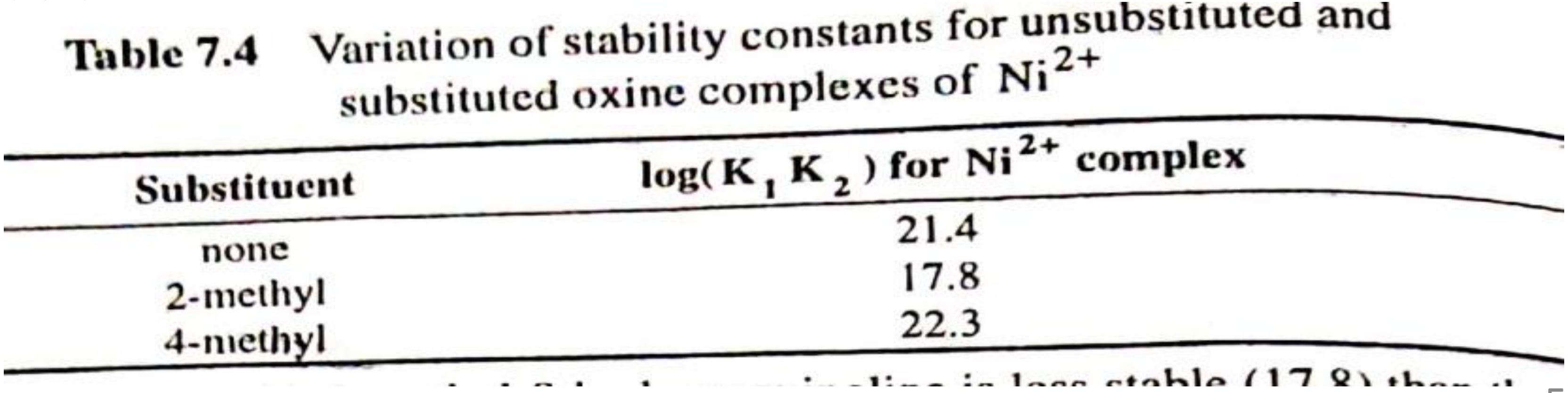


Table 7.4 Variation of stability constants for unsubstituted and substituted oxine complexes of Ni^{2+}

Substituent	$\log(K_1 K_2)$ for Ni^{2+} complex
none	21.4
2-methyl	17.8
4-methyl	22.3

The complex with 2-methyl-8-hydroxyquinoline is less stable (17.8) than those of either 8-hydroxyquinoline itself (21.4) or 4-methyl-8-hydroxyquinoline (22.3).

Generally, the more basic ligands are expected to form more stable complexes.

2-methyl-8-hydroxyquinoline is the most basic among these three chelating agents, but it forms the least stable chelate.

This is because in this ligand the bulky methyl group is present very near to the donor atom (nitrogen) to cause mutual repulsion between the ligands and thereby it decreases the stability of the chelate.

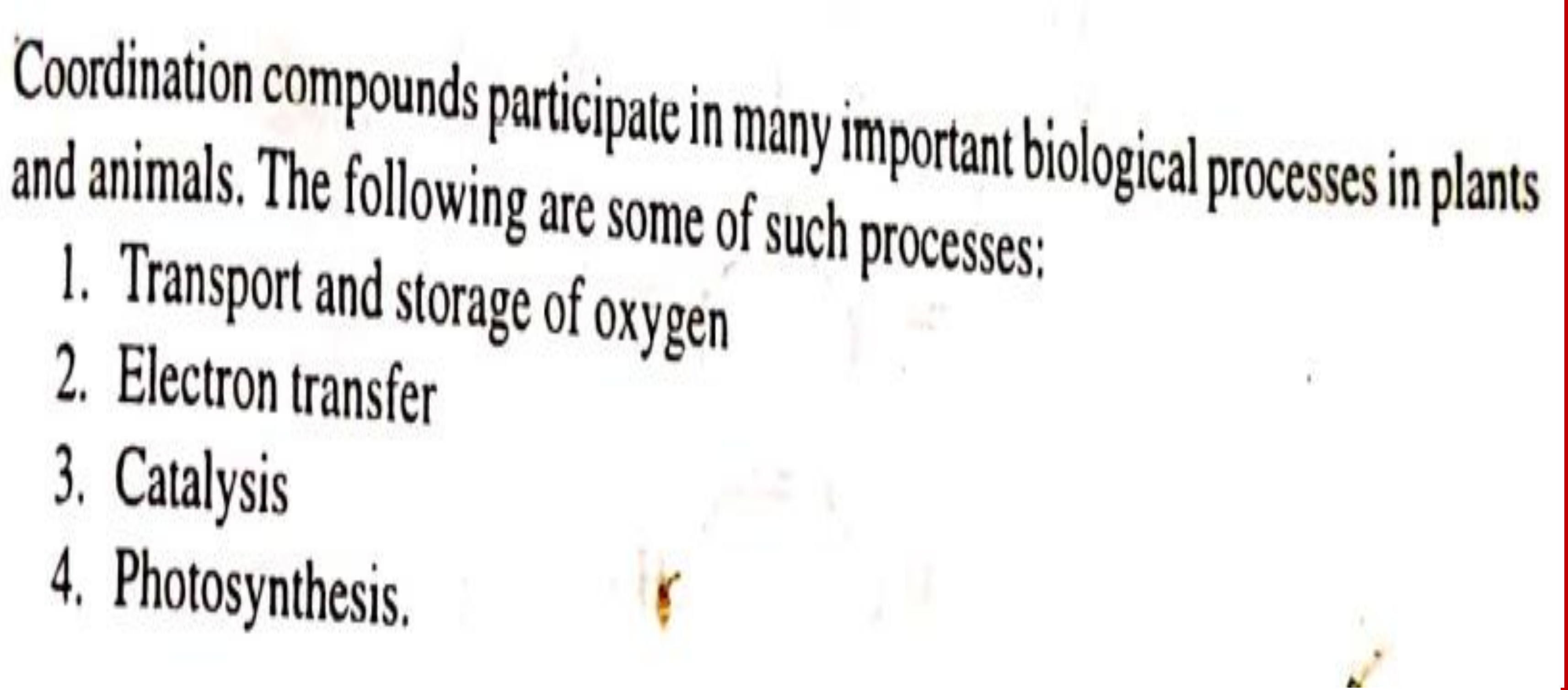
The 4-methyl derivative forms the most stable chelate.

This is attributed to its more basic nature than 8-hydroxyquinoline.

In this ligand, the bulky methyl group is far away from the donor nitrogen atom and hence it will not sterically hinder the approach of the second ligand.

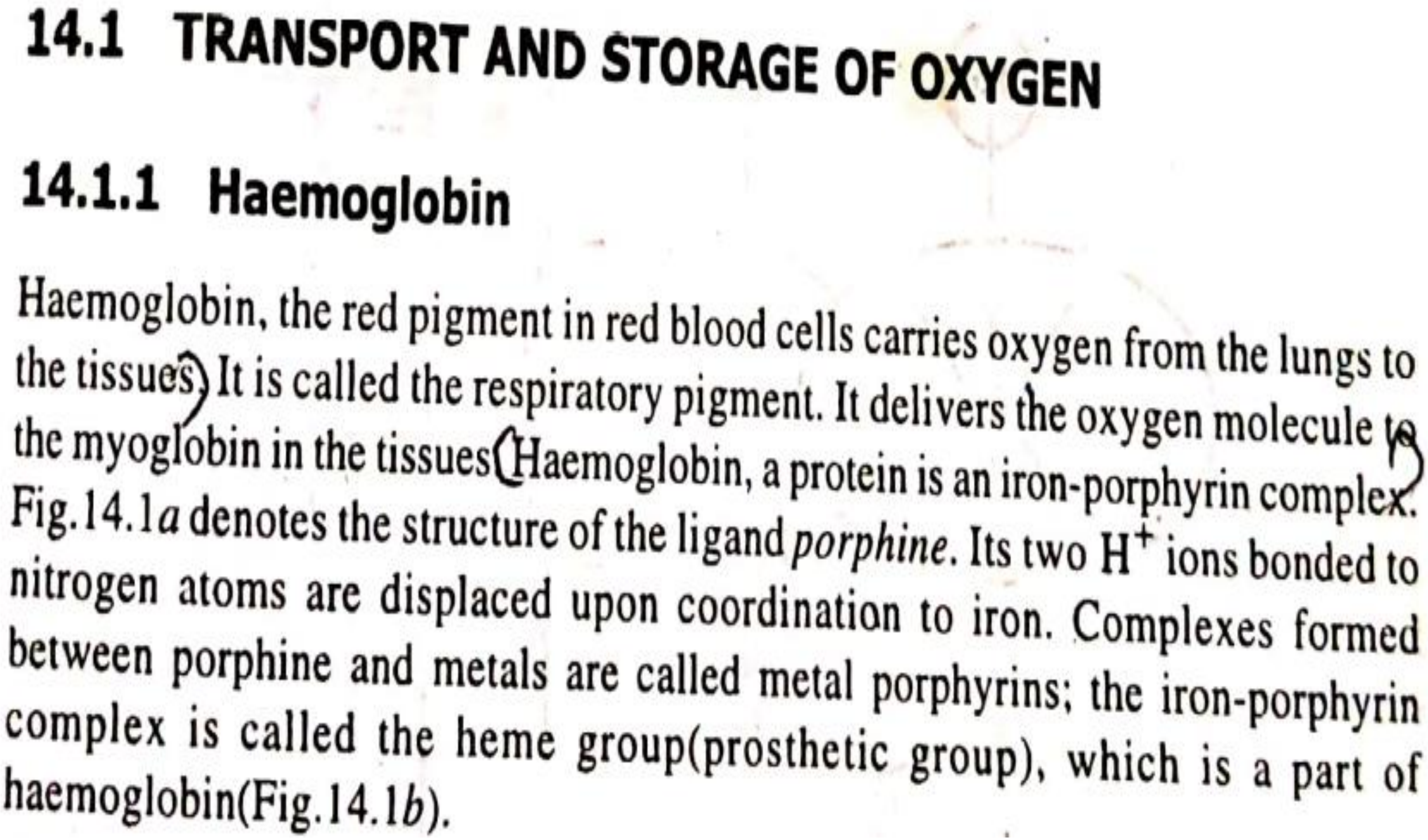
Hence it forms the most stable chelate among the three ligands. This is found to be true with many other metal ions such as Mn^{2+} , Co^{2+}, Zn^{2+}, etc.

Biological coordination compounds



Coordination compounds participate in many important biological processes in plants and animals. The following are some of such processes:

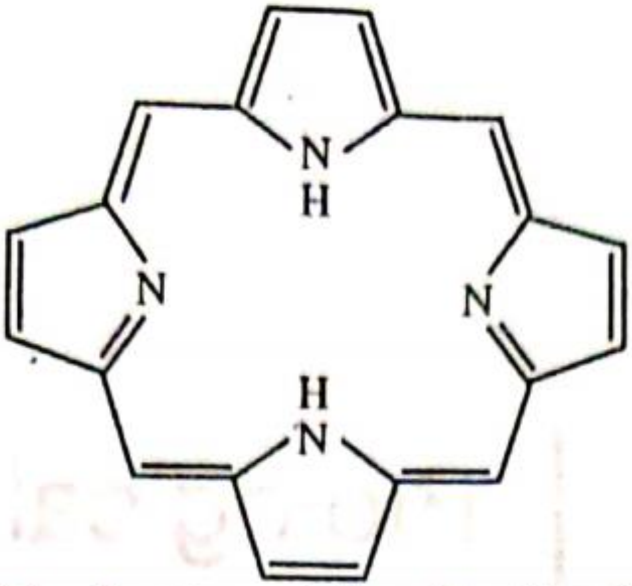
1. Transport and storage of oxygen
2. Electron transfer
3. Catalysis
4. Photosynthesis.



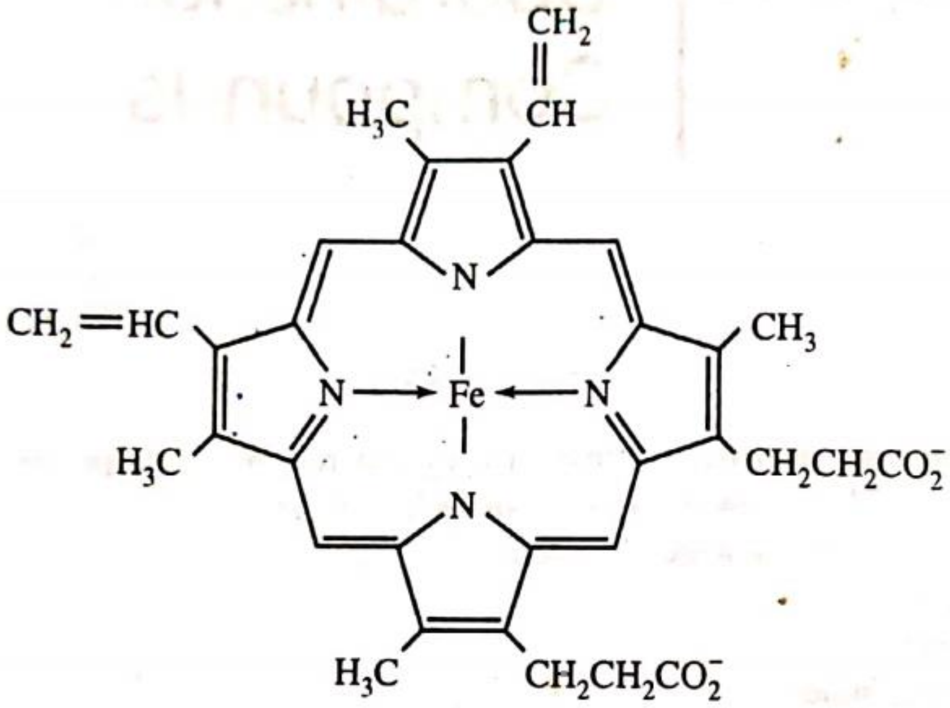
14.1 TRANSPORT AND STORAGE OF OXYGEN

14.1.1 Haemoglobin

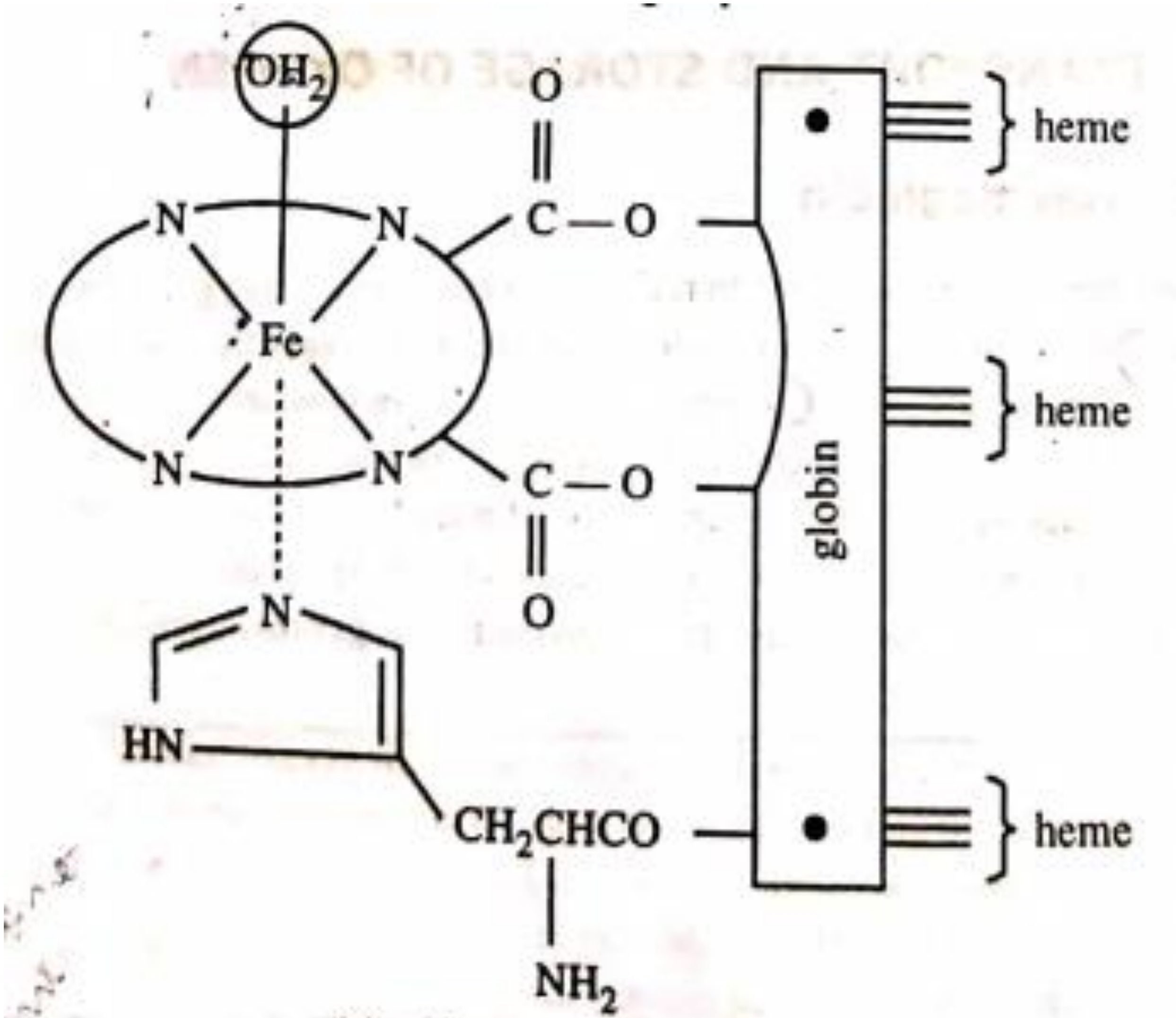
Haemoglobin, the red pigment in red blood cells carries oxygen from the lungs to the tissues. It is called the respiratory pigment. It delivers the oxygen molecule to the myoglobin in the tissues. Haemoglobin, a protein is an iron-porphyrin complex. Fig.14.1*a* denotes the structure of the ligand *porphine*. Its two H^+ ions bonded to nitrogen atoms are displaced upon coordination to iron. Complexes formed between porphine and metals are called metal porphyrins; the iron-porphyrin complex is called the heme group(prosthetic group), which is a part of haemoglobin(Fig.14.1*b*).



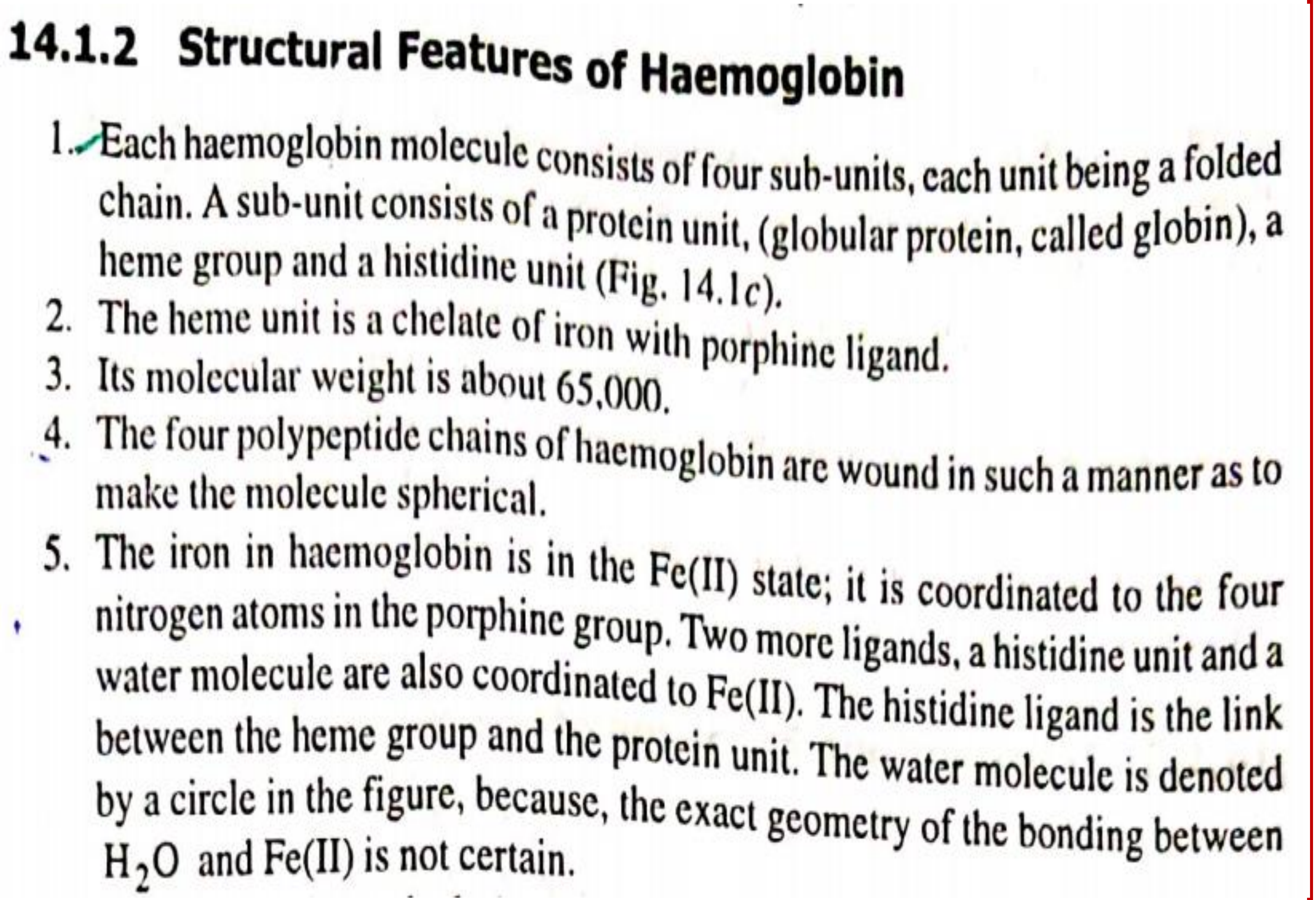
(*a*) *Structure of phorphine ligand*



(*b*) *Heme group*

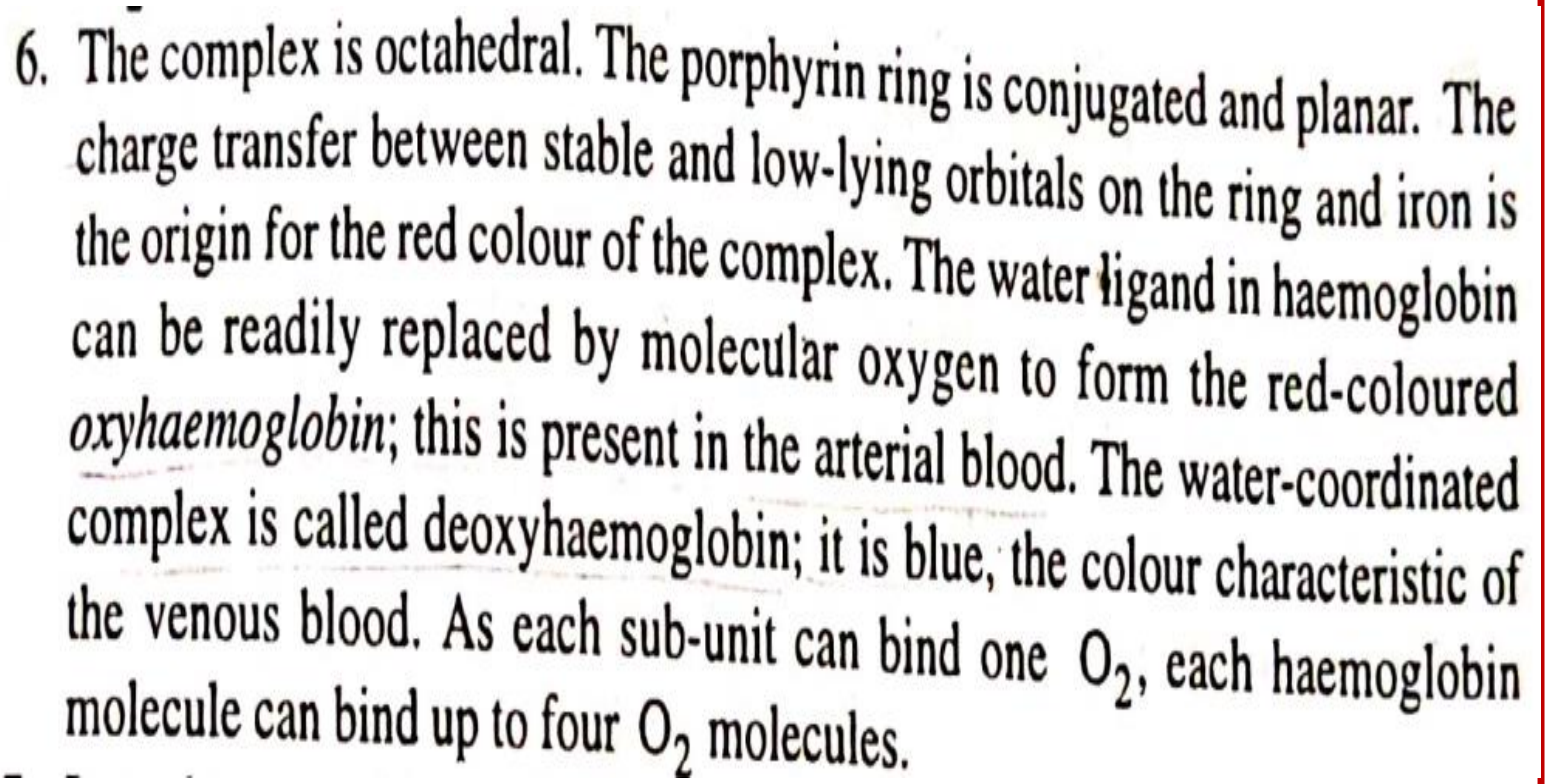


(c) *Haemoglobin sub-unit*



14.1.2 Structural Features of Haemoglobin

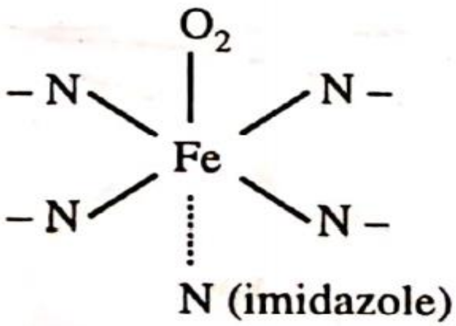
1. Each haemoglobin molecule consists of four sub-units, each unit being a folded chain. A sub-unit consists of a protein unit, (globular protein, called globin), a heme group and a histidine unit (Fig. 14.1*c*).
2. The heme unit is a chelate of iron with porphine ligand.
3. Its molecular weight is about 65,000.
4. The four polypeptide chains of haemoglobin are wound in such a manner as to make the molecule spherical.
5. The iron in haemoglobin is in the Fe(II) state; it is coordinated to the four nitrogen atoms in the porphine group. Two more ligands, a histidine unit and a water molecule are also coordinated to Fe(II). The histidine ligand is the link between the heme group and the protein unit. The water molecule is denoted by a circle in the figure, because, the exact geometry of the bonding between H_2O and Fe(II) is not certain.



6. The complex is octahedral. The porphyrin ring is conjugated and planar. The charge transfer between stable and low-lying orbitals on the ring and iron is the origin for the red colour of the complex. The water ligand in haemoglobin can be readily replaced by molecular oxygen to form the red-coloured *oxyhaemoglobin*; this is present in the arterial blood. The water-coordinated complex is called deoxyhaemoglobin; it is blue, the colour characteristic of the venous blood. As each sub-unit can bind one O_2, each haemoglobin molecule can bind up to four O_2 molecules.

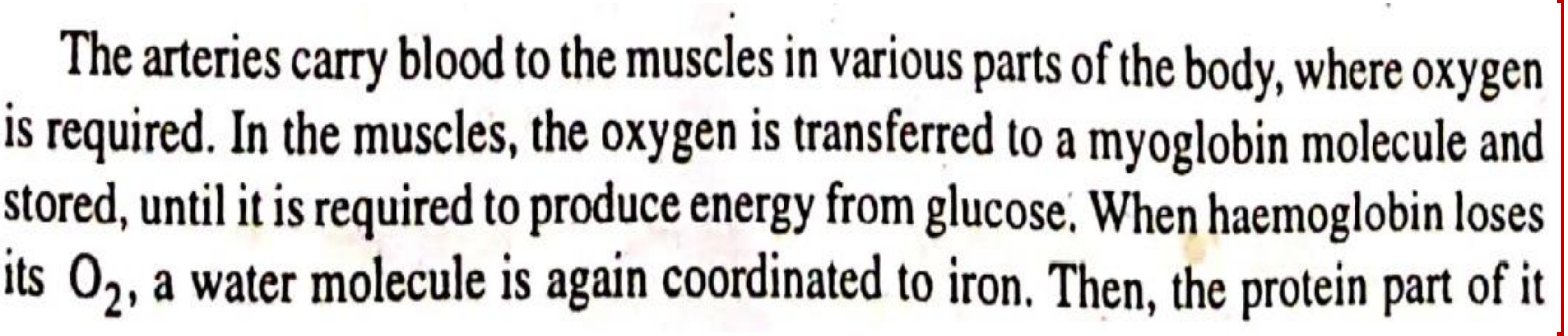
7. In oxyhaemoglobin, the Fe(II) is in the low-spin state and is diamagnetic; but in deoxyhaemoglobin, the Fe(II) is in the high-spin state and is paramagnetic. The size of Fe(II) is increased by about 30 per cent, when it changes from the diamagnetic to paramagnetic state. This increase in size distorts the bonds around Fe and also the shape of the complex. In oxyhaemoglobin, the Fe(II) is of the right size to get into the hole at the centre of the porphyrin ring; but in deoxyhaemoglobin, because of its enlargement, it is above the plane of the ring.

The O_2 molecule is bonded to the heme group as shown in Fig. 14.2.

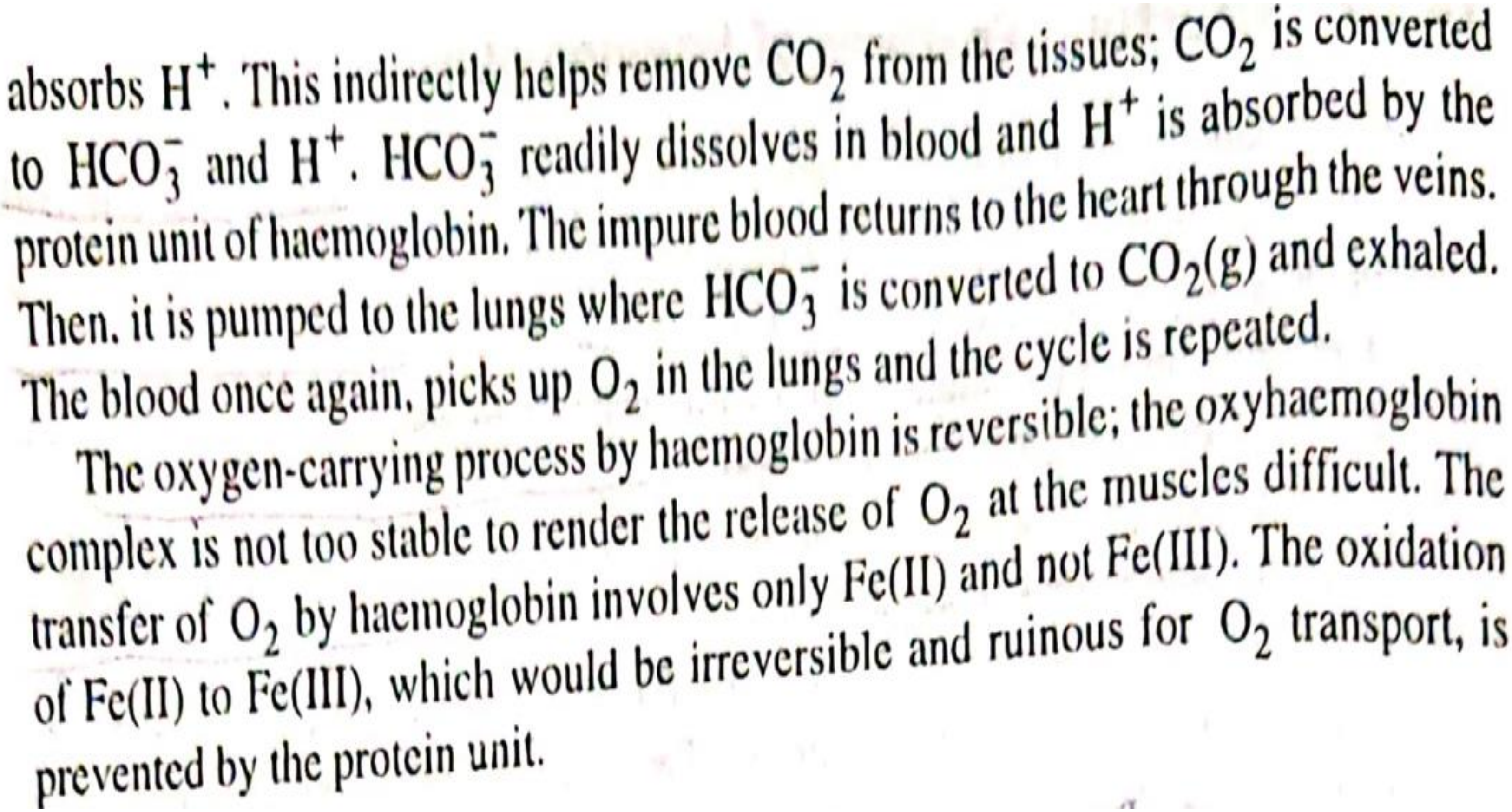


A portion of oxygenated haemoglobin

Fig. 14.2 *The bonding of the oxygen molecule with the heme unit of haemoglobin*

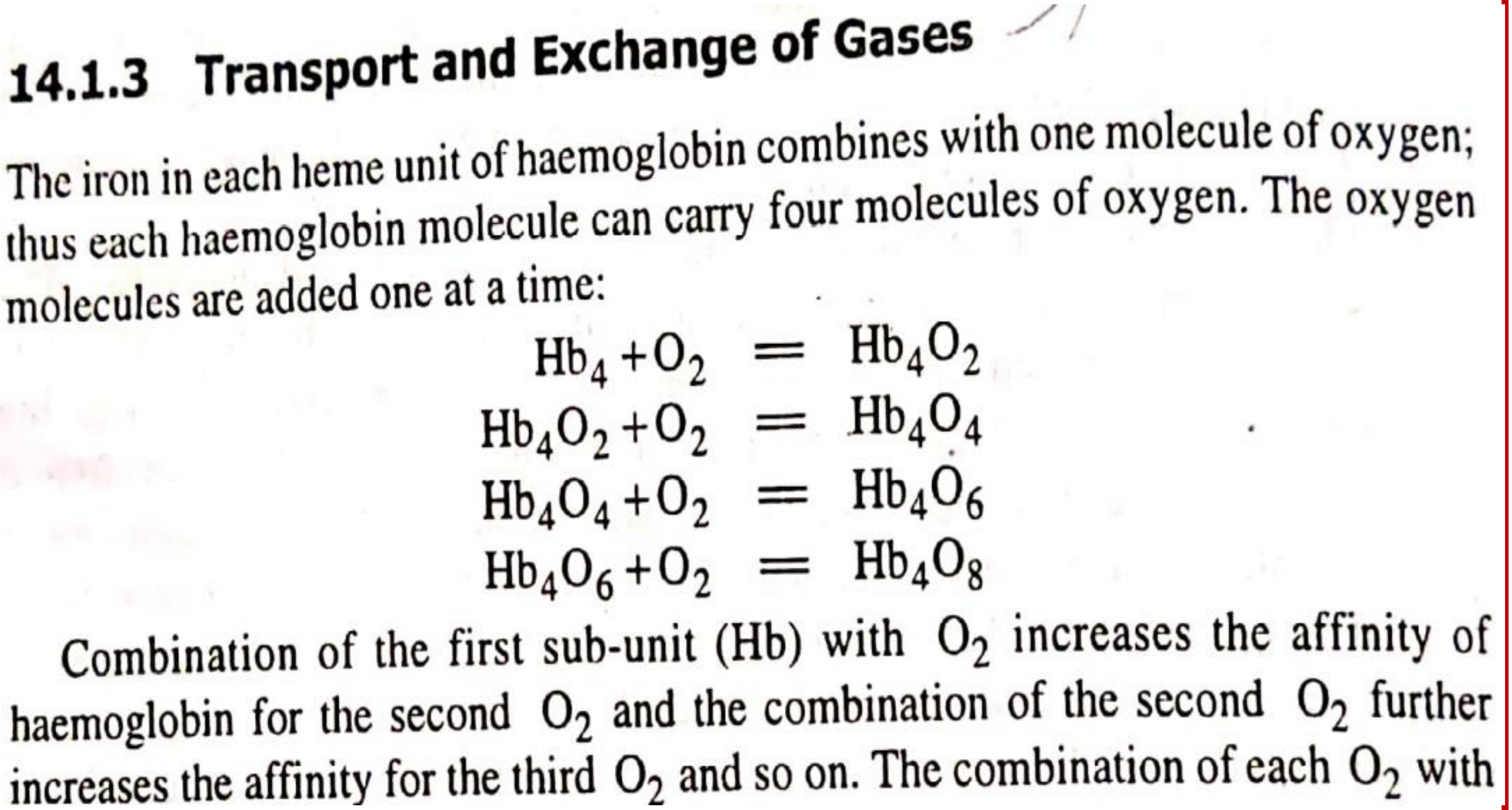


The arteries carry blood to the muscles in various parts of the body, where oxygen is required. In the muscles, the oxygen is transferred to a myoglobin molecule and stored, until it is required to produce energy from glucose. When haemoglobin loses its O_2, a water molecule is again coordinated to iron. Then, the protein part of it



absorbs H^+. This indirectly helps remove CO_2 from the tissues; CO_2 is converted to HCO_3^- and H^+. HCO_3^- readily dissolves in blood and H^+ is absorbed by the protein unit of haemoglobin. The impure blood returns to the heart through the veins. Then, it is pumped to the lungs where HCO_3^- is converted to $CO_2(g)$ and exhaled. The blood once again, picks up O_2 in the lungs and the cycle is repeated.

The oxygen-carrying process by haemoglobin is reversible; the oxyhaemoglobin complex is not too stable to render the release of O_2 at the muscles difficult. The transfer of O_2 by haemoglobin involves only Fe(II) and not Fe(III). The oxidation of Fe(II) to Fe(III), which would be irreversible and ruinous for O_2 transport, is prevented by the protein unit.

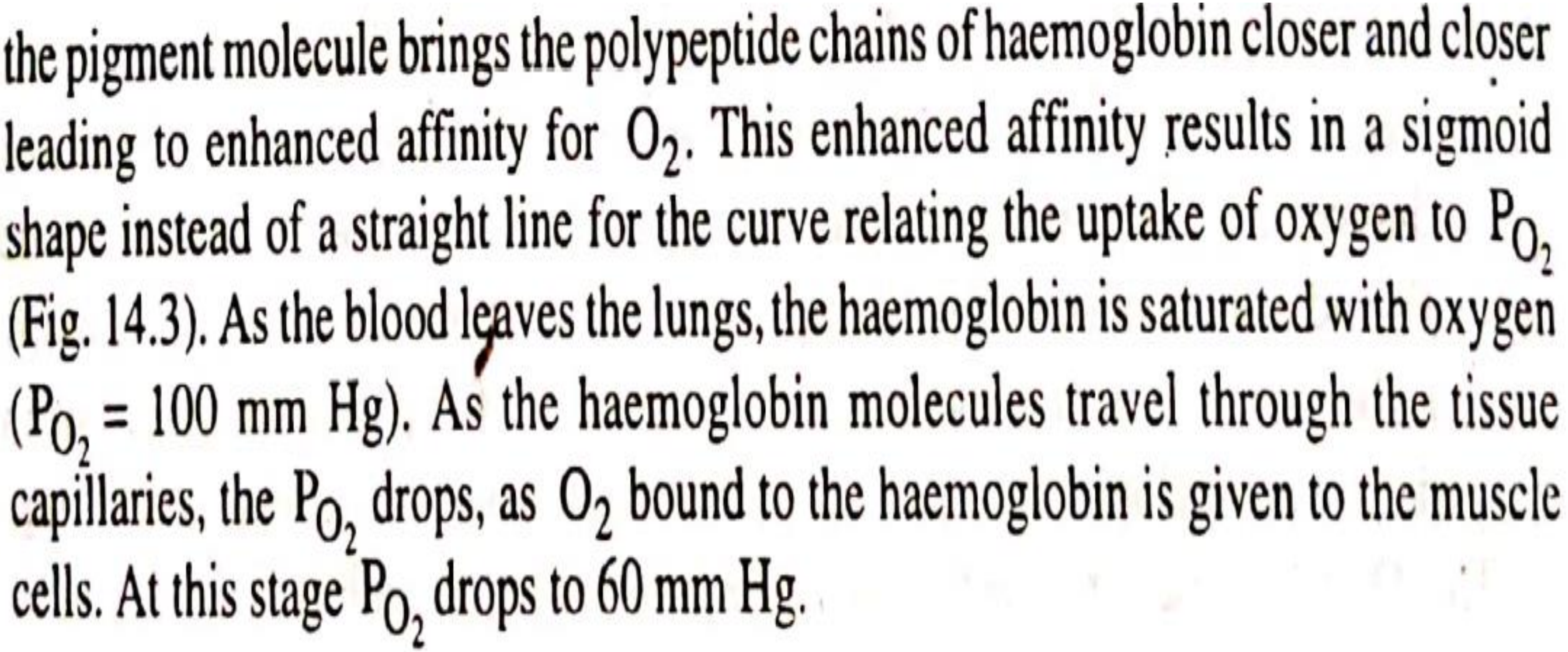


14.1.3 Transport and Exchange of Gases

The iron in each heme unit of haemoglobin combines with one molecule of oxygen; thus each haemoglobin molecule can carry four molecules of oxygen. The oxygen molecules are added one at a time:

$$\begin{aligned} Hb_4 + O_2 &= Hb_4O_2 \\ Hb_4O_2 + O_2 &= Hb_4O_4 \\ Hb_4O_4 + O_2 &= Hb_4O_6 \\ Hb_4O_6 + O_2 &= Hb_4O_8 \end{aligned}$$

Combination of the first sub-unit (Hb) with O_2 increases the affinity of haemoglobin for the second O_2 and the combination of the second O_2 further increases the affinity for the third O_2 and so on. The combination of each O_2 with



the pigment molecule brings the polypeptide chains of haemoglobin closer and closer leading to enhanced affinity for O_2. This enhanced affinity results in a sigmoid shape instead of a straight line for the curve relating the uptake of oxygen to P_{O_2} (Fig. 14.3). As the blood leaves the lungs, the haemoglobin is saturated with oxygen (P_{O_2} = 100 mm Hg). As the haemoglobin molecules travel through the tissue capillaries, the P_{O_2} drops, as O_2 bound to the haemoglobin is given to the muscle cells. At this stage P_{O_2} drops to 60 mm Hg.

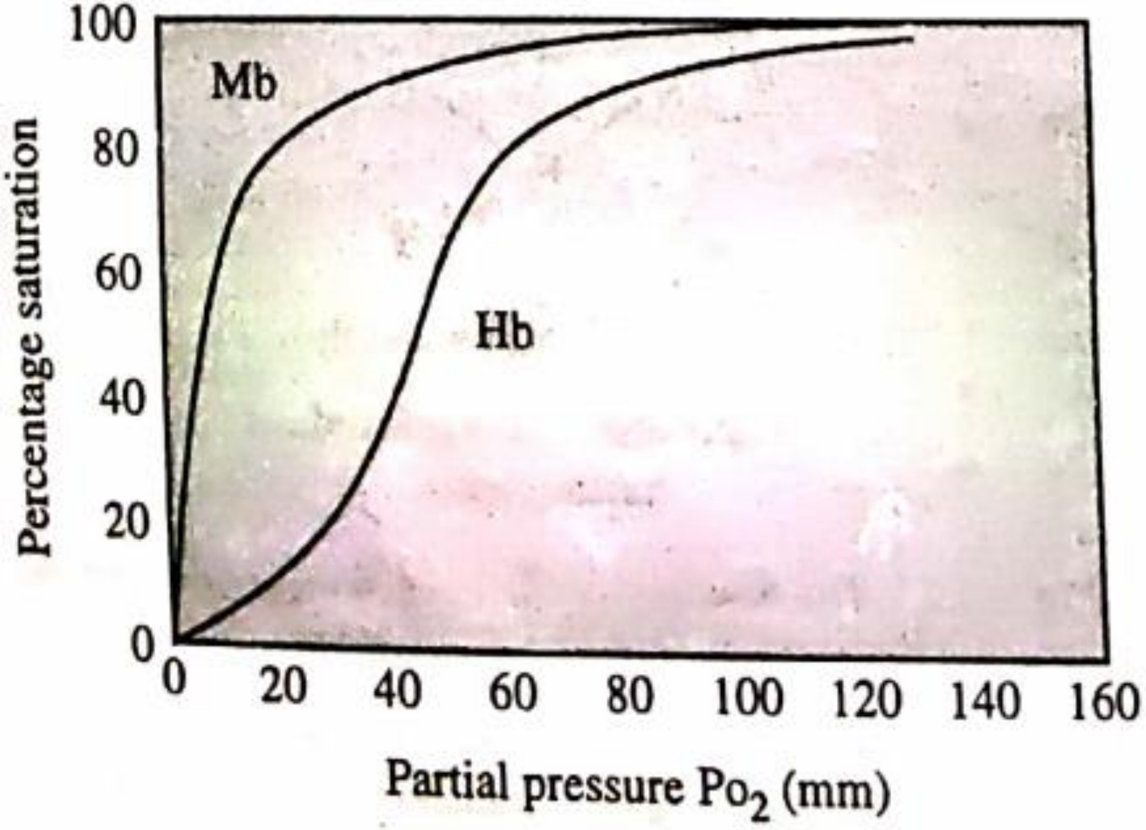
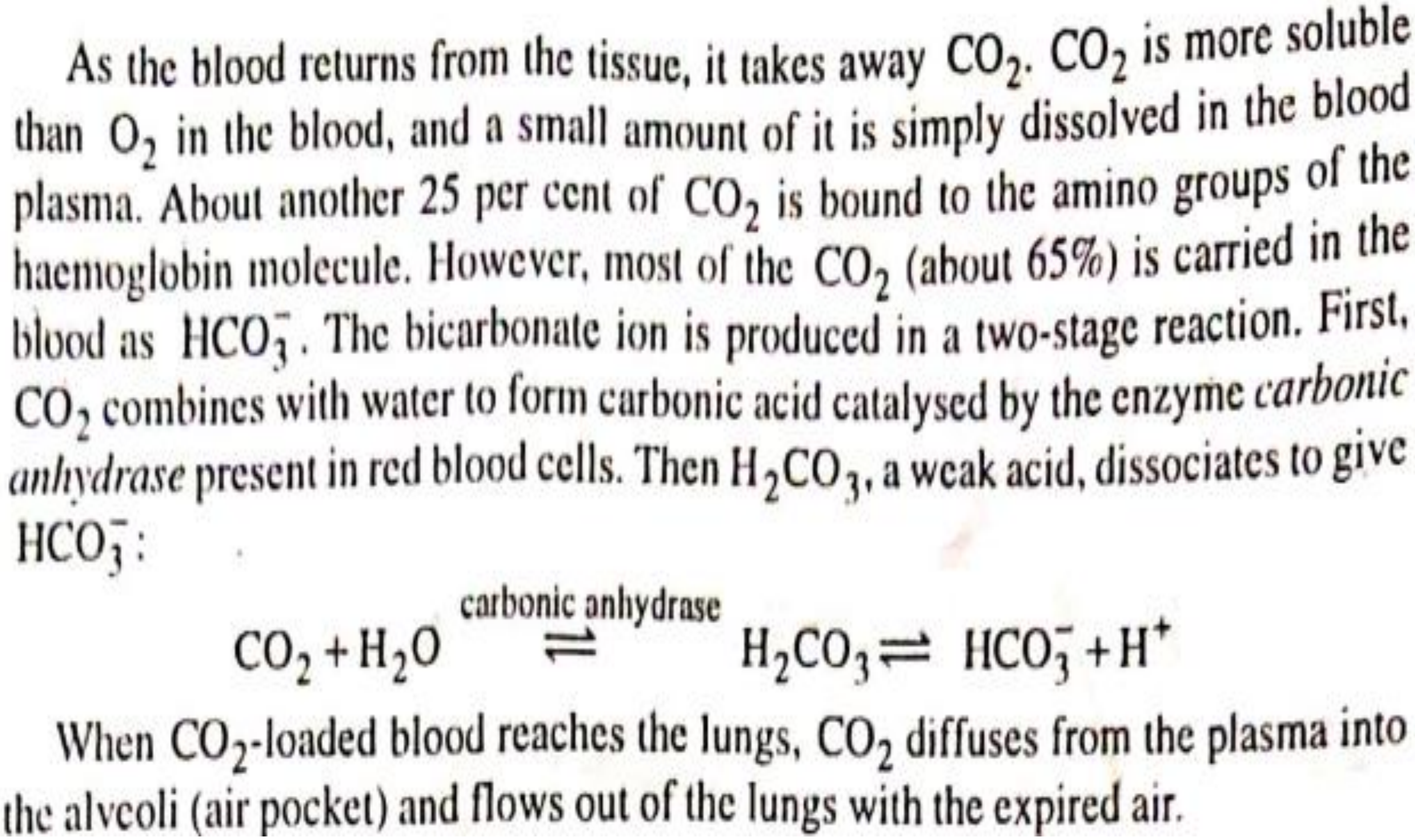


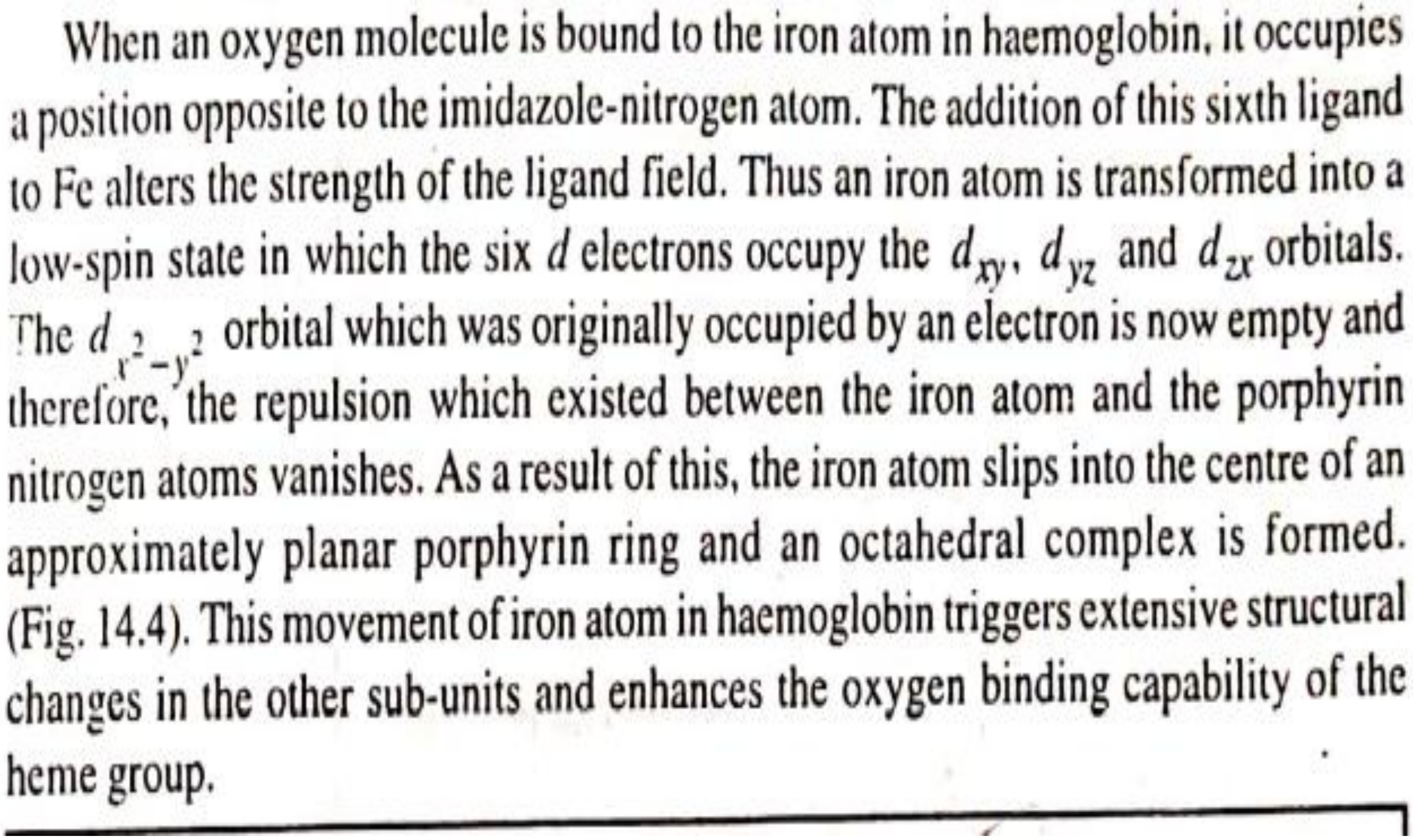
Fig. 14.3 *The oxygen-binding curves for myoglobin (Mb) and haemoglobin (Hb)*



As the blood returns from the tissue, it takes away CO_2. CO_2 is more soluble than O_2 in the blood, and a small amount of it is simply dissolved in the blood plasma. About another 25 per cent of CO_2 is bound to the amino groups of the haemoglobin molecule. However, most of the CO_2 (about 65%) is carried in the blood as HCO_3^-. The bicarbonate ion is produced in a two-stage reaction. First, CO_2 combines with water to form carbonic acid catalysed by the enzyme *carbonic anhydrase* present in red blood cells. Then H_2CO_3, a weak acid, dissociates to give HCO_3^-:

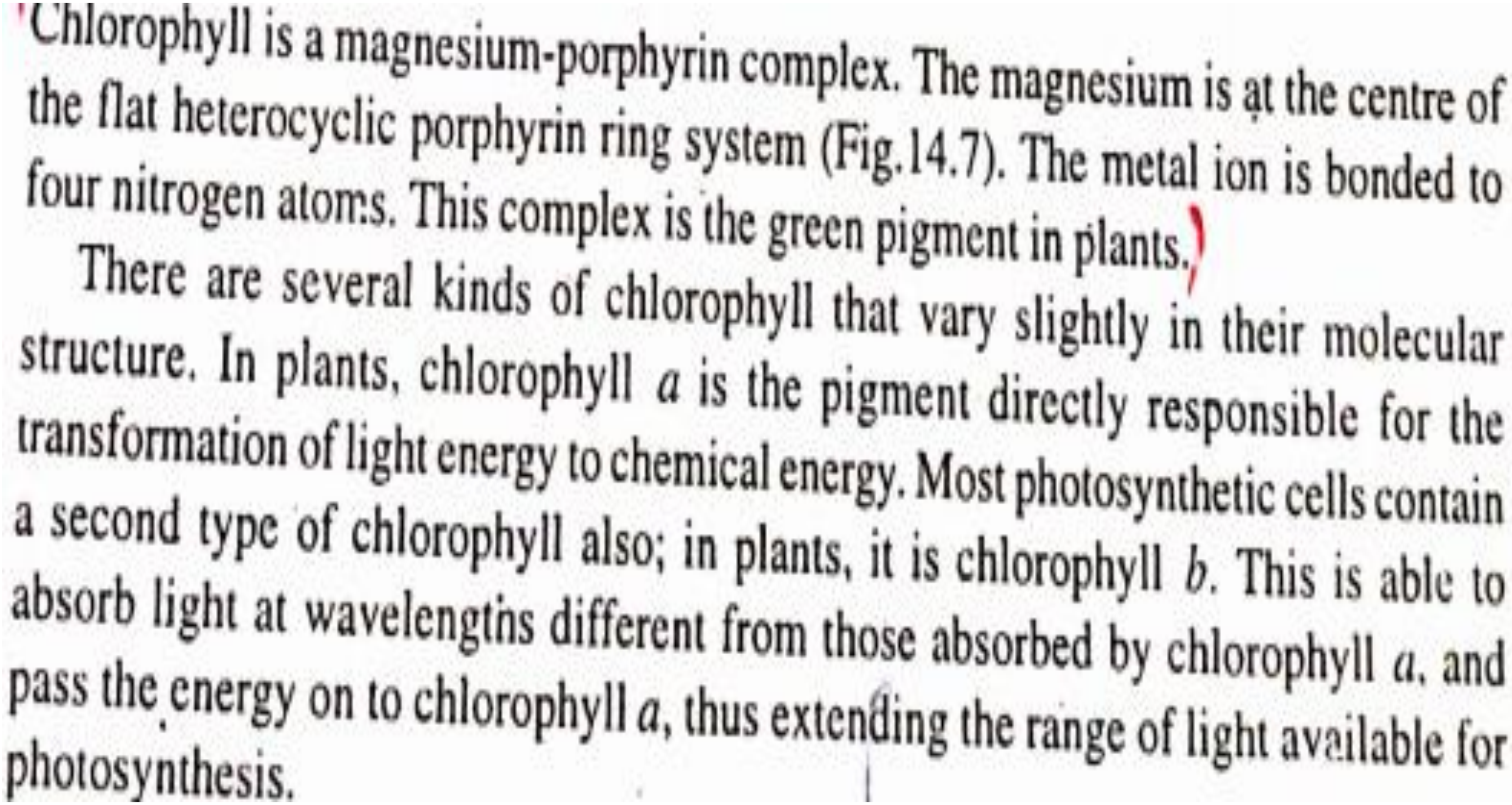
$$CO_2 + H_2O \overset{\text{carbonic anhydrase}}{\rightleftharpoons} H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

When CO_2-loaded blood reaches the lungs, CO_2 diffuses from the plasma into the alveoli (air pocket) and flows out of the lungs with the expired air.



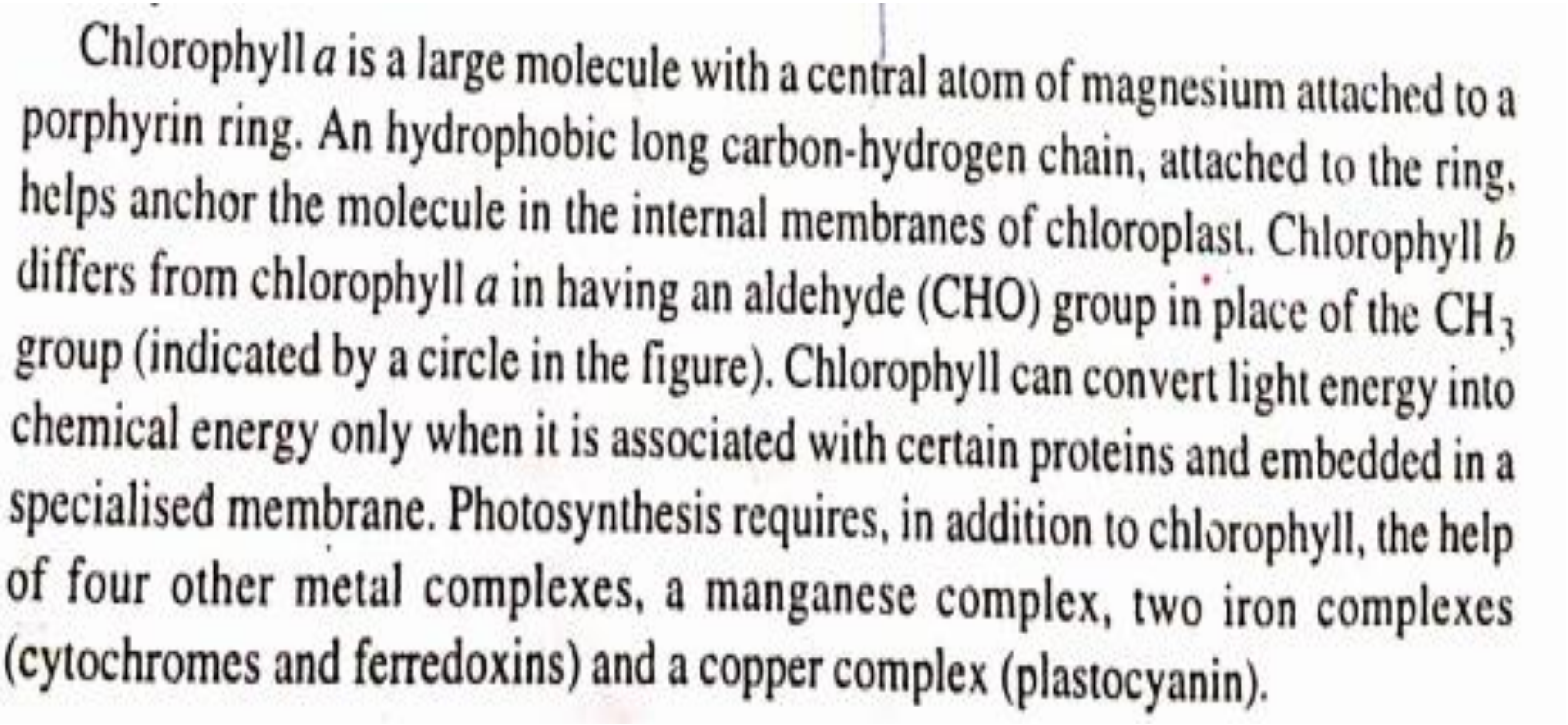
When an oxygen molecule is bound to the iron atom in haemoglobin, it occupies a position opposite to the imidazole-nitrogen atom. The addition of this sixth ligand to Fe alters the strength of the ligand field. Thus an iron atom is transformed into a low-spin state in which the six *d* electrons occupy the d_{xy}, d_{yz} and d_{zx} orbitals. The $d_{x^2-y^2}$ orbital which was originally occupied by an electron is now empty and therefore, the repulsion which existed between the iron atom and the porphyrin nitrogen atoms vanishes. As a result of this, the iron atom slips into the centre of an approximately planar porphyrin ring and an octahedral complex is formed. (Fig. 14.4). This movement of iron atom in haemoglobin triggers extensive structural changes in the other sub-units and enhances the oxygen binding capability of the heme group.

Chlorophyll



Chlorophyll is a magnesium-porphyrin complex. The magnesium is at the centre of the flat heterocyclic porphyrin ring system (Fig.14.7). The metal ion is bonded to four nitrogen atoms. This complex is the green pigment in plants.

There are several kinds of chlorophyll that vary slightly in their molecular structure. In plants, chlorophyll *a* is the pigment directly responsible for the transformation of light energy to chemical energy. Most photosynthetic cells contain a second type of chlorophyll also; in plants, it is chlorophyll *b*. This is able to absorb light at wavelengths different from those absorbed by chlorophyll *a*, and pass the energy on to chlorophyll *a*, thus extending the range of light available for photosynthesis.



Chlorophyll *a* is a large molecule with a central atom of magnesium attached to a porphyrin ring. An hydrophobic long carbon-hydrogen chain, attached to the ring, helps anchor the molecule in the internal membranes of chloroplast. Chlorophyll *b* differs from chlorophyll *a* in having an aldehyde (CHO) group in place of the CH_3 group (indicated by a circle in the figure). Chlorophyll can convert light energy into chemical energy only when it is associated with certain proteins and embedded in a specialised membrane. Photosynthesis requires, in addition to chlorophyll, the help of four other metal complexes, a manganese complex, two iron complexes (cytochromes and ferredoxins) and a copper complex (plastocyanin).

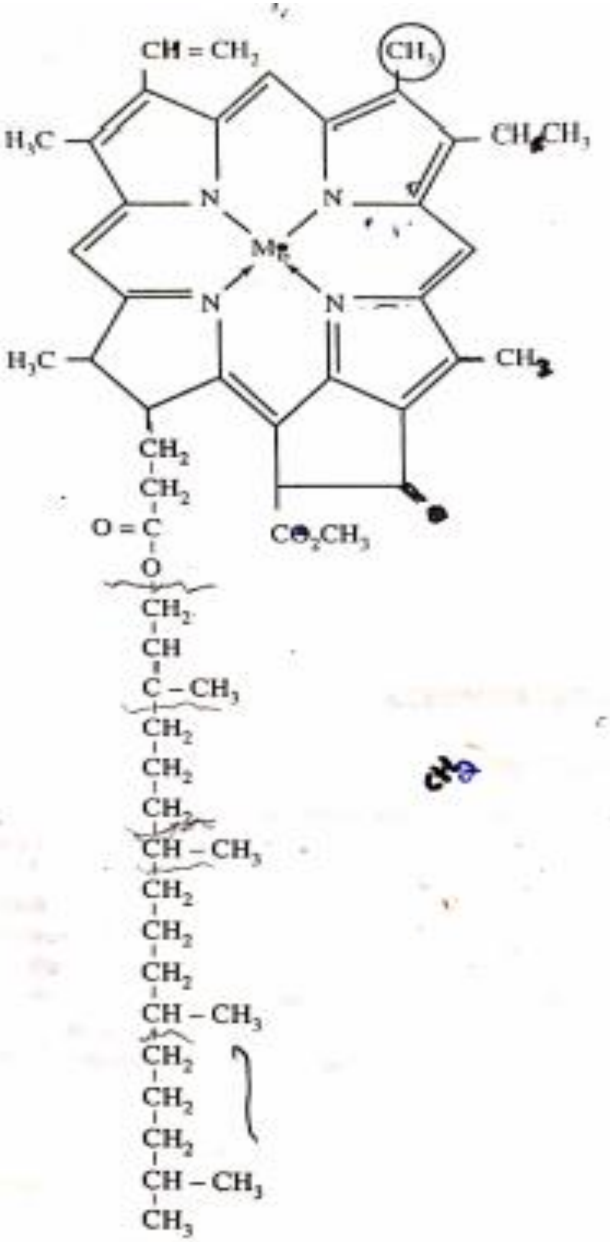


Fig. 14.7 *Structure of chlorophyll*

(Chlorophyll *a* is a large molecule with a central atom of magnesium held in a porphyrin ring. Attached to the ring is a long, hydrophobic carbon-hydrogen chain that may help to anchor the molecule in the internal membranes of the chloroplast.)

Chlorophyll *b* differs from chlorophyll *a* in having an aldehyde (CHO) group in place of the CH_3 group.

(i) Chlorophyll absorbs light in the red region (near 700 nm) from the sunlight and supplies the absorbed energy for photosynthesis; in this synthesis, CO_2 is converted into sugars.

$$x\,CO_2 + y\,H_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} \underbrace{C_x(H_2O)_y}_{\text{carbohydrate}} + x\,O_2$$

chlorophyll

CO_2 is "fixed" and oxygen is a by-product in this process. Photosynthesis occurs not only in higher plants but also in algae and certain bacteria. It involves the conversion of light energy into chemical energy.

6

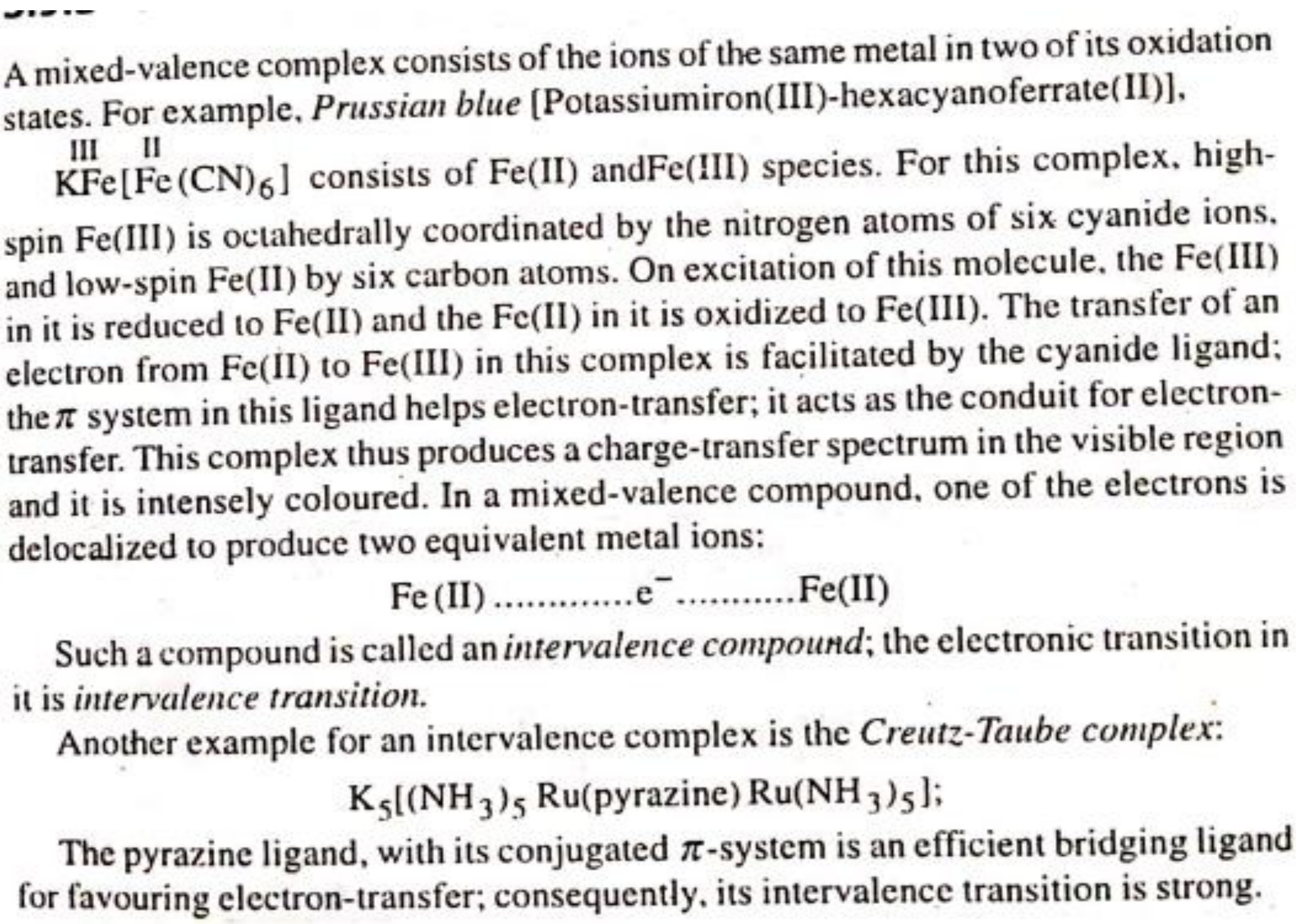
(ii) Many individual enzyme-catalysed reactions occur in photosynthesis. The process begins with the absorption of light by chlorophyll. The green colour of chlorophyll and, therefore, its capacity to absorb sunlight in the visible region, is primarily due to its extended conjugated system. Chlorophyll traps photons of sunlight and supplies these to the plant cells to reduce carbon dioxide to carbohydrates and to oxidise water to oxygen.

(iii) Magnesium in it makes the molecule rigid so that the energy absorbed is not lost thermally through molecular vibrations. In addition, it enhances the rate at which the short-lived excited state initially formed by photon absorption is transformed into the corresponding triplet state; the triplet state has a longer lifetime and therefore can transfer its excitation energy into the redox chain.

(iv) Photosynthesis involves a series of redox reactions. At the initial stage of the electron-transfer sequence, a manganese complex undergoes reversible redox reaction. At other stages, iron-containing cytochromes and ferredoxins, and copper-containing plastocyanin participate in redox reactions. The chain of these redox processes ultimately releases molecular oxygen.

The structure of chlorophyll-*a* was established by H.Fischer, R.Willstater and J.B. Conant. R.B. Woodward first synthesised chlorophyll from simple organic molecules in 1960. He was awarded the Nobel Prize in 1965 for his excellent contribution to synthetic organic chemistry.

Prussian blue



A mixed-valence complex consists of the ions of the same metal in two of its oxidation states. For example, *Prussian blue* [Potassiumiron(III)-hexacyanoferrate(II)], $K\overset{III}{Fe}[\overset{II}{Fe}(CN)_6]$ consists of Fe(II) andFe(III) species. For this complex, high-spin Fe(III) is octahedrally coordinated by the nitrogen atoms of six cyanide ions, and low-spin Fe(II) by six carbon atoms. On excitation of this molecule, the Fe(III) in it is reduced to Fe(II) and the Fe(II) in it is oxidized to Fe(III). The transfer of an electron from Fe(II) to Fe(III) in this complex is facilitated by the cyanide ligand; the π system in this ligand helps electron-transfer; it acts as the conduit for electron-transfer. This complex thus produces a charge-transfer spectrum in the visible region and it is intensely coloured. In a mixed-valence compound, one of the electrons is delocalized to produce two equivalent metal ions:

$$\mathrm{Fe(II)} \ldots\ldots\ldots\ldots e^{-} \ldots\ldots\ldots\ldots \mathrm{Fe(II)}$$

Such a compound is called an *intervalence compound*; the electronic transition in it is *intervalence transition.*

Another example for an intervalence complex is the *Creutz-Taube complex*:

$$K_5[(NH_3)_5\,Ru(pyrazine)\,Ru(NH_3)_5];$$

The pyrazine ligand, with its conjugated π-system is an efficient bridging ligand for favouring electron-transfer; consequently, its intervalence transition is strong.

Application

Importance of chelates in Biology

In biology, many widely divergent chemical and biological processes are closely related to the formation of chelate rings. Many metals, which are essential for the normal growth and maintenance of life in both animals and plants are present in the form of their chelates in the organisms.

1. Haemoglobin, which is the oxygen carrier in the blood is an iron chelate.
2. Chlorophyll, which is essential for photosynthesis in plants is a magnesium chelate.
3. Oxygen carriers in the blood of various invertebrates are the chelate compounds of the elements such as manganese and vanadium.
4. Vitamin B12, which is an anti-pernicious anaemia factor, is a cobalt chelate.

5. Cytochromes, which are electron carriers are ion chelates.

6. Plastocyanins, which are also electron carriers are copper chelates.

7. Metal poisoning due to lead, mercury, copper, etc. is attributed to the formation of very stable , toxic chelates of these metals with biologically important substances like adrenalin, citric acid, cortisone, etc. thereby affecting their normal metabolisms.

Such metal poisoning can be treated by drinking an aqueous solution of EDTA.

This chelating agent complexes with the poisoning lead, mercury, copper, etc. and these toxic chelates are excreted in the urine.

But unfortunately EDTA also complexes the essential calcium in the body and the complex is excreted in urine.

This problem may be partly overcome by using Ca-EDTA complex as the antidote in the place of EDTA.

Chelates in Analytical chemistry

Chelates are of great importance in analytical chemistry.

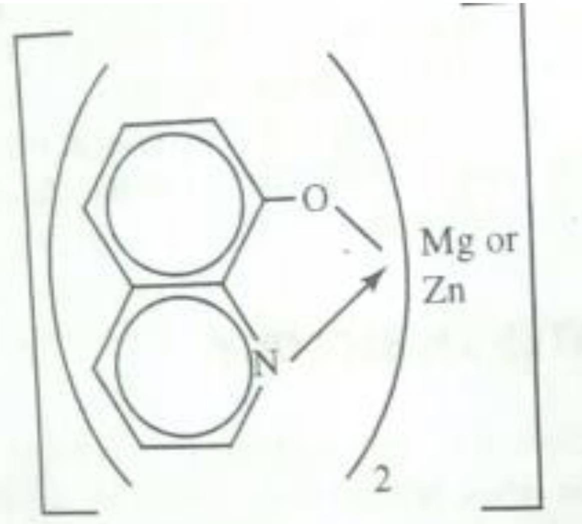
1. In qualitative analysis, nickel can be readily identified as its DMG chelate which gets precipitated as a rosy red solid in ammoniacal medium.

2. Magneium, aluminium and zinc ions can also be identified as their stable and intensely colored chelates.

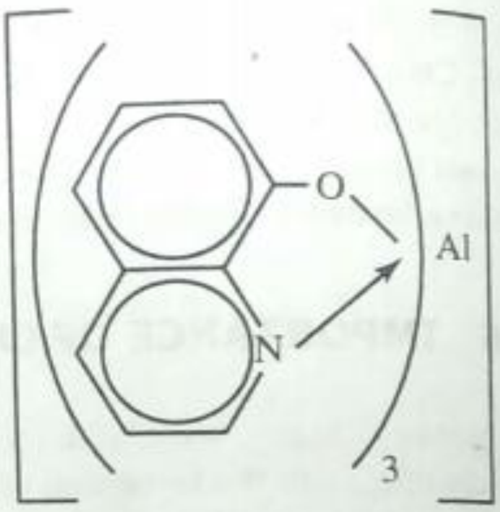
3. In gravimetric anlaysis, magnesium, aluminium and zinc are precipitated quatitatively as their 8-hydroxyquinoline chelates called the oxinates.

4. $Ni^{2+}$is quantitatively precipitated as its dimethyl glyoxime chelte in ammonical medium.

5. In volumetric analysis, certain metal chelates are used as indicators. For example [Fe^{II} (*o*-phen)$_3$] chelate, called ferroin, is used as the indicator in the titration of $Cr_2O_7^{2-}$, or Ce^{4+} with Fe^{2+}.



(**a**) *Mg or Zn oxinate chelate*



(**b**) *Al oxinate chelate*

6. The formation of Ca2+ and Mg2+ - EDTA chelates is used in the determination of the total hardness of water.

7. In certain, analytical separations, chelating agents are used as masking agents. A masking agent is defined as a substance that hides certain metal ions from other reagents with which their interactions are undesired.

For example, in the gravimetric determination of Ni2+, as its DMG complex, the presence of Fe3+ gives Fe(OH)3 precipitate. Thus Fe3+ interferes in this determination.

To avoid the formation of Fe(OH)3, before the addition of DMG and ammonium hydroxide, a slight excess of tartaric acid or citric acid is added as masking agent. Fe3+ forms a very stable, water soluble Fe3+ -tartrate or Fe3+-citrate chelate complex in which iron forms a part of a complex anion.

Hence, the reaction between OH- and this complex anion is avoided. Thus the interference of Fe3+ is avoided.

Reference books

- “Concise Coordination Chemistry” by R Gopalan and V Ramalingam,2008
- “Coordination Chemistry” by D Banerjea, III rd edition, 2009.