كيمياء لاعضوية

Forurth stage students

Chemistry Department

College of science

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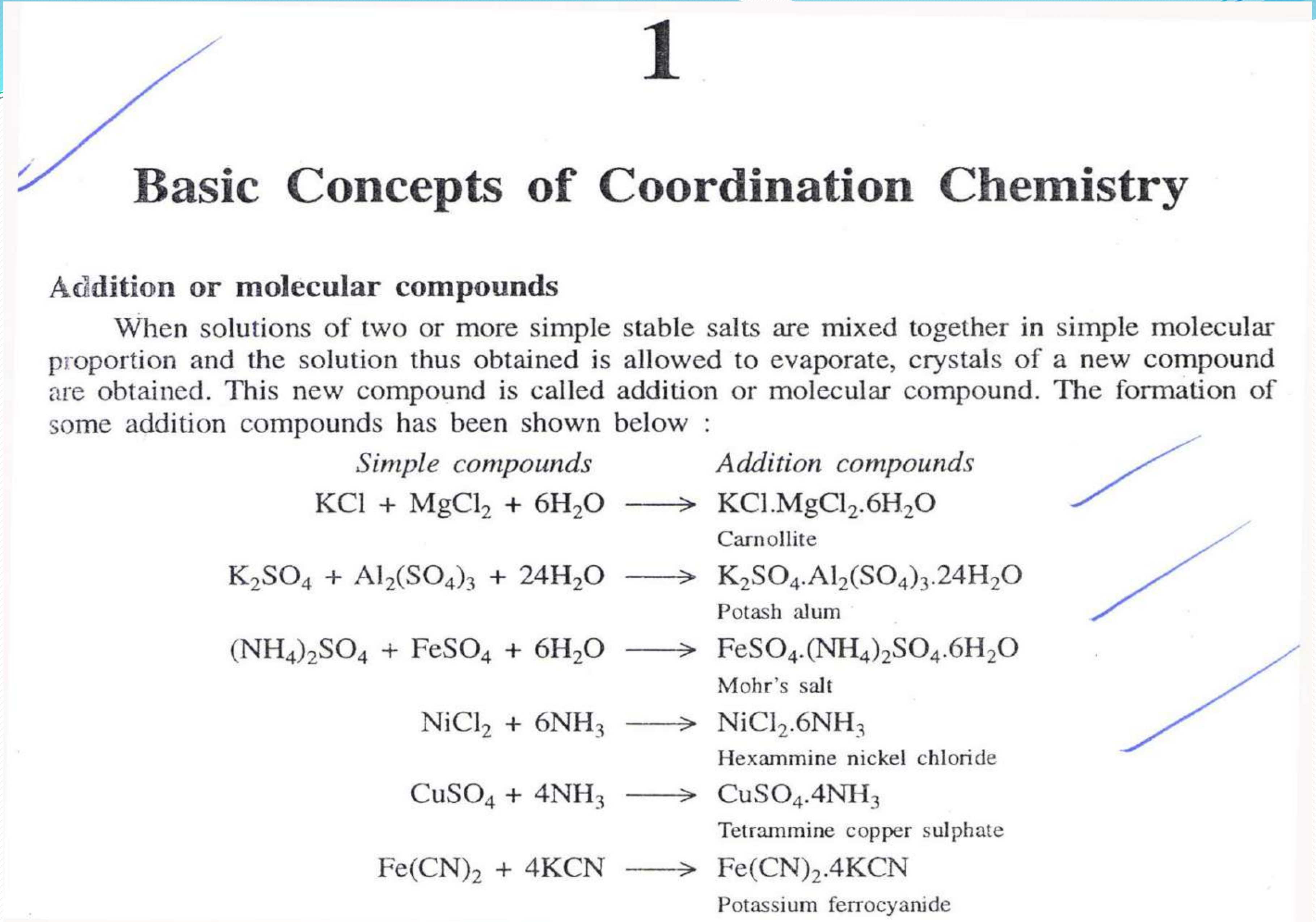

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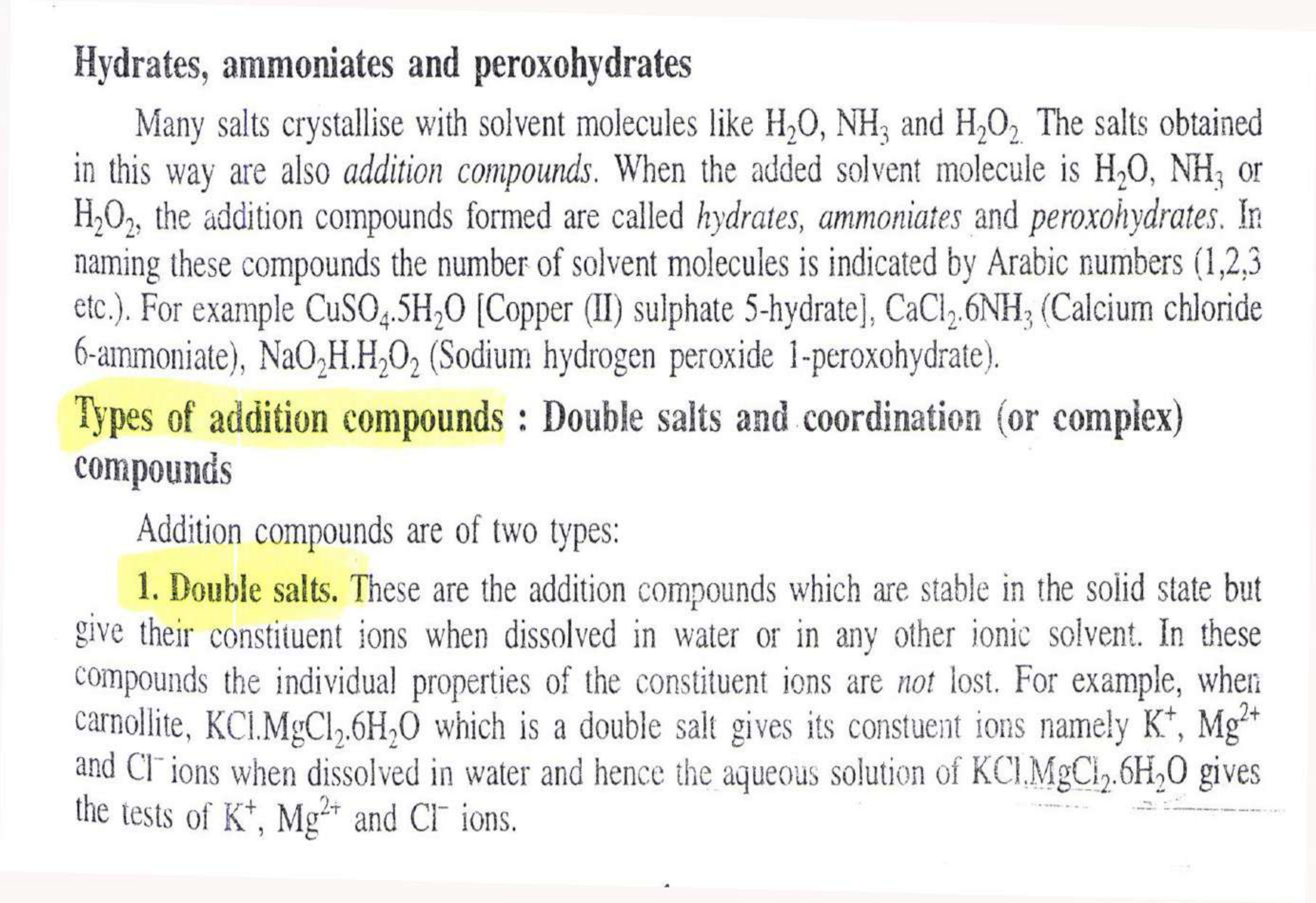
Basic Concepts of Coordination Chemistry

Addition or molecular compounds

When solutions of two or more simple stable salts are mixed together in simple molecular proportion and the solution thus obtained is allowed to evaporate, crystals of a new compound are obtained. This new compound is called addition or molecular compound. The formation of some addition compounds has been shown below :

Simple compounds		*Addition compounds*
$KCl + MgCl_2 + 6H_2O$	$\longrightarrow$	$KCl.MgCl_2.6H_2O$ Carnollite
$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$	$\longrightarrow$	$K_2SO_4.Al_2(SO_4)_3.24H_2O$ Potash alum
$(NH_4)_2SO_4 + FeSO_4 + 6H_2O$	$\longrightarrow$	$FeSO_4.(NH_4)_2SO_4.6H_2O$ Mohr's salt
$NiCl_2 + 6NH_3$	$\longrightarrow$	$NiCl_2.6NH_3$ Hexammine nickel chloride
$CuSO_4 + 4NH_3$	$\longrightarrow$	$CuSO_4.4NH_3$ Tetrammine copper sulphate
$Fe(CN)_2 + 4KCN$	$\longrightarrow$	$Fe(CN)_2.4KCN$ Potassium ferrocyanide



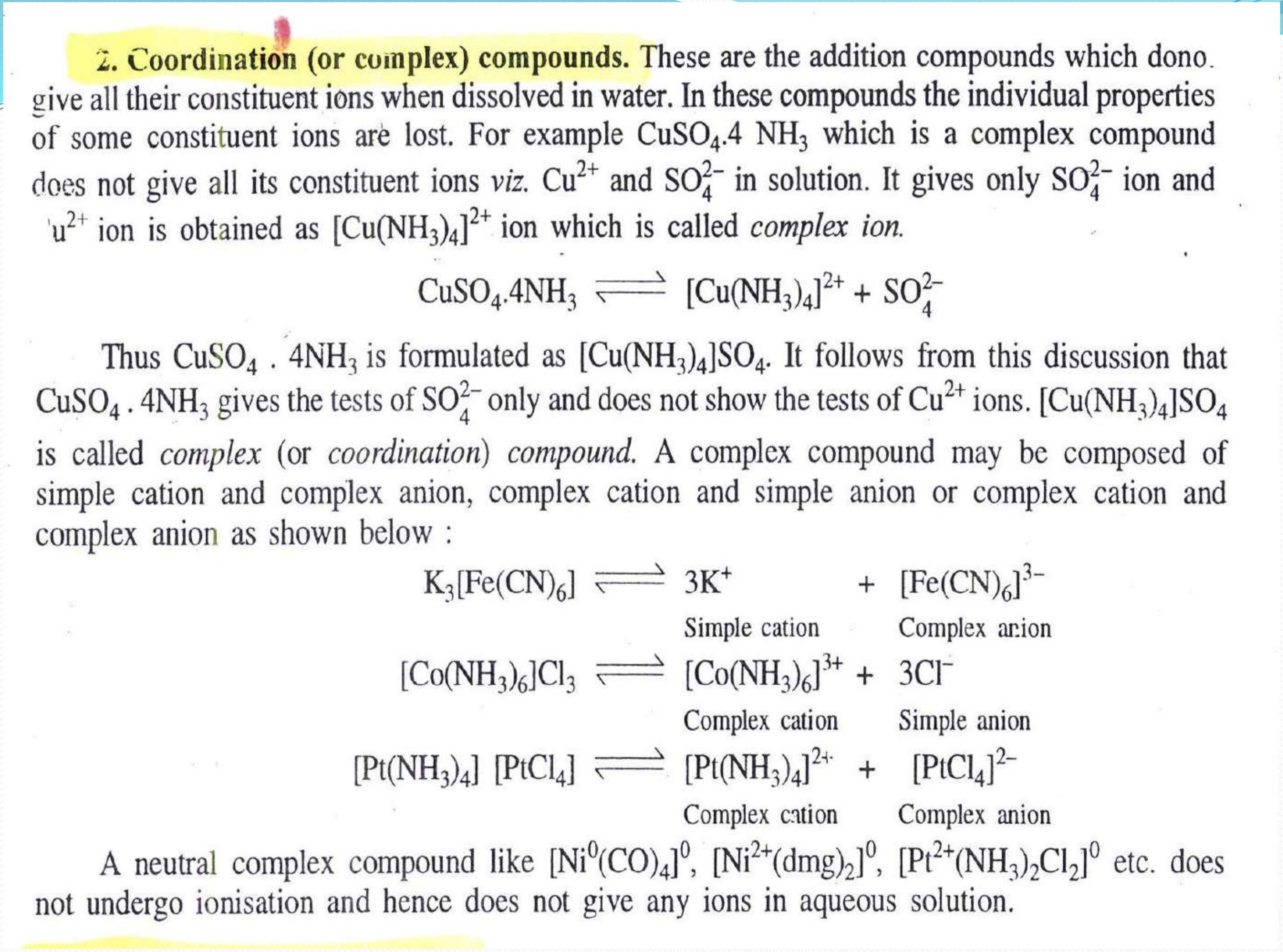
Hydrates, ammoniates and peroxohydrates

Many salts crystallise with solvent molecules like H_2O, NH_3 and H_2O_2. The salts obtained in this way are also *addition compounds*. When the added solvent molecule is H_2O, NH_3 or H_2O_2, the addition compounds formed are called *hydrates, ammoniates* and *peroxohydrates*. In naming these compounds the number of solvent molecules is indicated by Arabic numbers (1,2,3 etc.). For example $CuSO_4.5H_2O$ [Copper (II) sulphate 5-hydrate], $CaCl_2.6NH_3$ (Calcium chloride 6-ammoniate), $NaO_2H.H_2O_2$ (Sodium hydrogen peroxide 1-peroxohydrate).

Types of addition compounds : Double salts and coordination (or complex) compounds

Addition compounds are of two types:

1. Double salts. These are the addition compounds which are stable in the solid state but give their constituent ions when dissolved in water or in any other ionic solvent. In these compounds the individual properties of the constituent ions are *not* lost. For example, when carnollite, $KCl.MgCl_2.6H_2O$ which is a double salt gives its constuent ions namely K^+, Mg^{2+} and Cl^- ions when dissolved in water and hence the aqueous solution of $KCl.MgCl_2.6H_2O$ gives the tests of K^+, Mg^{2+} and Cl^- ions.



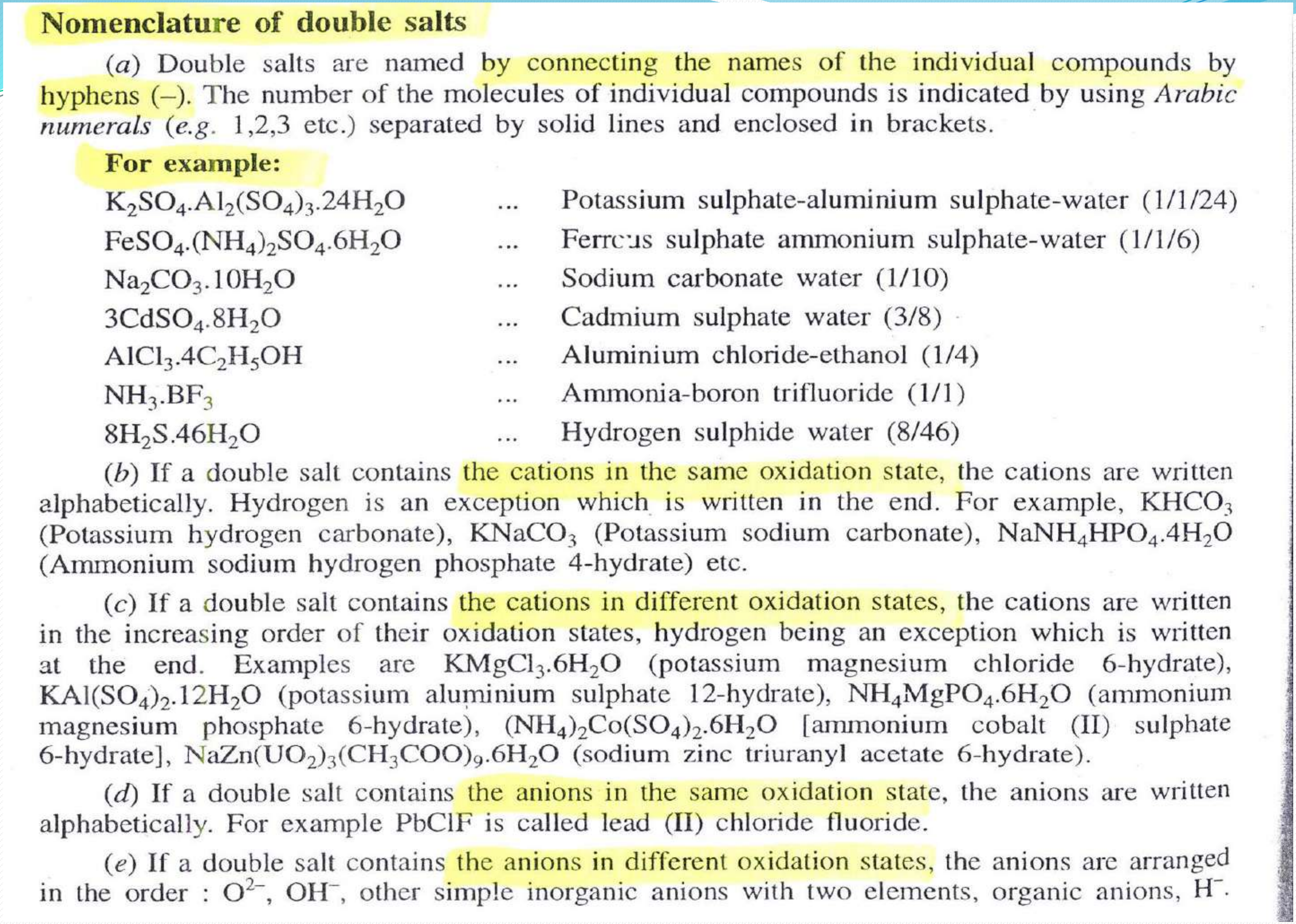
2. Coordination (or complex) compounds. These are the addition compounds which dono. give all their constituent ions when dissolved in water. In these compounds the individual properties of some constituent ions are lost. For example $CuSO_4.4\ NH_3$ which is a complex compound does not give all its constituent ions *viz.* Cu^{2+} and SO_4^{2-} in solution. It gives only SO_4^{2-} ion and u^{2+} ion is obtained as $[Cu(NH_3)_4]^{2+}$ ion which is called *complex ion.*

$$CuSO_4.4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

Thus $CuSO_4 \ .\ 4NH_3$ is formulated as $[Cu(NH_3)_4]SO_4$. It follows from this discussion that $CuSO_4\ .\ 4NH_3$ gives the tests of SO_4^{2-} only and does not show the tests of Cu^{2+} ions. $[Cu(NH_3)_4]SO_4$ is called *complex* (or *coordination*) *compound.* A complex compound may be composed of simple cation and complex anion, complex cation and simple anion or complex cation and complex anion as shown below :

$$\begin{array}{lcll} K_3[Fe(CN)_6] & \rightleftharpoons & 3K^+ & +\ [Fe(CN)_6]^{3-} \\ & & \text{Simple cation} & \text{Complex anion} \\ [Co(NH_3)_6]Cl_3 & \rightleftharpoons & [Co(NH_3)_6]^{3+} & +\ 3Cl^- \\ & & \text{Complex cation} & \text{Simple anion} \\ [Pt(NH_3)_4]\ [PtCl_4] & \rightleftharpoons & [Pt(NH_3)_4]^{2+} & +\ [PtCl_4]^{2-} \\ & & \text{Complex cation} & \text{Complex anion} \end{array}$$

A neutral complex compound like $[Ni^0(CO)_4]^0$, $[Ni^{2+}(dmg)_2]^0$, $[Pt^{2+}(NH_3)_2Cl_2]^0$ etc. does not undergo ionisation and hence does not give any ions in aqueous solution.



Nomenclature of double salts

(*a*) Double salts are named by connecting the names of the individual compounds by hyphens (–). The number of the molecules of individual compounds is indicated by using *Arabic numerals* (*e.g.* 1,2,3 etc.) separated by solid lines and enclosed in brackets.

For example:

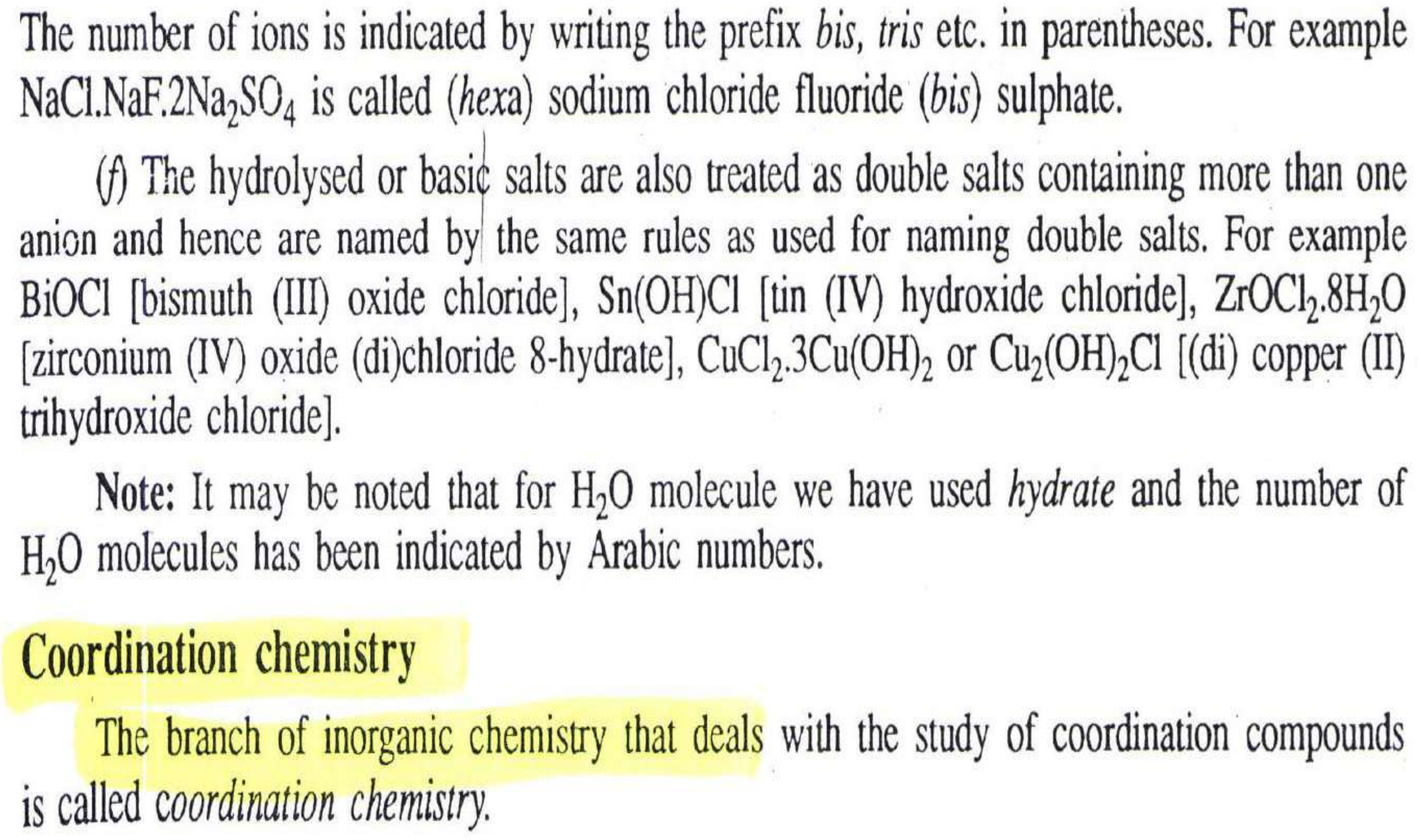
$K_2SO_4.Al_2(SO_4)_3.24H_2O$	...	Potassium sulphate-aluminium sulphate-water (1/1/24)
$FeSO_4.(NH_4)_2SO_4.6H_2O$	...	Ferrous sulphate ammonium sulphate-water (1/1/6)
$Na_2CO_3.10H_2O$	...	Sodium carbonate water (1/10)
$3CdSO_4.8H_2O$	...	Cadmium sulphate water (3/8)
$AlCl_3.4C_2H_5OH$	...	Aluminium chloride-ethanol (1/4)
$NH_3.BF_3$	...	Ammonia-boron trifluoride (1/1)
$8H_2S.46H_2O$	...	Hydrogen sulphide water (8/46)

(*b*) If a double salt contains the cations in the same oxidation state, the cations are written alphabetically. Hydrogen is an exception which is written in the end. For example, $KHCO_3$ (Potassium hydrogen carbonate), $KNaCO_3$ (Potassium sodium carbonate), $NaNH_4HPO_4.4H_2O$ (Ammonium sodium hydrogen phosphate 4-hydrate) etc.

(*c*) If a double salt contains the cations in different oxidation states, the cations are written in the increasing order of their oxidation states, hydrogen being an exception which is written at the end. Examples are $KMgCl_3.6H_2O$ (potassium magnesium chloride 6-hydrate), $KAl(SO_4)_2.12H_2O$ (potassium aluminium sulphate 12-hydrate), $NH_4MgPO_4.6H_2O$ (ammonium magnesium phosphate 6-hydrate), $(NH_4)_2Co(SO_4)_2.6H_2O$ [ammonium cobalt (II) sulphate 6-hydrate], $NaZn(UO_2)_3(CH_3COO)_9.6H_2O$ (sodium zinc triuranyl acetate 6-hydrate).

(*d*) If a double salt contains the anions in the same oxidation state, the anions are written alphabetically. For example PbClF is called lead (II) chloride fluoride.

(*e*) If a double salt contains the anions in different oxidation states, the anions are arranged in the order : O^{2-}, OH^-, other simple inorganic anions with two elements, organic anions, H^-.



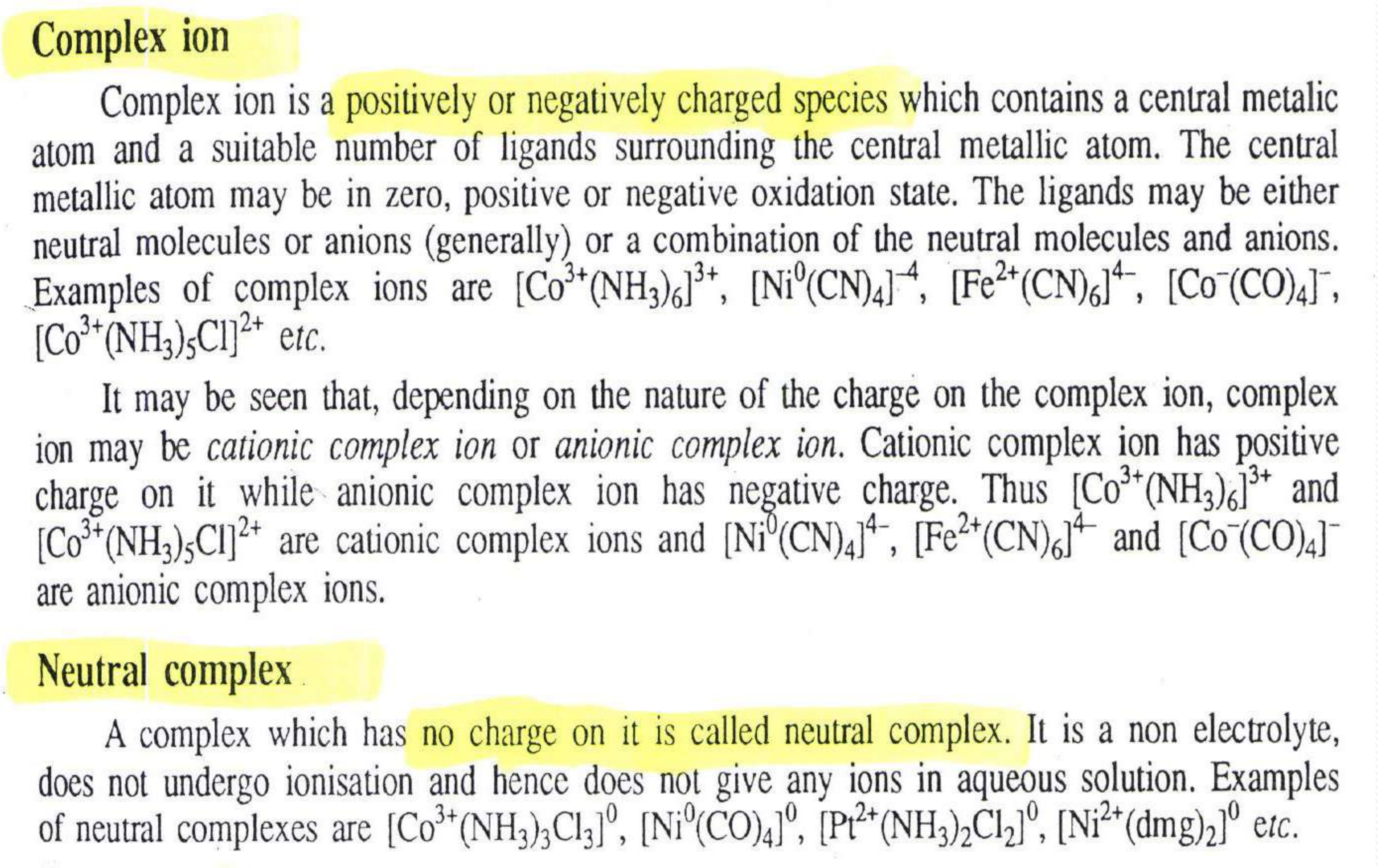
The number of ions is indicated by writing the prefix *bis*, *tris* etc. in parentheses. For example $NaCl.NaF.2Na_2SO_4$ is called (*hexa*) sodium chloride fluoride (*bis*) sulphate.

(*f*) The hydrolysed or basic salts are also treated as double salts containing more than one anion and hence are named by the same rules as used for naming double salts. For example BiOCl [bismuth (III) oxide chloride], Sn(OH)Cl [tin (IV) hydroxide chloride], $ZrOCl_2.8H_2O$ [zirconium (IV) oxide (di)chloride 8-hydrate], $CuCl_2.3Cu(OH)_2$ or $Cu_2(OH)_2Cl$ [(di) copper (II) trihydroxide chloride].

Note: It may be noted that for H_2O molecule we have used *hydrate* and the number of H_2O molecules has been indicated by Arabic numbers.

Coordination chemistry

The branch of inorganic chemistry that deals with the study of coordination compounds is called *coordination chemistry*.



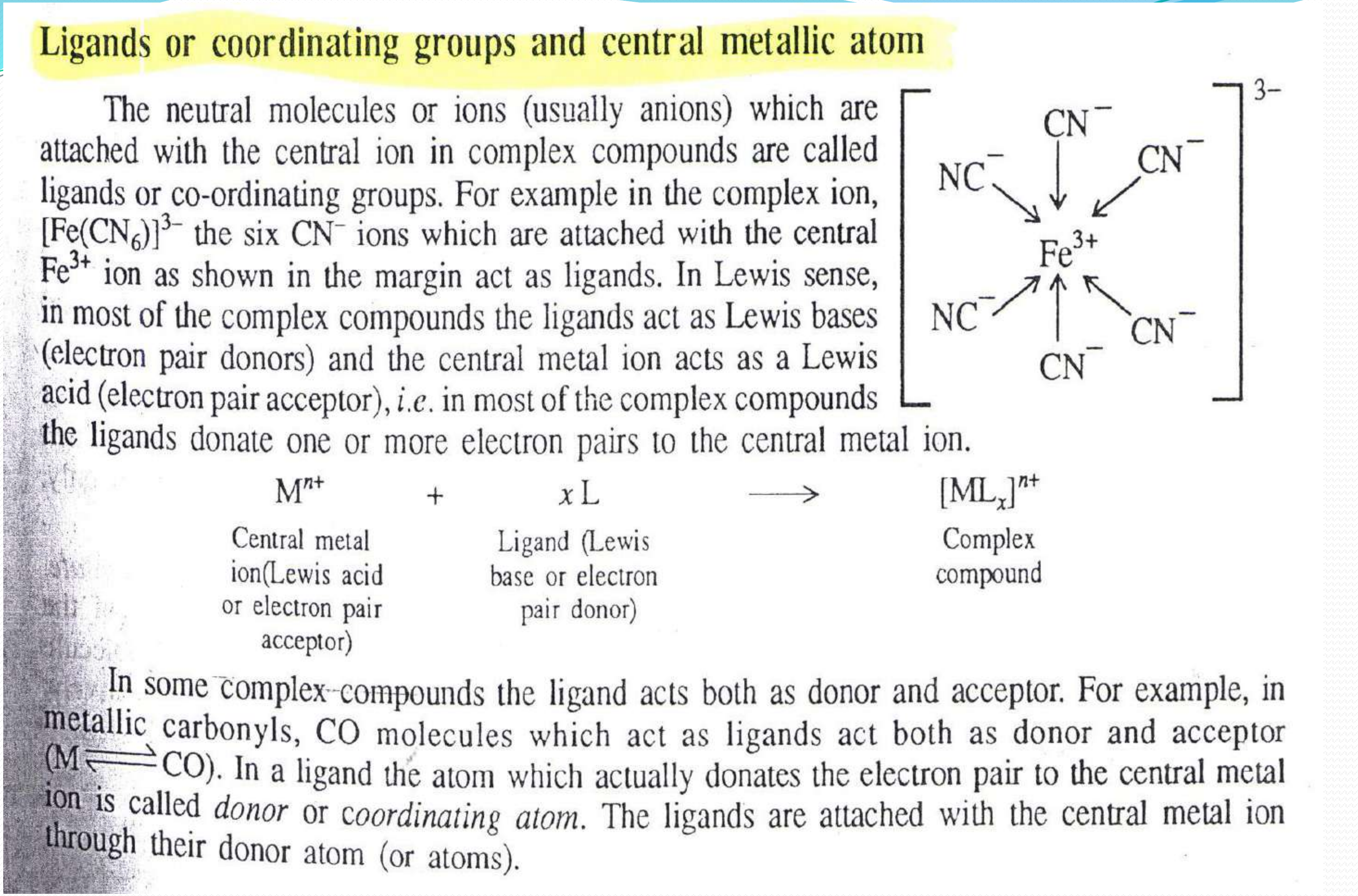
Complex ion

Complex ion is a positively or negatively charged species which contains a central metalic atom and a suitable number of ligands surrounding the central metallic atom. The central metallic atom may be in zero, positive or negative oxidation state. The ligands may be either neutral molecules or anions (generally) or a combination of the neutral molecules and anions. Examples of complex ions are $[Co^{3+}(NH_3)_6]^{3+}$, $[Ni^0(CN)_4]^{-4}$, $[Fe^{2+}(CN)_6]^{4-}$, $[Co^-(CO)_4]^-$, $[Co^{3+}(NH_3)_5Cl]^{2+}$ *etc.*

It may be seen that, depending on the nature of the charge on the complex ion, complex ion may be *cationic complex ion* or *anionic complex ion*. Cationic complex ion has positive charge on it while anionic complex ion has negative charge. Thus $[Co^{3+}(NH_3)_6]^{3+}$ and $[Co^{3+}(NH_3)_5Cl]^{2+}$ are cationic complex ions and $[Ni^0(CN)_4]^{4-}$, $[Fe^{2+}(CN)_6]^{4-}$ and $[Co^-(CO)_4]^-$ are anionic complex ions.

Neutral complex

A complex which has no charge on it is called neutral complex. It is a non electrolyte, does not undergo ionisation and hence does not give any ions in aqueous solution. Examples of neutral complexes are $[Co^{3+}(NH_3)_3Cl_3]^0$, $[Ni^0(CO)_4]^0$, $[Pt^{2+}(NH_3)_2Cl_2]^0$, $[Ni^{2+}(dmg)_2]^0$ *etc.*

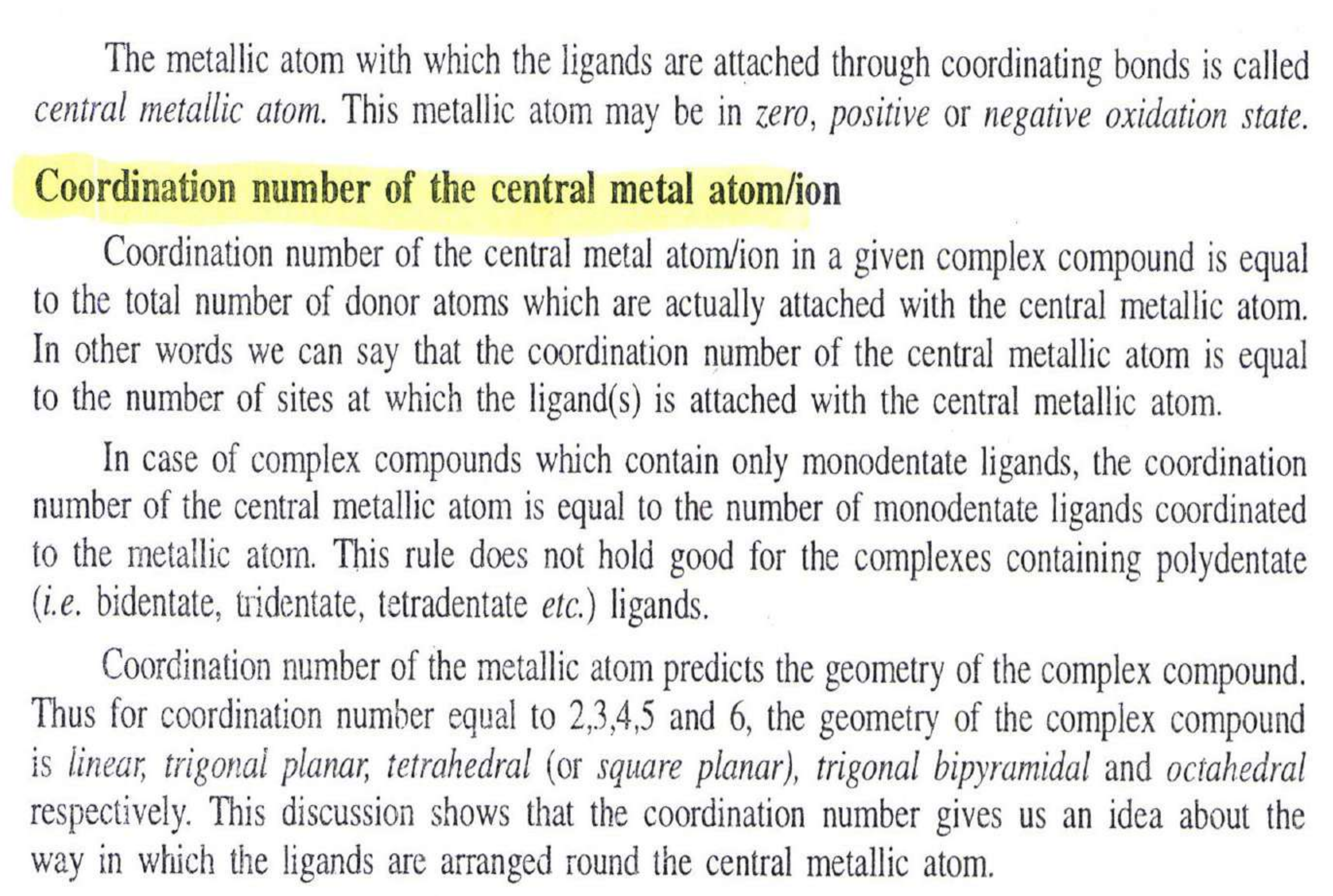


Ligands or coordinating groups and central metallic atom

The neutral molecules or ions (usually anions) which are attached with the central ion in complex compounds are called ligands or co-ordinating groups. For example in the complex ion, $[Fe(CN_6)]^{3-}$ the six CN^- ions which are attached with the central Fe^{3+} ion as shown in the margin act as ligands. In Lewis sense, in most of the complex compounds the ligands act as Lewis bases (electron pair donors) and the central metal ion acts as a Lewis acid (electron pair acceptor), *i.e.* in most of the complex compounds the ligands donate one or more electron pairs to the central metal ion.

$$\underset{\text{Central metal ion(Lewis acid or electron pair acceptor)}}{M^{n+}} + \underset{\text{Ligand (Lewis base or electron pair donor)}}{x\,L} \longrightarrow \underset{\text{Complex compound}}{[ML_x]^{n+}}$$

In some complex compounds the ligand acts both as donor and acceptor. For example, in metallic carbonyls, CO molecules which act as ligands act both as donor and acceptor ($M \rightleftarrows CO$). In a ligand the atom which actually donates the electron pair to the central metal ion is called *donor* or *coordinating atom*. The ligands are attached with the central metal ion through their donor atom (or atoms).



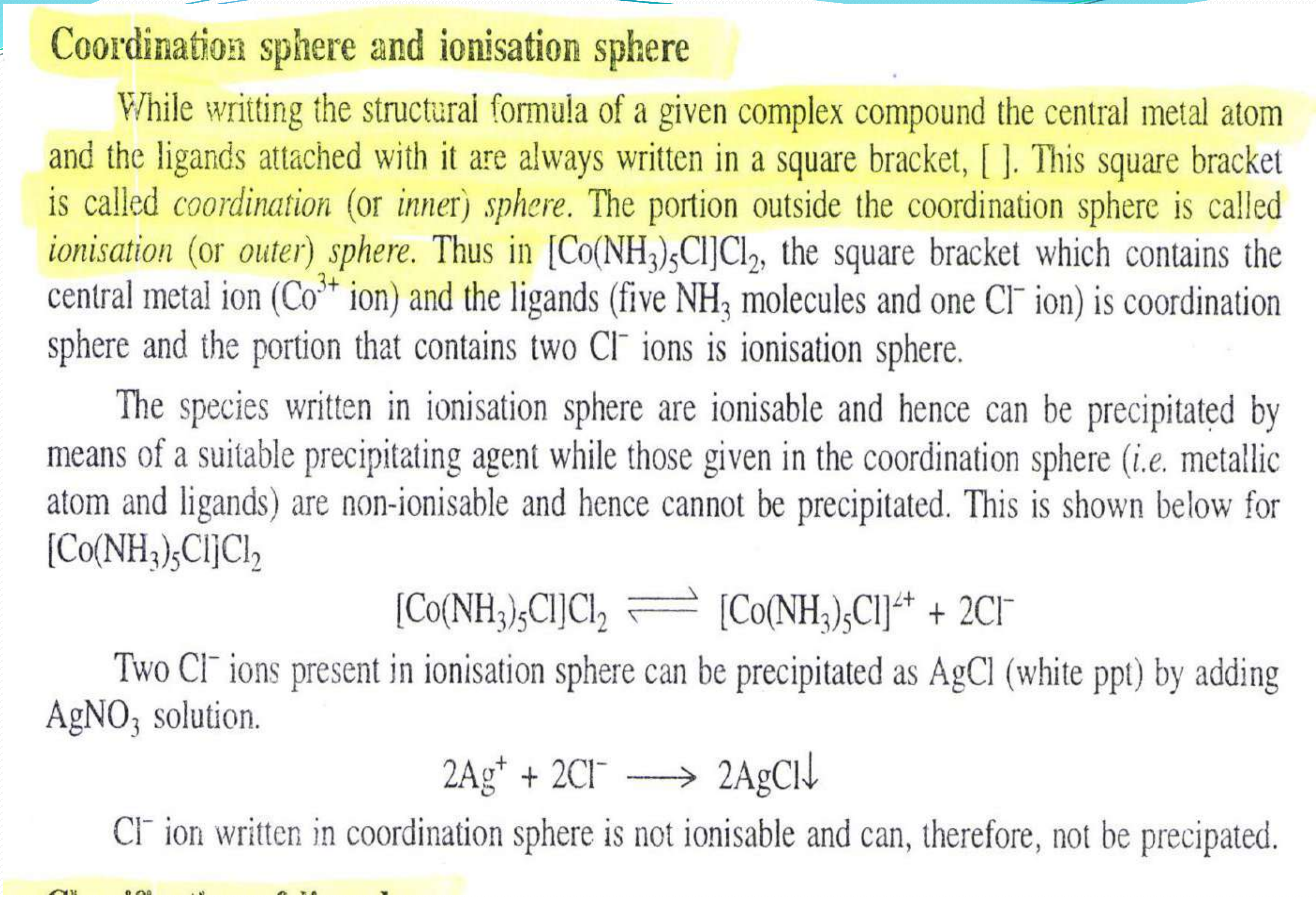
The metallic atom with which the ligands are attached through coordinating bonds is called *central metallic atom*. This metallic atom may be in *zero*, *positive* or *negative oxidation state.*

Coordination number of the central metal atom/ion

Coordination number of the central metal atom/ion in a given complex compound is equal to the total number of donor atoms which are actually attached with the central metallic atom. In other words we can say that the coordination number of the central metallic atom is equal to the number of sites at which the ligand(s) is attached with the central metallic atom.

In case of complex compounds which contain only monodentate ligands, the coordination number of the central metallic atom is equal to the number of monodentate ligands coordinated to the metallic atom. This rule does not hold good for the complexes containing polydentate (*i.e.* bidentate, tridentate, tetradentate *etc.*) ligands.

Coordination number of the metallic atom predicts the geometry of the complex compound. Thus for coordination number equal to 2,3,4,5 and 6, the geometry of the complex compound is *linear, trigonal planar, tetrahedral* (or *square planar*), *trigonal bipyramidal* and *octahedral* respectively. This discussion shows that the coordination number gives us an idea about the way in which the ligands are arranged round the central metallic atom.



Coordination sphere and ionisation sphere

While writting the structural formula of a given complex compound the central metal atom and the ligands attached with it are always written in a square bracket, [ ]. This square bracket is called *coordination* (or *inner*) *sphere*. The portion outside the coordination sphere is called *ionisation* (or *outer*) *sphere*. Thus in $[Co(NH_3)_5Cl]Cl_2$, the square bracket which contains the central metal ion (Co^{3+} ion) and the ligands (five NH_3 molecules and one Cl^- ion) is coordination sphere and the portion that contains two Cl^- ions is ionisation sphere.

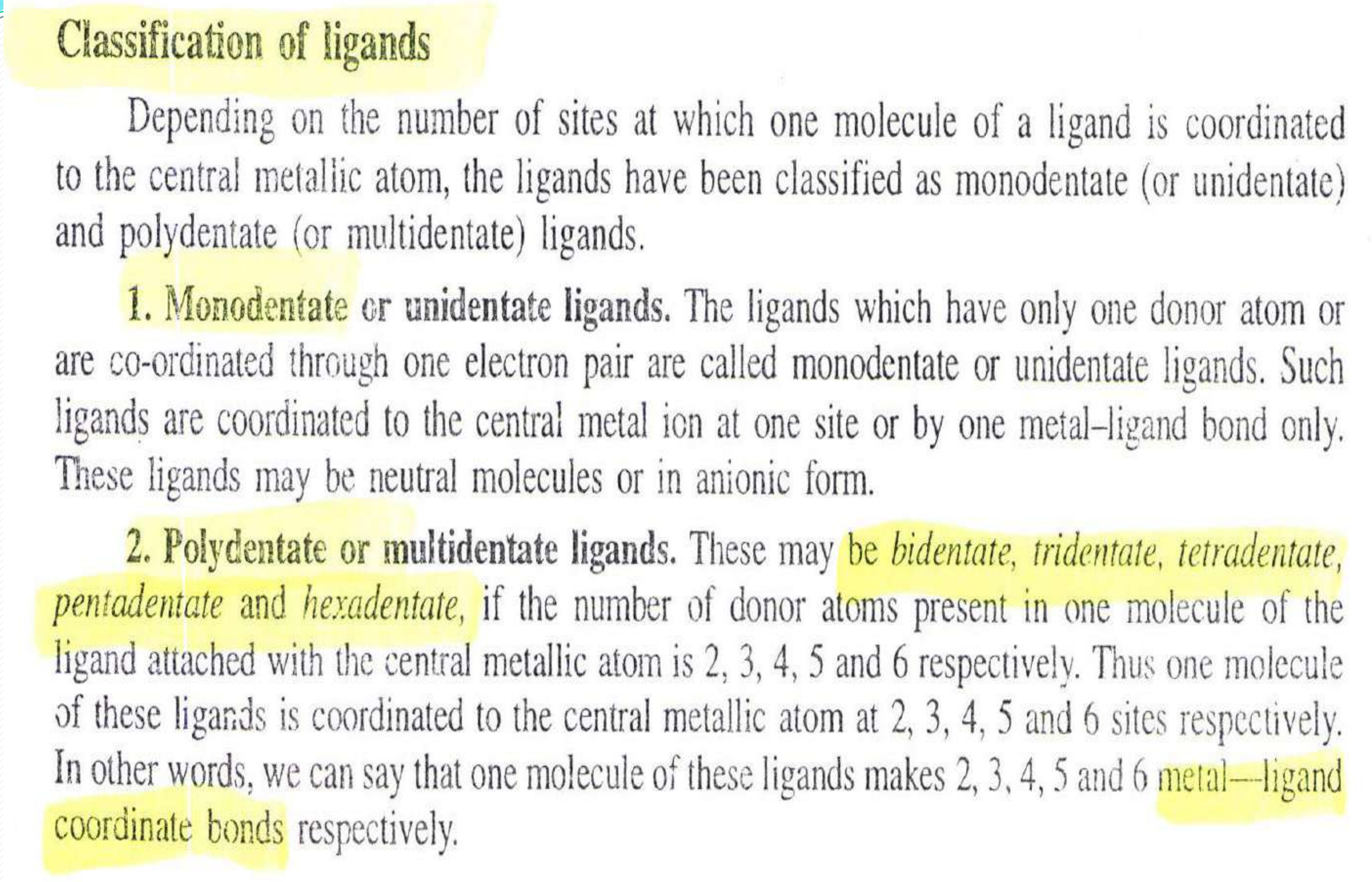
The species written in ionisation sphere are ionisable and hence can be precipitated by means of a suitable precipitating agent while those given in the coordination sphere (*i.e.* metallic atom and ligands) are non-ionisable and hence cannot be precipitated. This is shown below for $[Co(NH_3)_5Cl]Cl_2$

$$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

Two Cl^- ions present in ionisation sphere can be precipitated as AgCl (white ppt) by adding $AgNO_3$ solution.

$$2Ag^+ + 2Cl^- \longrightarrow 2AgCl\downarrow$$

Cl^- ion written in coordination sphere is not ionisable and can, therefore, not be precipated.

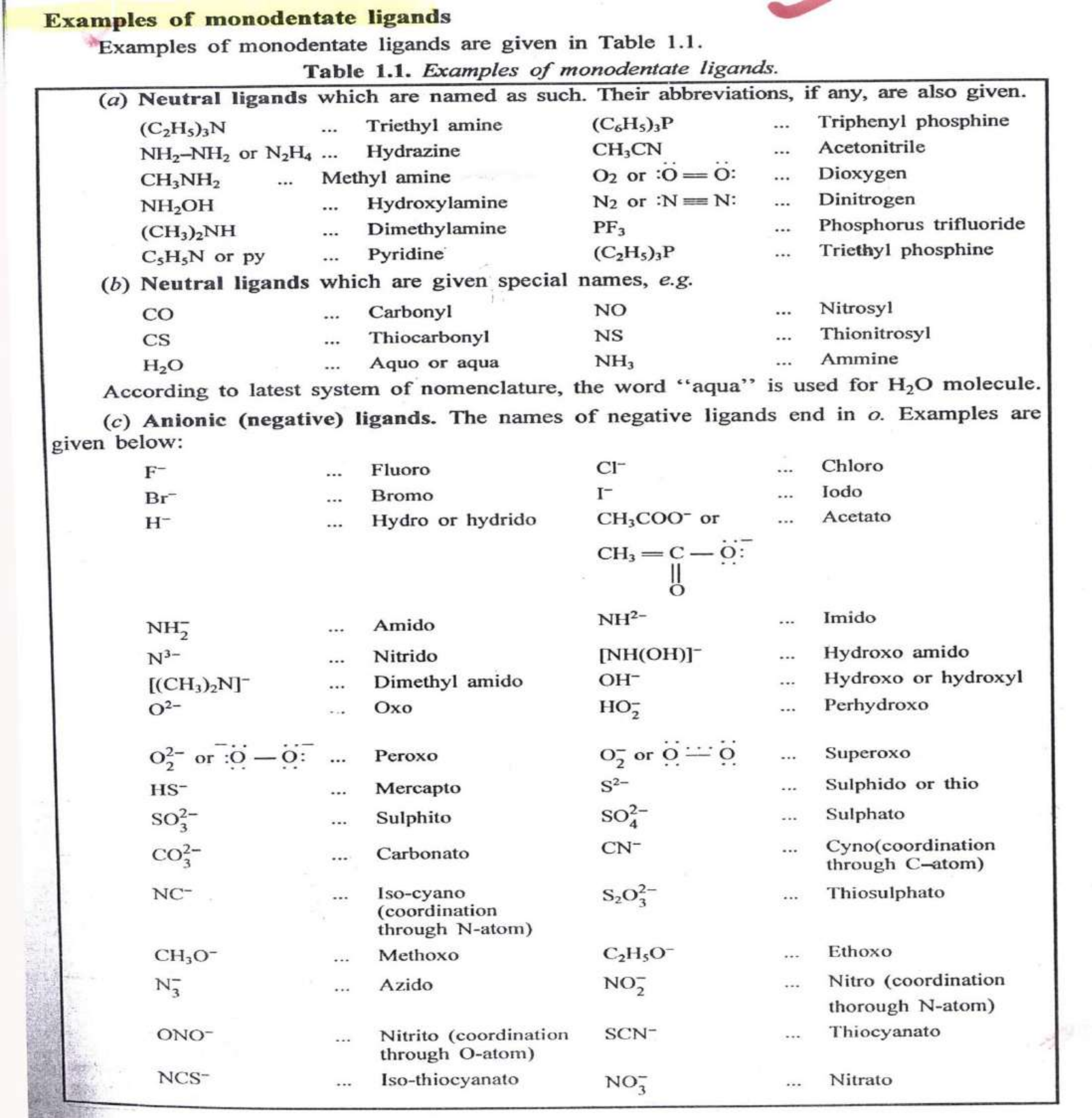


Classification of ligands

Depending on the number of sites at which one molecule of a ligand is coordinated to the central metallic atom, the ligands have been classified as monodentate (or unidentate) and polydentate (or multidentate) ligands.

1. Monodentate or unidentate ligands. The ligands which have only one donor atom or are co-ordinated through one electron pair are called monodentate or unidentate ligands. Such ligands are coordinated to the central metal ion at one site or by one metal–ligand bond only. These ligands may be neutral molecules or in anionic form.

2. Polydentate or multidentate ligands. These may be *bidentate*, *tridentate*, *tetradentate*, *pentadentate* and *hexadentate*, if the number of donor atoms present in one molecule of the ligand attached with the central metallic atom is 2, 3, 4, 5 and 6 respectively. Thus one molecule of these ligands is coordinated to the central metallic atom at 2, 3, 4, 5 and 6 sites respectively. In other words, we can say that one molecule of these ligands makes 2, 3, 4, 5 and 6 metal—ligand coordinate bonds respectively.



Examples of monodentate ligands

Examples of monodentate ligands are given in Table 1.1.

Table 1.1. *Examples of monodentate ligands.*

(*a*) **Neutral ligands** which are named as such. Their abbreviations, if any, are also given.

$(C_2H_5)_3N$	Triethyl amine	$(C_6H_5)_3P$	Triphenyl phosphine
$NH_2{-}NH_2$ or N_2H_4	Hydrazine	CH_3CN	Acetonitrile
CH_3NH_2	Methyl amine	O_2 or $:\ddot{O}=\ddot{O}:$	Dioxygen
NH_2OH	Hydroxylamine	N_2 or $:N\equiv N:$	Dinitrogen
$(CH_3)_2NH$	Dimethylamine	PF_3	Phosphorus trifluoride
C_5H_5N or py	Pyridine	$(C_2H_5)_3P$	Triethyl phosphine

(*b*) **Neutral ligands** which are given special names, *e.g.*

CO	Carbonyl	NO	Nitrosyl
CS	Thiocarbonyl	NS	Thionitrosyl
H_2O	Aquo or aqua	NH_3	Ammine

According to latest system of nomenclature, the word "aqua" is used for H_2O molecule.

(*c*) **Anionic (negative) ligands.** The names of negative ligands end in *o*. Examples are given below:

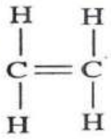
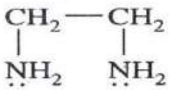
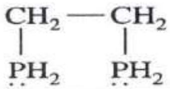
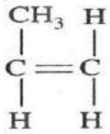
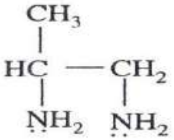
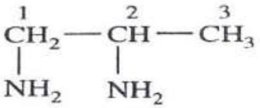
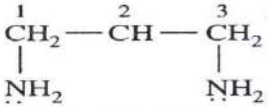
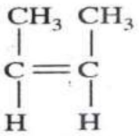
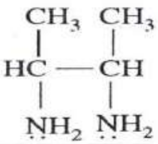
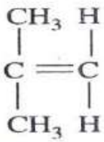
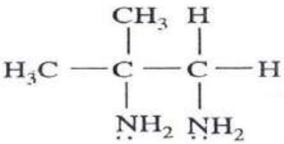
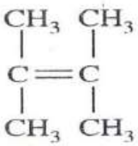
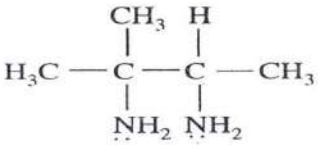
F^-	Fluoro	Cl^-	Chloro
Br^-	Bromo	I^-	Iodo
H^-	Hydro or hydrido	CH_3COO^- or $CH_3=\underset{\underset{O}{\Vert}}{C}-\ddot{O}:^-$	Acetato
NH_2^-	Amido	NH^{2-}	Imido
N^{3-}	Nitrido	$[NH(OH)]^-$	Hydroxo amido
$[(CH_3)_2N]^-$	Dimethyl amido	OH^-	Hydroxo or hydroxyl
O^{2-}	Oxo	HO_2^-	Perhydroxo
O_2^{2-} or $^-:\ddot{O}-\ddot{O}:^-$	Peroxo	O_2^- or $\ddot{O}\cdots\ddot{O}$	Superoxo
HS^-	Mercapto	S^{2-}	Sulphido or thio
SO_3^{2-}	Sulphito	SO_4^{2-}	Sulphato
CO_3^{2-}	Carbonato	CN^-	Cyno(coordination through C–atom)
NC^-	Iso-cyano (coordination through N-atom)	$S_2O_3^{2-}$	Thiosulphato
CH_3O^-	Methoxo	$C_2H_5O^-$	Ethoxo
N_3^-	Azido	NO_2^-	Nitro (coordination thorough N-atom)
ONO^-	Nitrito (coordination through O-atom)	SCN^-	Thiocyanato
NCS^-	Iso-thiocyanato	NO_3^-	Nitrato

Examples of bidentate ligands

Bidentate ligends may be neutral molecules or anions.

1. Alkenes like ethylene, propylene, butylene and isobutylene give a number of diamine derivatives which have been found to act as bidentate ligands as shown in Table 1.2.

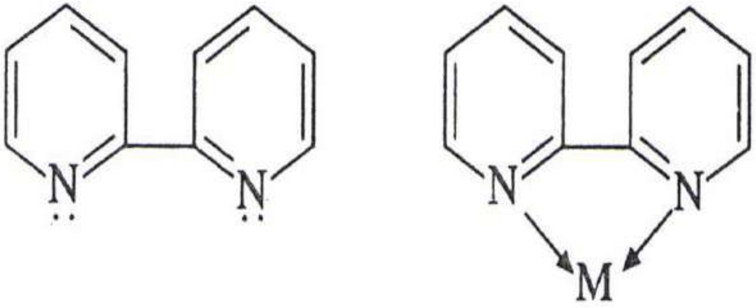
Table 1.2. *Bidentate ligands derived from alkenes.*

Alkenes	*Bidentate ligands*
Ethylene  $\begin{array}{ccc} H & & H \\ \vert & & \vert \\ C & = & C \\ \vert & & \vert \\ H & & H \end{array}$	Ethylene diamine (*en*)  $\begin{array}{ccc} CH_2 & - & CH_2 \\ \vert & & \vert \\ NH_2 & & NH_2 \end{array}$ Ethylene diphosphine (*diphos*)  $\begin{array}{ccc} CH_2 & - & CH_2 \\ \vert & & \vert \\ PH_2 & & PH_2 \end{array}$
Propylene  $\begin{array}{ccc} CH_3 & & H \\ \vert & & \vert \\ C & = & C \\ \vert & & \vert \\ H & & H \end{array}$	Propylene diamine (*pn*)  $\begin{array}{ccc} CH_3 & & \\ \vert & & \\ HC & - & CH_2 \\ \vert & & \vert \\ NH_2 & & NH_2 \end{array}$ This compound is also called 1, 2-diamino propane (*pn*)  $\begin{array}{ccccc} \overset{1}{CH_2} & - & \overset{2}{CH} & - & \overset{3}{CH_3} \\ \vert & & \vert & & \\ NH_2 & & NH_2 & & \end{array}$, since the structure of propane is $CH_3-CH_2-CH_3$ 1, 3-diamino propane or trimethylene diamine (*tn*)  $\begin{array}{ccccc} \overset{1}{CH_2} & - & \overset{2}{CH} & - & \overset{3}{CH_2} \\ \vert & & & & \vert \\ NH_2 & & & & NH_2 \end{array}$
Butylene  $\begin{array}{ccc} CH_3 & & CH_3 \\ \vert & & \vert \\ C & = & C \\ \vert & & \vert \\ H & & H \end{array}$	Butylene diamine (*bn*)  $\begin{array}{ccc} CH_3 & & CH_3 \\ \vert & & \vert \\ HC & - & CH \\ \vert & & \vert \\ NH_2 & & NH_2 \end{array}$
Isobutylene  $\begin{array}{ccc} CH_3 & & H \\ \vert & & \vert \\ C & = & C \\ \vert & & \vert \\ CH_3 & & H \end{array}$	Isobutylene diamine (*i-bn*)  $\begin{array}{ccccccc} & & CH_3 & & H & & \\ & & \vert & & \vert & & \\ H_3C & - & C & - & C & - & H \\ & & \vert & & \vert & & \\ & & NH_2 & & NH_2 & & \end{array}$
Tetramethyl ethylene  $\begin{array}{ccc} CH_3 & & CH_3 \\ \vert & & \vert \\ C & = & C \\ \vert & & \vert \\ CH_3 & & CH_3 \end{array}$	Tetramethyl ethylene diamine (*tetrameen*)  $\begin{array}{ccccccc} & & CH_3 & & H & & \\ & & \vert & & \vert & & \\ H_3C & - & C & - & C & - & CH_3 \\ & & \vert & & \vert & & \\ & & NH_2 & & NH_2 & & \end{array}$

Ethylene diphosphine (*diphos*) has two P-atoms which oct as donor atoms, since they have one lone pair of electrons each. The coordination of this ligand to the central metal atom takes place through these two P-atoms, leading to the formation of one 5-membered ring.

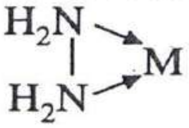
Each of the diamines gets attached with the central metal atom through its two N-atoms (donor atoms), forming one 5-membered ring including the central metal atom. This is evident from the structures of $[Co^{3+}(en)_2Cl_2]^+$ and $[Pt^{2+}(bn)_2]^{2+}$ ions given in Fig. 1.20 (see symmetrical and unsymmetrical bidentate ligands).

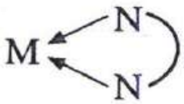
2. 2, 2-bipyridine (bipy) (also called **bipyridyl**). It is a neutral molecule and has two N-atoms which act as donor atoms as shown at (*a*) of Fig. 1.1. When this ligand gets linked with a metal atom M, 5-membered ring is obtained [See (*b*) of Fig. 1.1].

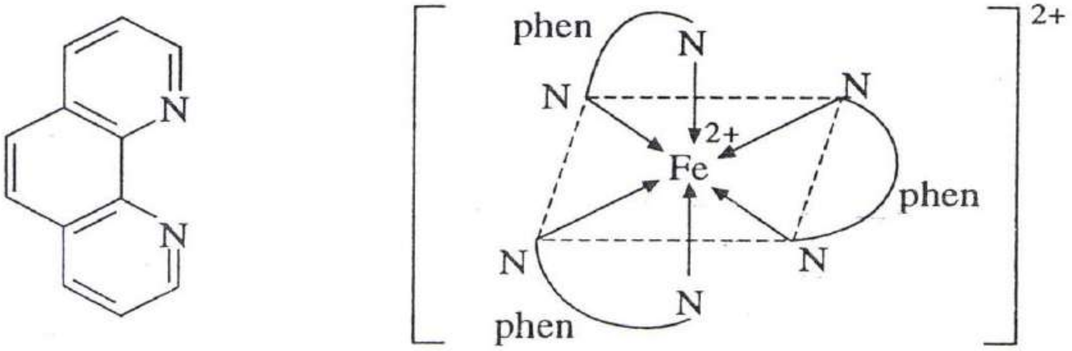


(*a*) (*b*)

Fig. 1.1. (*a*) Structure of 2,2′-bipyridine (bipy) or bipyridyl (*b*) Attachment of bipy with the central metal atom, M.

3. Hydrazine, $\ddot{N}H_2$—$\ddot{N}H_2$. Its attachment to a metal atom occurs through its two N-atoms, forming one 3-membered ring which can be represented as  . This ring is very strained and hence is unstable.

4. o-phenanthroline or 1, 10-phenanthroline (o-phen or phen or phenan). It is a neutral symmetrical bidentate ligand, since its two donor atoms *viz.* N-atoms are similar atoms. Its structure is given at (*a*) of Fig. 1.2. It is abbreviated as *phen* or *phenan*. When it gets attached with a metal atom, it is denoted as  *phen* and its attachment to a metal atom, *M* is indicated as  *phen*. For example this ligand gets attached with Fe^{2+} ion and gives $[Fe(phen)_3]^{2+}$ complex ion whose structure is given at (*b*) of Fig. 1.2.



(*a*) (*b*)

Fig. 1.2. (*a*) Structure of o-phenonthroline (phen or phenon) (*b*) structure of $[Fe(phen)_3]^{2+}$ ion.

5. o-phenylene bis dimethyl arsine (diars or D). The structure and the mode of its attachment with the central metal atom in complexes are shown in Fig. 1.3. Here two As atoms are donor atoms.

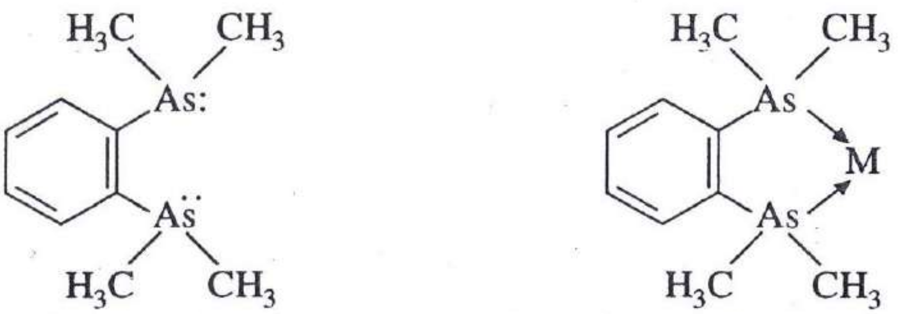
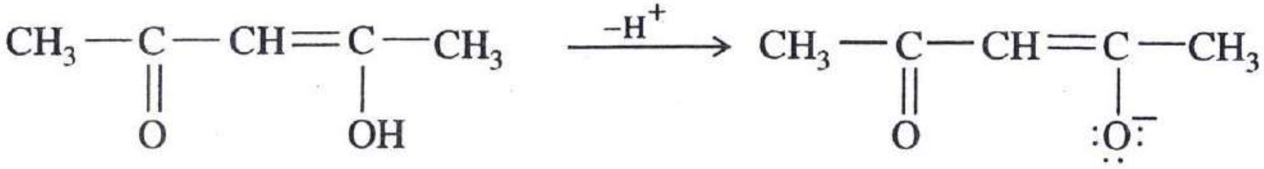


Fig. 1.3. (*a*) Structure of *o*-phenylene *bis* dimethyl arsine (diars or D) (*b*) Mode of attachment of diars with a metal atom, M in complex compounds.

6. Acetylacetonato ion (acac⁻). This ion is obtained when one molecule of the enol form of acetyl acetone (Hacac) loses a proton, H^+ (see Fig. 1.4).



$$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CH_3 \xrightarrow{-H^+} CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{:\ddot{O}:^-}{|}}{C}-CH_3$$

Fig. 1.4. To get *acac*⁻ ion from Hacac molecule.

This ligand gets attached with the central metal atom through its two O-atoms and forms a chelated complex having one 6-membered ring as shown in Fig. 1.5.

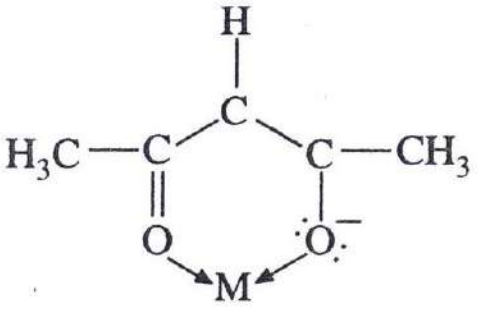
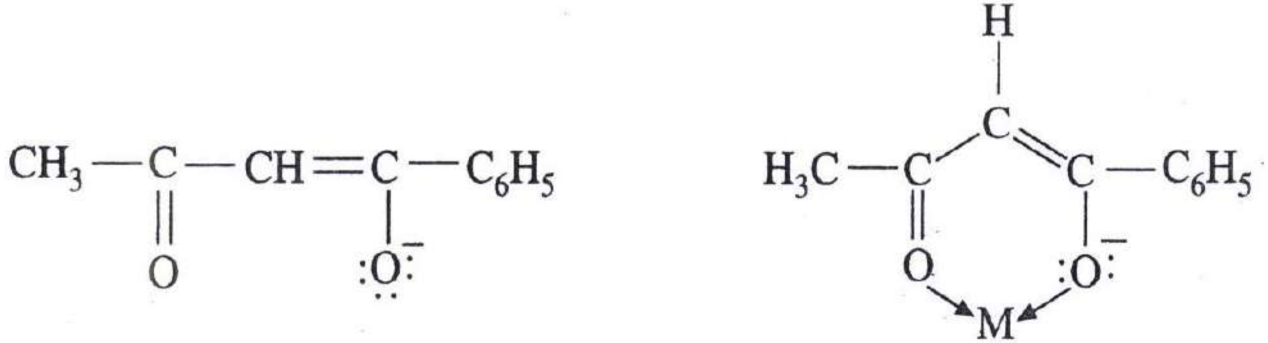


Fig. 1.5. Mode of attachment of acetylacetonato ion to the metal atom, M.

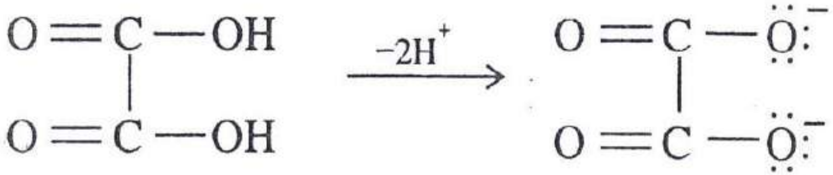
7. Benzoyl acetonato ion. The structure of this ligand and the mode of its attachment with the cental metal atom can be shown as depicted in Fig. 1.6.



(*a*) (*b*)

Fig. 1.6. (*a*) Structure of benzoyl acetonato ion (*b*) Mode of attachment of benzoyl acetonato ion to the metal atom, M.

8. Oxalato ion, $C_2O_4^{2-}$ (**ox^{2-}**). This ion can be obtained when one molecule of oxalic acid ($H_2C_2O_4$ or H_2*ox*) loses two protons (see Fig. 1.7).

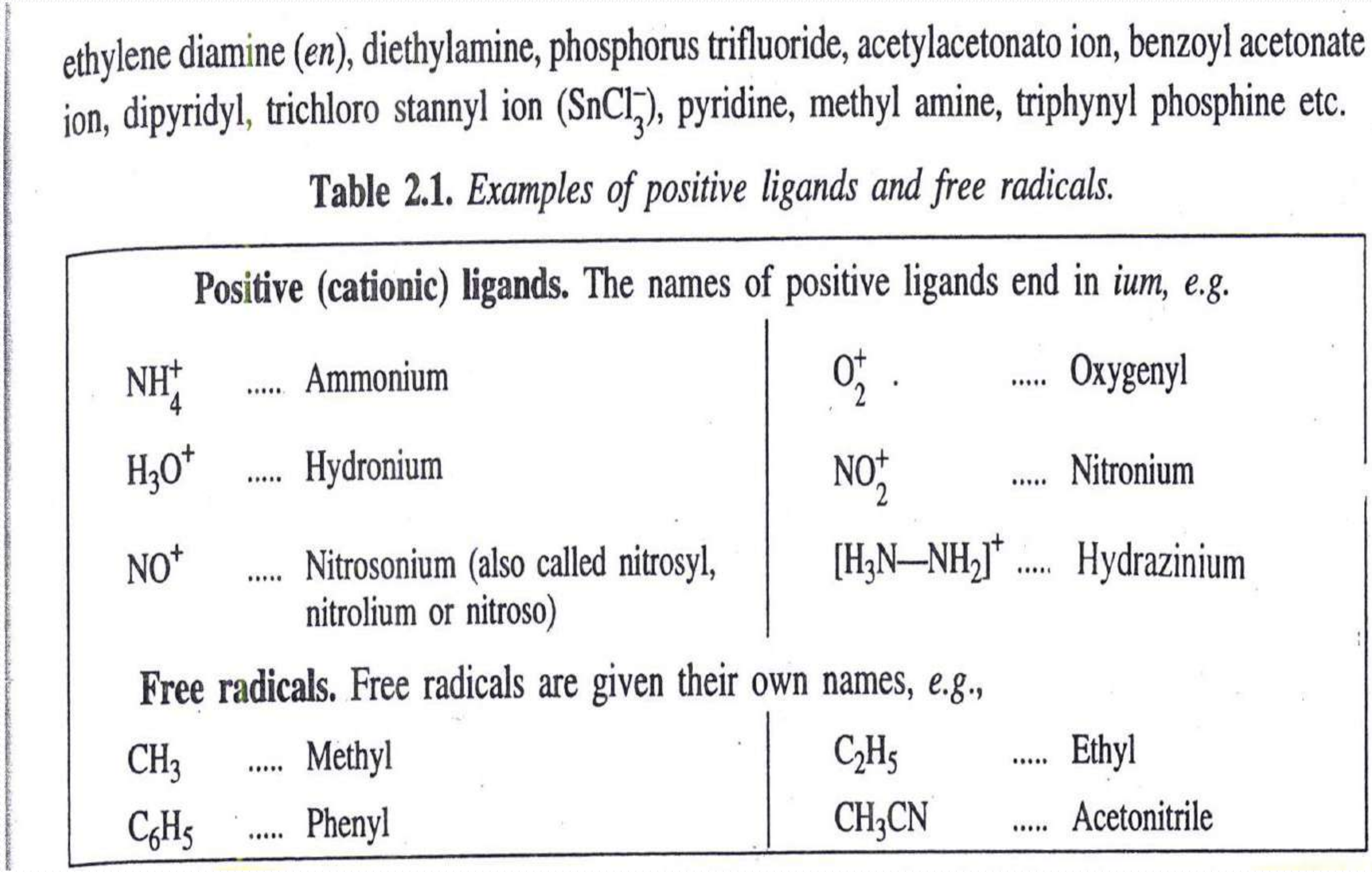


H_2*ox* molecule

ox^{2-} molecule

Fig. 1.7. To get *ox*$^{2-}$ ion from H2*ox* molecule.

$C_2O_4^{2-}$ (ox^{2-}) is a bidentate dibasic ligand and its coordination to the central metal atom



ethylene diamine (*en*), diethylamine, phosphorus trifluoride, acetylacetonato ion, benzoyl acetonate ion, dipyridyl, trichloro stannyl ion ($SnCl_3^-$), pyridine, methyl amine, triphynyl phosphine etc.

Table 2.1. *Examples of positive ligands and free radicals.*

Positive (cationic) ligands. The names of positive ligands end in *ium, e.g.*

NH_4^+	Ammonium	O_2^+	Oxygenyl
H_3O^+	Hydronium	NO_2^+	Nitronium
NO^+	Nitrosonium (also called nitrosyl, nitrolium or nitroso)	$[H_3N—NH_2]^+$	Hydrazinium

Free radicals. Free radicals are given their own names, *e.g.*,

CH_3	Methyl	C_2H_5	Ethyl
C_6H_5	Phenyl	CH_3CN	Acetonitrile

The attachment of oxine$^-$ ion with a metal atom (M) in complex compounds takes place as shown in Fig. 1.10. By this type of attachment a 5-membered ring is formed.

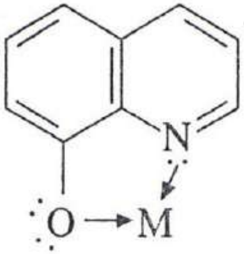
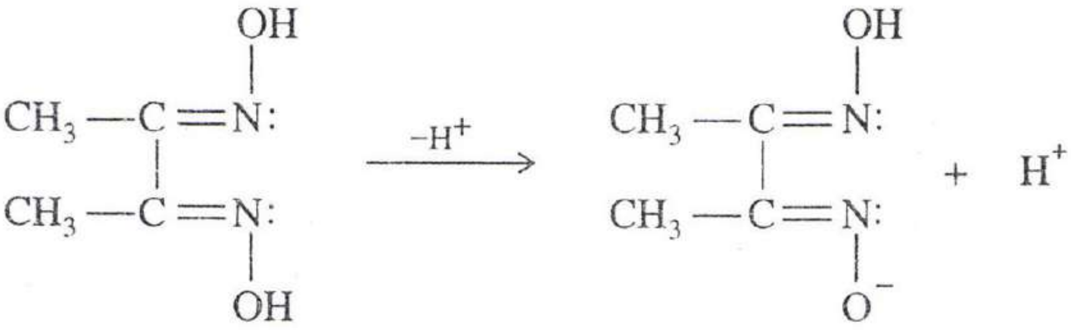


Fig. 1.10. Attachment of oxine$^-$ ion to a metal atom (M) in complex compounds.

10. Dimethyl glyoximato ion (dmg$^-$ or DMG$^-$). This ion is obtained when one OH group attached with N-atom in Hdmg molecule loses a proton (Fig. 1.11).



Dimethyl glyoxime (Hdmg or HDMG)

dmg$^-$ or DMG$^-$

Fig. 1.11. To get dmg$^-$ ion from Hdmg molecule.

Two dmg$^-$ ions react with Ni^{2+} or Pd^{2+} ion in ammoniacal solution and form an insoluble neutral red chelated complex, $[M(dmg)_2]^0$ ($M = Ni^{2+}$, Pd^{2+}) which has two 5-membered and two 6-membered rings. The formation of $[Ni(dmg)_2]^0$ has been shown in Fig. 1.12.

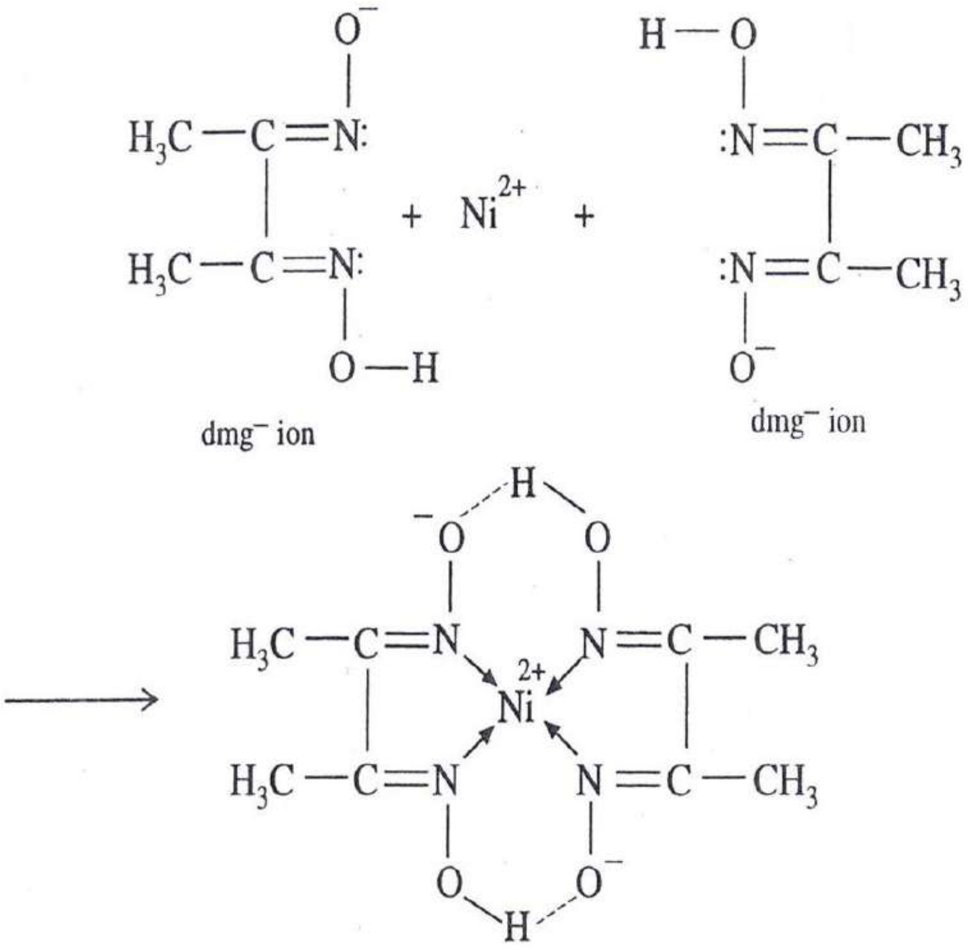


Fig. 1.12. Formation of $[\mathrm{Ni(dmg)_2}]^0$ (chelated complex).

11. α-nitroso β-naphthol anion. This anion is obtained when α-nitroso β-naphthol molecule loses a proton (H^+) from OH group (see Fig. 1.13).

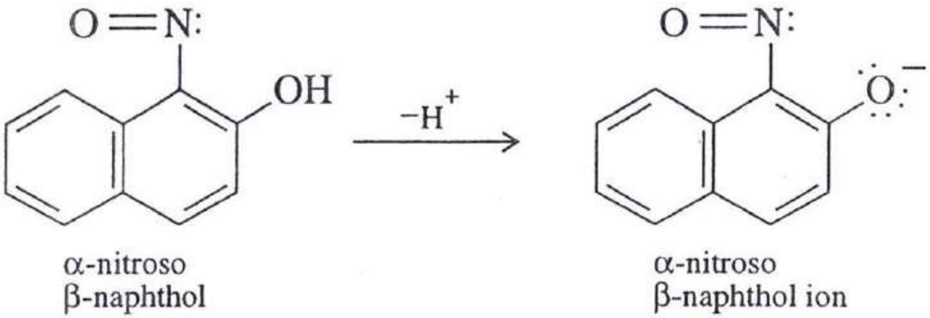


Fig. 1.13 To get α-introso β-naphthol ion from α-nitroso β-naphthol molecule.

This ion gets linked with metal atom, M through its N-atom of NO group and negatively charged O-atom. A 5-membered ring is fomed at M atom (Fig. 1.14).

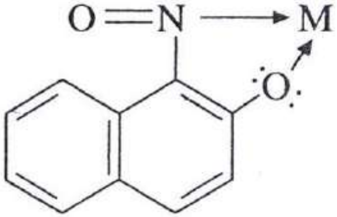
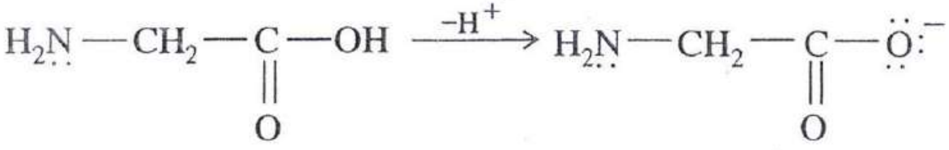


Fig. 1.14. Chelated complex formed by α-nitroso β-naphthol ion with metal atom, M.

12. Glycinato ion (gly⁻). This ion is derived by removing one proton from one molecule of glycine (amino acetic acid), $H_2N—CH_2—COOH$ (Hgly) as shown in Fig. 1.15.



$$H_2\underset{..}{N}-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{-H^+} H_2\underset{..}{N}-CH_2-\underset{\underset{O}{\|}}{C}-\ddot{\underset{..}{O}}:^-$$

Glycine molecule (Hgly)　　Glycinato ion (gly⁻)

Fig. 1.15. To get gly⁻ ion from Hgly molecule.

Glycinato ion (gly⁻) is a bidentate monobasic ligand and its co-ordination to the metal ion occurs through neutral N-atom (neutral donor atom) and negatively-charged O-atom (acidic donor atom), forming a 5-membered ring as is evident from the strucuture of *cis*-and *trans*-isomers of octahedral triglycinato chromium (III), $[\mathrm{Cr(NH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}O)_3}]^0$ or $[\mathrm{Cr(gly)_3}]^0$ shown in Fig. 1.21 (see symmetrical and unsymmetrical bidentate ligands).

13. Biguanido ion (big⁻). This ion is obtained when biguanide molecule loses H-atom of NH group in C=NH unit (see Fig. 1.16).

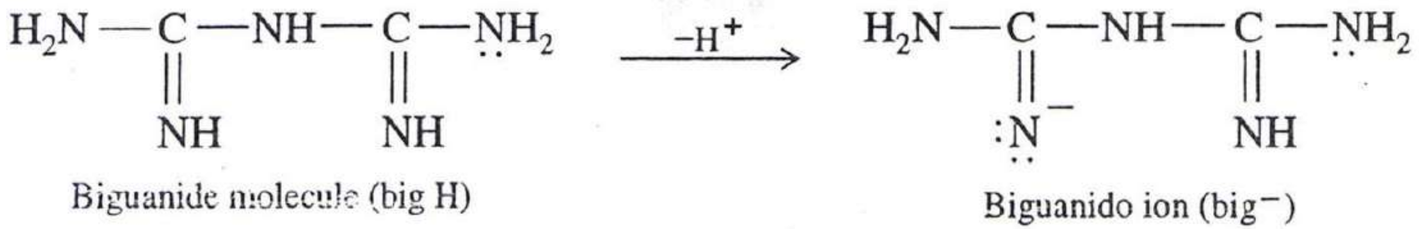


Fig. 1.16. To get big⁻ ion from Hbig molecule.

This ion gets attached with the central metal atom through its negatively-charged N-atom and N-atom of NH_2 group and forms a chelated complex containing 6-membered ring as shown in Fig. 1.17.

14. Carbonato (CO_3^{2-}), nitrato (NO_3^-) and sulphato (SO_4^{2-}). The structure of these ions and the way in which they are coordinated to the metal atom are shown below in Fig. 1.18.

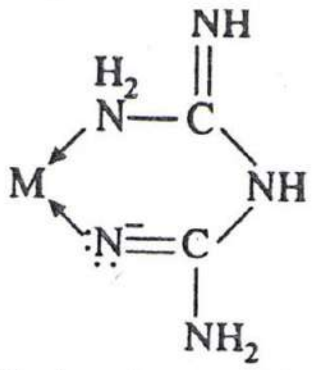


Fig. 1.17. Attachment of biguanido ion with metallic atom

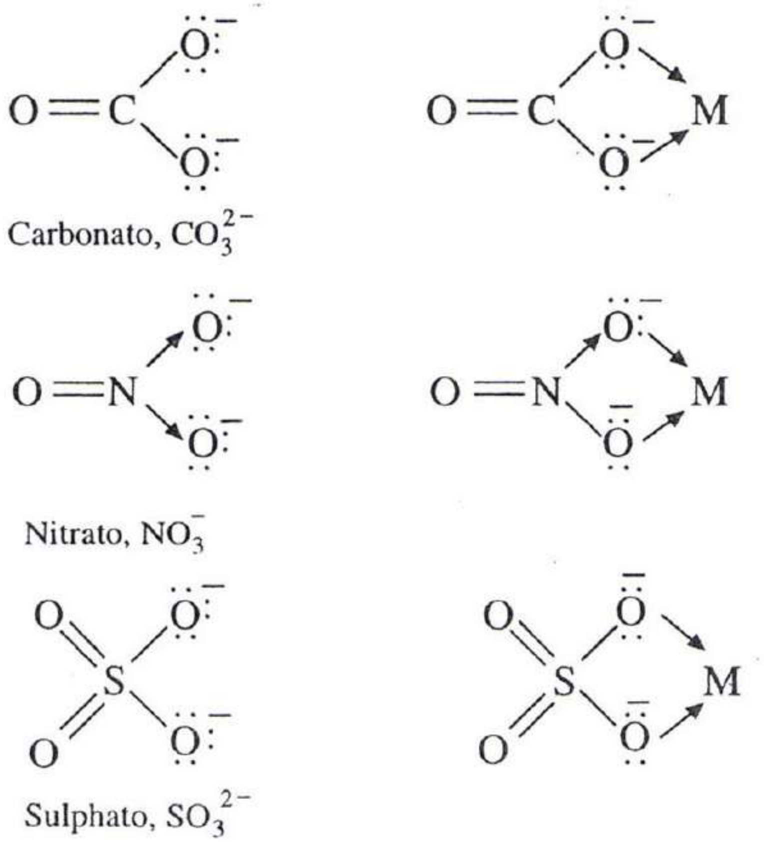


Fig. 1.18. Structure of CO_3^{2-}, NO_3^- and SO_4^{2-} ions and their attachment with metal atom, M.

Note. Carbonato, nitrato and sulphato ligands also act as monodentate ligands as is evident from the following complex ions.

$[Co^{3+}(NH_3)_5(CO_3)]^+$ ... Pentammine carbonato cobalt (III) ion (octahedral)
$[Co^{3+}(NH_3)_5(SO_4)]^+$ ... Pentammine sulphato cobalt (III) ion (octahedral)
$[Ti^{4+}(NO_3)_4]^0$ ... Tetranitrato titanium (IV) (square planar)

$[Co^{3+}(en)_2(NO_3)_2]^+$ ... Bis-(ethylene diamine) dinitrato cobalt (III) ion (octahedral)

15. Peroxo, O_2^{2-}. This ligand can be supposed to have been obtained by eliminating two protons from H_2O_2 molecule (Fig. 1.19).

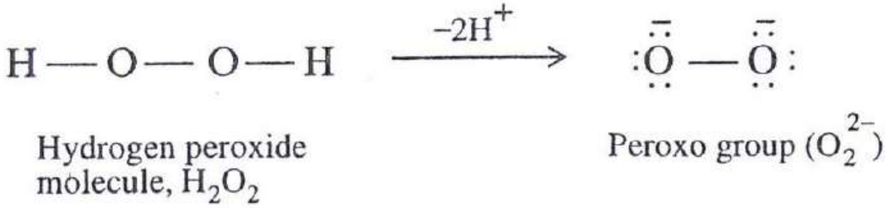
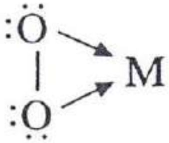


Fig. 1.19. To get peroxo ion (O_2^{2-}) from hydrogen peroxide molecule (H_2O_2)

O_2^{2-} group gets coordinated to the central metal atom as



Classification of bidentate ligands

Bidentate ligands have been clasified into the following two ways:

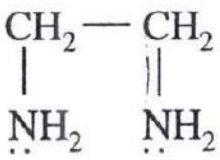
Classification I. This classification gives the following three types of bidentate ligands.

1. Bidentate ligands whose both donor atoms are neutral atoms. Examples of such ligands are ethylene diamine (N, N), dipyridyl (N, N), o-phenylene bis dimethyl arsine (As, As) etc. The symbols given in bracket are the donor atoms.

2. Bidentate ligands which have one neutral and one anionic donor atom. Examples of such ligands are acetyl acetonate ion (O, O^-), 8-hydroxy quinolinate ion (N, O^-), α-nitroso β-naphthol ion (N, O^-) etc.

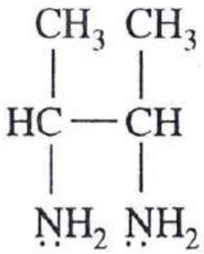
3. Bidentate ligand which have both anionic donor atoms, *e.g.* oxalate ion (O^-, O^-), carbonate ion (O^-, O^-), sulphate ion (O^-, O^-) etc.

Classification II. According to this classification, bidentate ligands may be **symmetrical** bidentate ligands or **unsymmetrical** bidentate ligands. Symmetrical bidentate ligands are those in which the two donor atoms are the **same** while unsymmetrical bidentate ligands are those in which the two donor atoms are **different.** Thus a symmetrical bidentate ligand is denoted by (*AA*) in which two *A*'s are two similar donor atoms while an unsymmetrical bidentate ligand is denoted as (*AB*) in which *A* and *B* are two different donor atoms. Examples of symmetrical bidentate ligands are given below. Donor atoms have been shown in bracket.



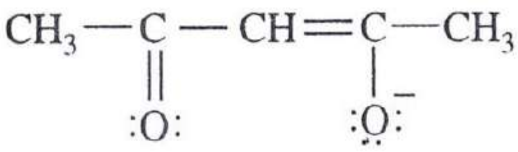
$\underset{\underset{\ddot{N}H_2}{|}}{CH_2}-\underset{\underset{\ddot{N}H_2}{|}}{CH_2}$

Ethylene diamine, *en*
(N, N)



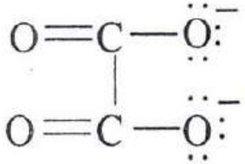
$\underset{\underset{\ddot{N}H_2}{|}}{\overset{\overset{CH_3}{|}}{HC}}-\underset{\underset{\ddot{N}H_2}{|}}{\overset{\overset{CH_3}{|}}{CH}}$

Butylene diamine, *bn*
(N, N)



$CH_3-\underset{\underset{:\ddot{O}:}{\|}}{C}-CH=\underset{\underset{:\ddot{O}:^-}{|}}{C}-CH_3$

Acetylacetonato, *acac*⁻
(O, O⁻)



$\begin{matrix}O=C-\ddot{\underset{..}{O}}:^- \\ | \\ O=C-\ddot{\underset{..}{O}}:^-\end{matrix}$ *or* $C_2O_4^{2-}$

Oxatato, *ox*$^{2-}$
(O, O⁻)

The attachment of a symmetrical bidentate ligand to the central metal atom is shown by a curve $\left.\begin{matrix}A\\A\end{matrix}\right)L$ where where *L* is the abbrevation of the symmetrical bidentate ligand and two *A*'s are two (similar) donor atoms.

For example the attachment of two molecules of ethylene diamine, $NH_2—CH_2—CH_2—NH_2$ (en) to Co^{3+} ion to form *trans*-isomer of $[Co(en)_2Cl_2]^+$ ion (octahedral ion) can be shown as depicted at (*a*) of Fig. 1.20. Similarly, the attachment of two molecules of butylene diamine, $NH_2—CH(CH_3)—CH(CH_3)—NH_2$ (bn) to Pt^{2+} ion to form square planar $[Pt(en)_2]^{2+}$ ion can be shown at (*b*) of Fig. 1.20.

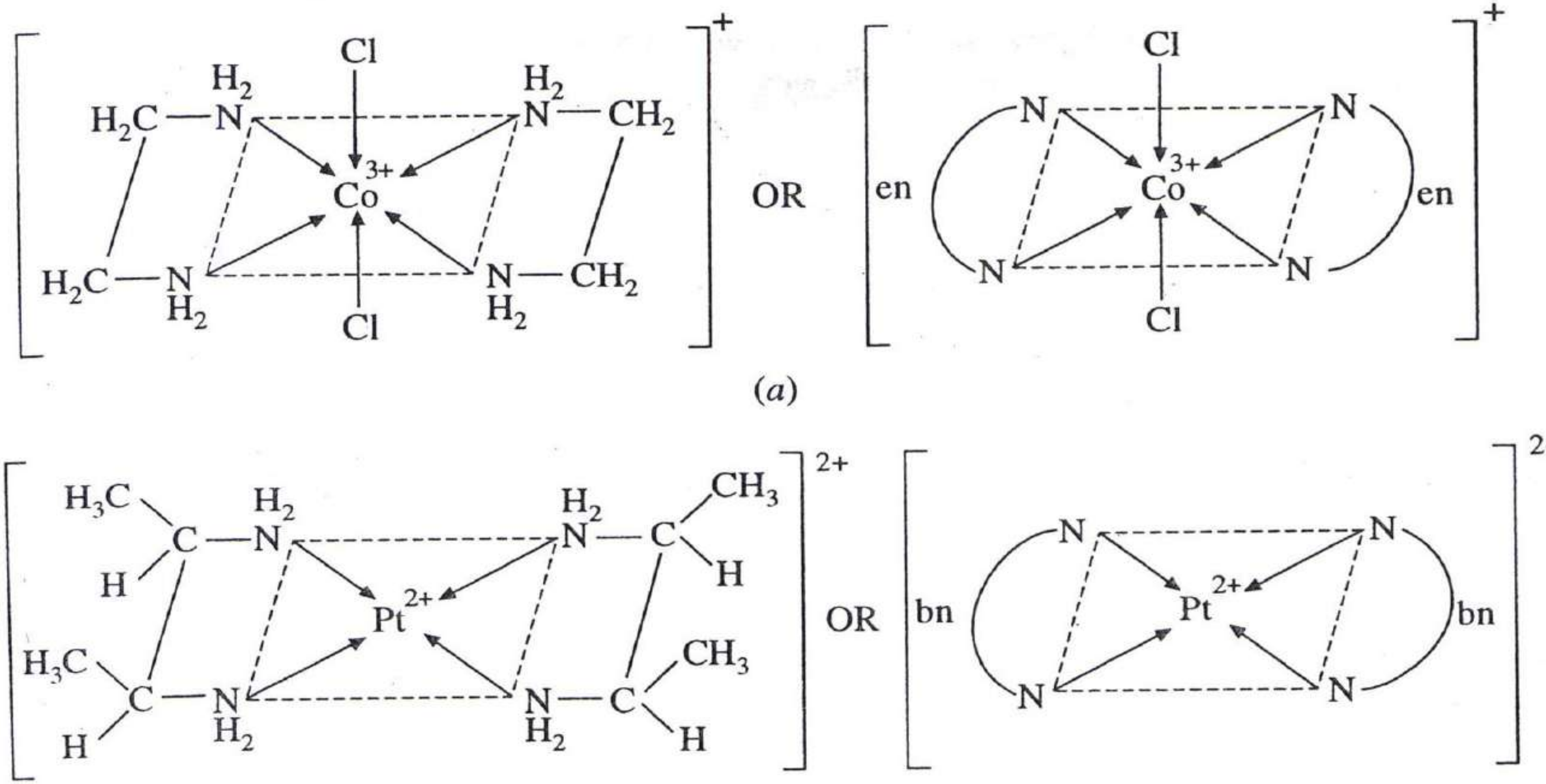
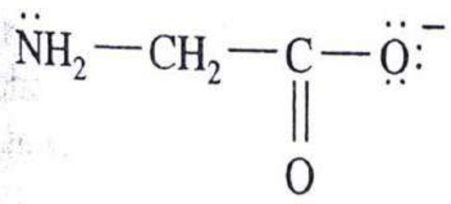


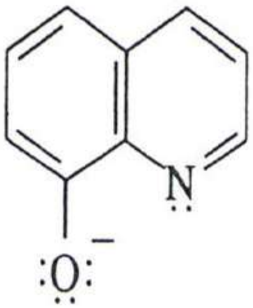
Fig. 1.20. Structure of trans-isomer of bis (ethylene diamine) dichloro cobalt (III) ion, $[Co(NH_2—CH_2—CH_2—NH_2)_2Cl_2]^+$ or $[Co(en)_2 Cl_2]^+$ (octahedral ion) [shown at (*a*)] and bis (butylene diamine) platinum (II) ion, $[Pt\{NH_2—CH(CH_3)—CH(CH_3)—NH_2\}_2]^{2+}$ or $[Pt(bn)_2]^{2+}$ (square planar ion) [shown at (*b*)].

Examples of unsymmetrical bidentate ligands are given below. Donor atoms are given in bracket.

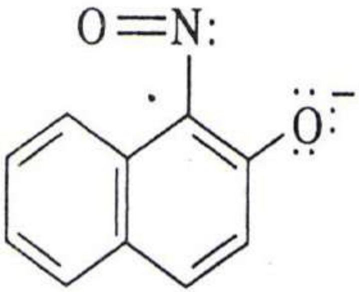


$$\ddot{N}H_2-CH_2-\underset{\underset{O}{\|}}{C}-\ddot{\underset{..}{O}}:^{-}$$

Glycinato ion, *gly*$^-$
(N, O^-)

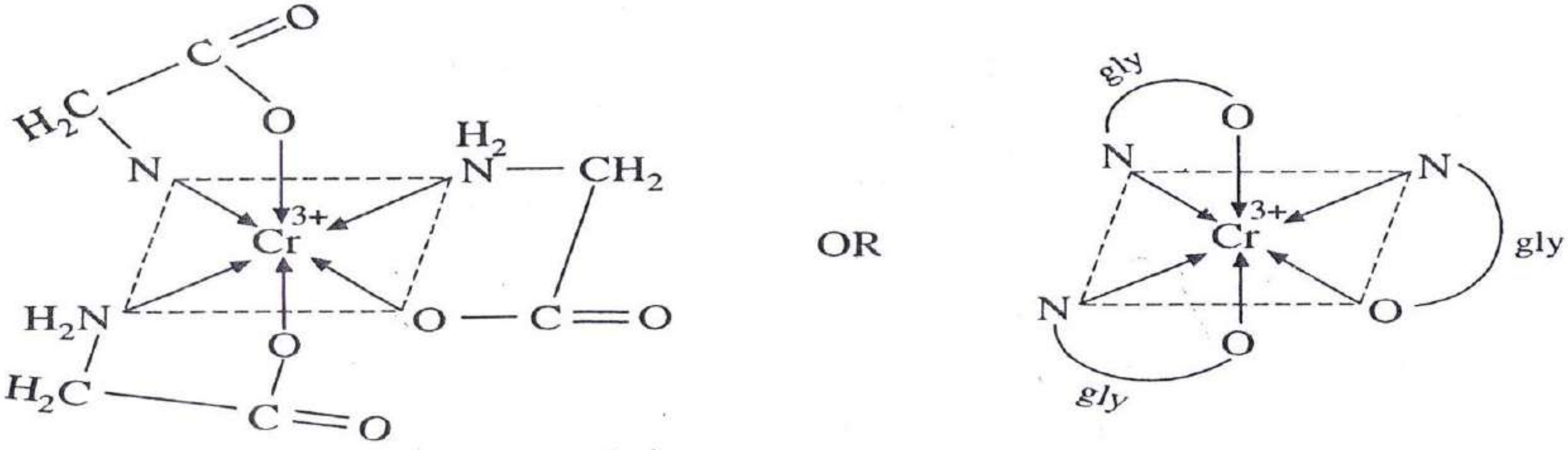


8-hydroxy quinolinato ion
(N, O^-)

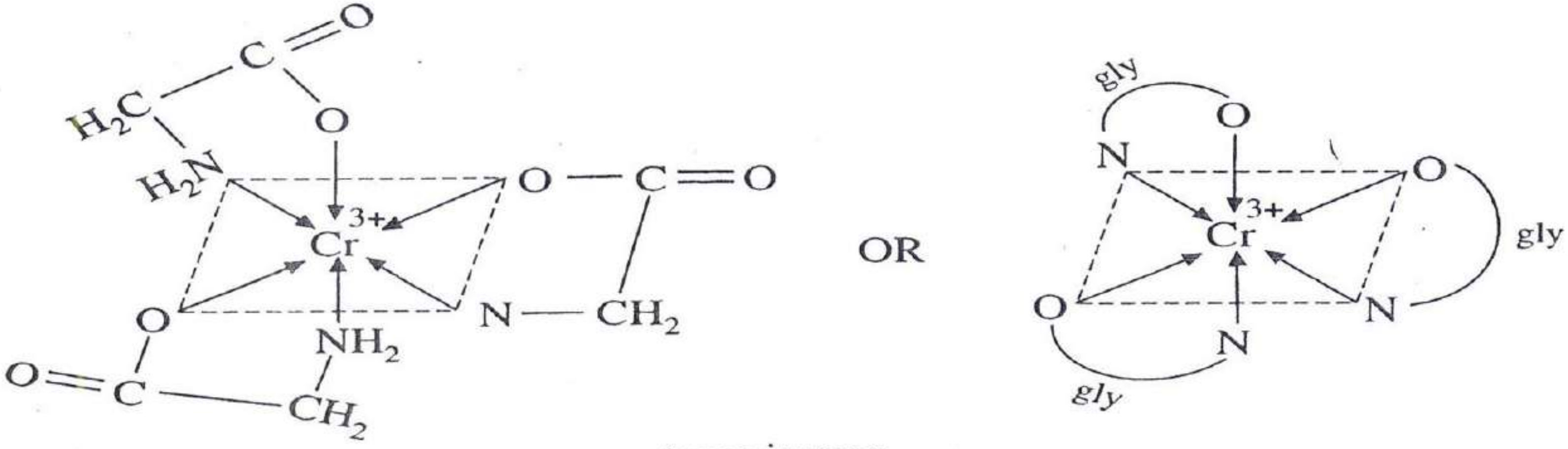


α-nitroso β-naphthol ion
(N, O^-)

The attachment of an unsymmetrical bidentate ligand to the central metal atom is shown by a curve $\left.\begin{matrix}A\\ \\B\end{matrix}\right)L$ where *L* is the abbreviation of the ligand and *A* and *B* are two (different) donor atoms. For example, the attachment of three glycinate ions, $NH_2-CH_2-\underset{\underset{O}{\|}}{C}-O^-$ (gly$^-$) to Cr^{3+} ion to form *cis*-and *trans*-isomers of octahedral $[Cr(gly)_3]^0$ can be shown as depicted in Fig. 1.21.



cis-isomer



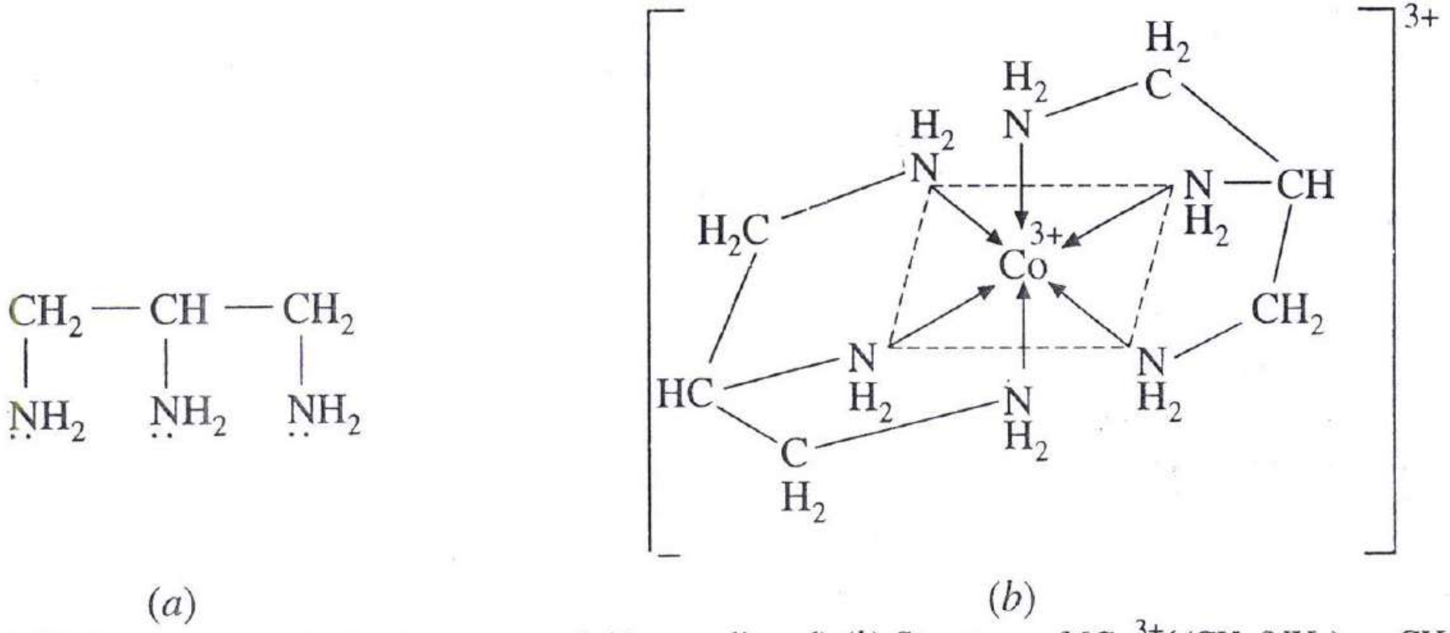
trans-isomer

Fig. 1.21. Structure of *cis*-and *trans*-isomers of $[\mathrm{Cr}(\mathrm{NH_2} - \mathrm{CH_2} - \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}} - \mathrm{O})_3]^0$ or $[\mathrm{Cr(gly)_3}]^0$

Examples of tridentate ligands

These ligands may be neutral molecules or anionic species. Important examples are given below:

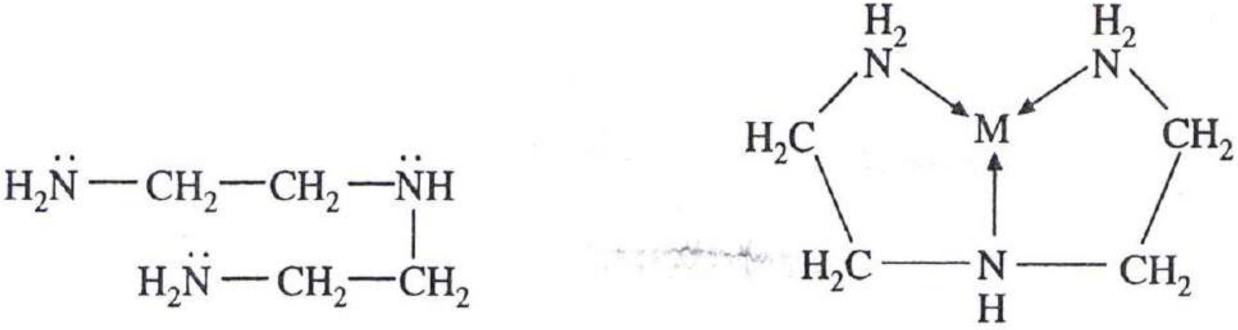
1. Triaminopropane. The structure of this ligand is given at (*a*) of Fig. 1.22 which shows that it has three N-atoms as its donor atoms. The coordination of this ligand to the central metal atom takes place through its three N-atoms (donor atoms), leading to the formation of two 5-membered rings as is evident from the structure of $[Co^{3+}\{(CH_2(NH_2)—CH(NH_2)—CH_2(NH_2)\}_2]^{3+}$ ion (a chelated complex ion) given at (*b*) of Fig. 1.22.



(*a*) (*b*)

Fig. 1.22. (*a*) Structure of triaminopropane (tridentate ligand) (*b*) Structure of $[Co^{3+}\{(CH_2(NH_2)—CH(NH_2)—CH_2(NH_2)\}_2]^{3+}$ ion (octahedral chelated complexion).

2. Diethylene triamine (dien). Its structure is given in Fig. 1.23 (*a*). This ligand gets attached with the central metal atom through its three N-atoms (donor atoms) and forms a chelate which contains two 5-membered rings. [See Fig. 1.23 (*b*)].



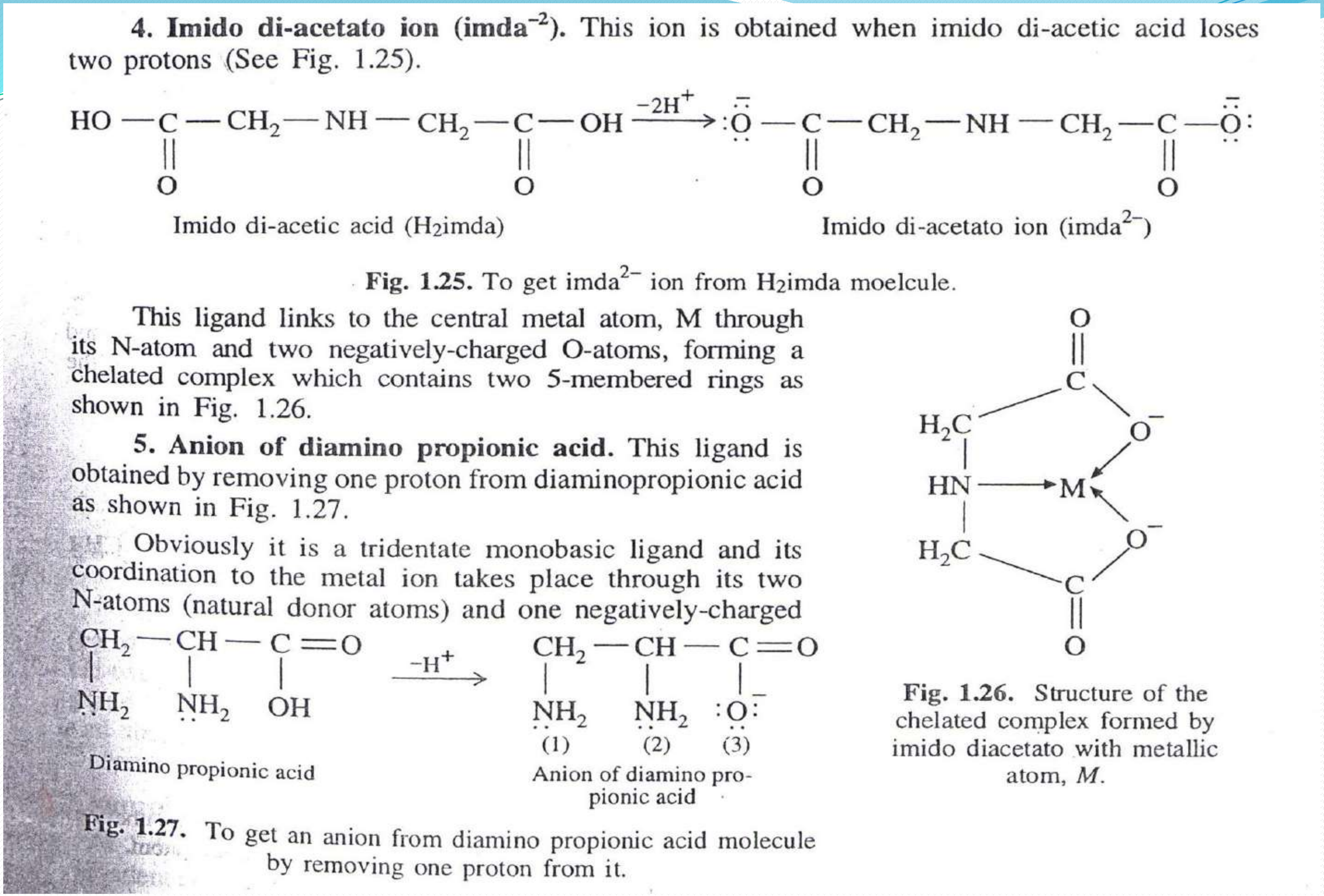
(*a*) (*b*)

Fig. 1.23. (*a*) Structure of diethylene triamine (dien) (*b*) chelated complex formed by dien with a metallic atom, M.

3. 2, 2′, 2″-terpyridine or terpyridyl (terpy). Its structure and its mode of linking with the central metal atom are shown below in Fig. 1.24.

(*a*) (*b*)

Fig. 1.24. (*a*) Structure of 2, 2′, 2″-terpyridine (terpy) (*b*) Mode of attachment of terpy with the central metal atom, M.



4. Imido di-acetato ion (imda^{-2}). This ion is obtained when imido di-acetic acid loses two protons (See Fig. 1.25).

$$HO-\underset{\underset{O}{\|}}{C}-CH_2-NH-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{-2H^+} :\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}-\underset{\underset{O}{\|}}{C}-CH_2-NH-CH_2-\underset{\underset{O}{\|}}{C}-\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$$

Imido di-acetic acid (H2imda) Imido di-acetato ion (imda^{2-})

Fig. 1.25. To get imda^{2-} ion from H2imda moelcule.

This ligand links to the central metal atom, M through its N-atom and two negatively-charged O-atoms, forming a chelated complex which contains two 5-membered rings as shown in Fig. 1.26.

5. Anion of diamino propionic acid. This ligand is obtained by removing one proton from diaminopropionic acid as shown in Fig. 1.27.

Obviously it is a tridentate monobasic ligand and its coordination to the metal ion takes place through its two N-atoms (natural donor atoms) and one negatively-charged

$$\underset{\underset{NH_2}{|}}{CH_2}-\underset{\underset{NH_2}{|}}{CH}-\underset{\underset{OH}{|}}{C}=O \xrightarrow{-H^+} \underset{\underset{\underset{(1)}{\underset{\cdot\cdot}{N}H_2}}{|}}{CH_2}-\underset{\underset{\underset{(2)}{\underset{\cdot\cdot}{N}H_2}}{|}}{CH}-\underset{\underset{\underset{(3)}{:\overset{-}{\underset{\cdot\cdot}{O}}:}}{|}}{C}=O$$

Diamino propionic acid Anion of diamino propionic acid

Fig. 1.27. To get an anion from diamino propionic acid molecule by removing one proton from it.

Fig. 1.26. Structure of the chelated complex formed by imido diacetato with metallic atom, *M*.

O-atom (acidic donor atom) as is evident from the structure of the chelate formed by this ligand with Co^{3+} ion as shown in Fig. 1.28.

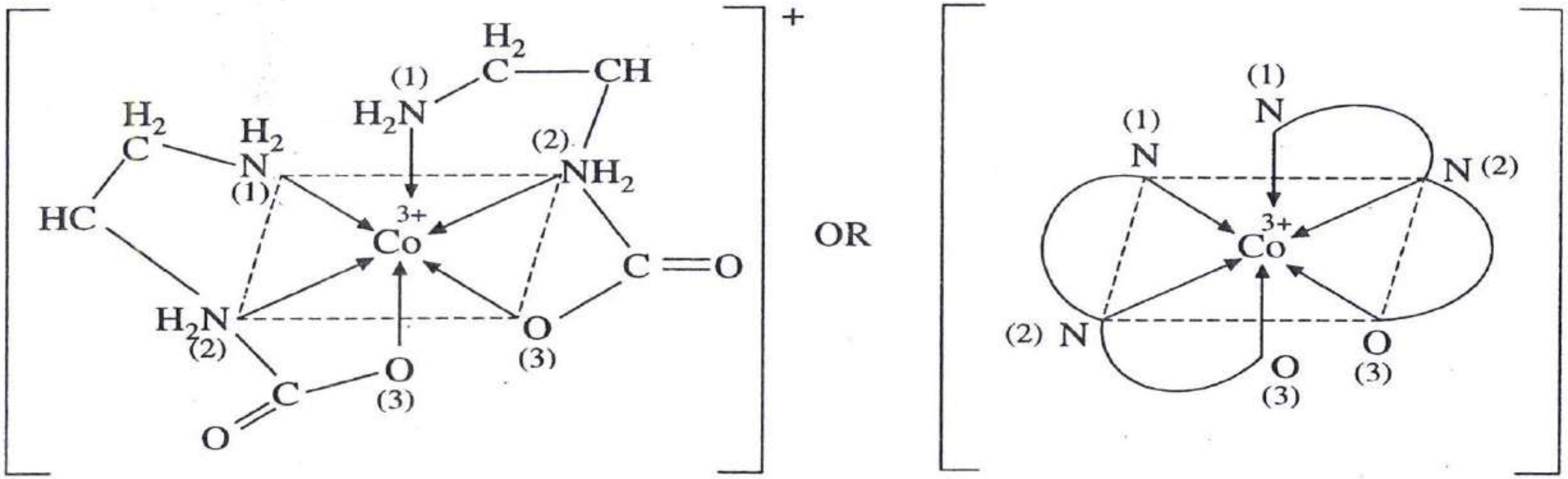


Fig. 1.28. Structure of $[Co^{3+}\{(CH_2(NH_2)—CH(NH_2)—COO\}_2]^+$ ion (chelated complex ion).

Examples of tetradentate ligands

Important examples of these ligands are given below:

1. Triethylene tetramine (trien). The structure of this ligand is given at (*a*) of Fig. 1.29. This structure shows that this ligand has four N-atoms as its donor atoms (neutral donor atoms). Coordination of this ligand to the metal ion takes place through these N-atoms, forming a chelated complex containing three 5-membered rings as shown at (*b*) of Fig. 1.29.

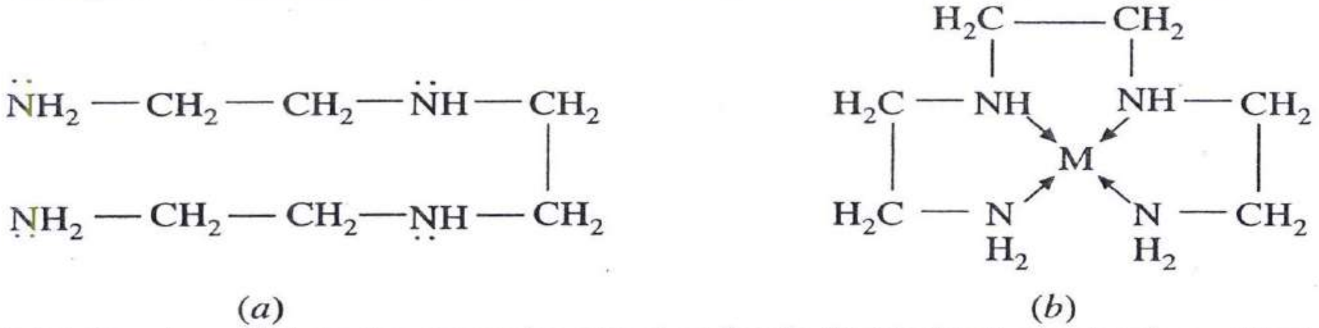
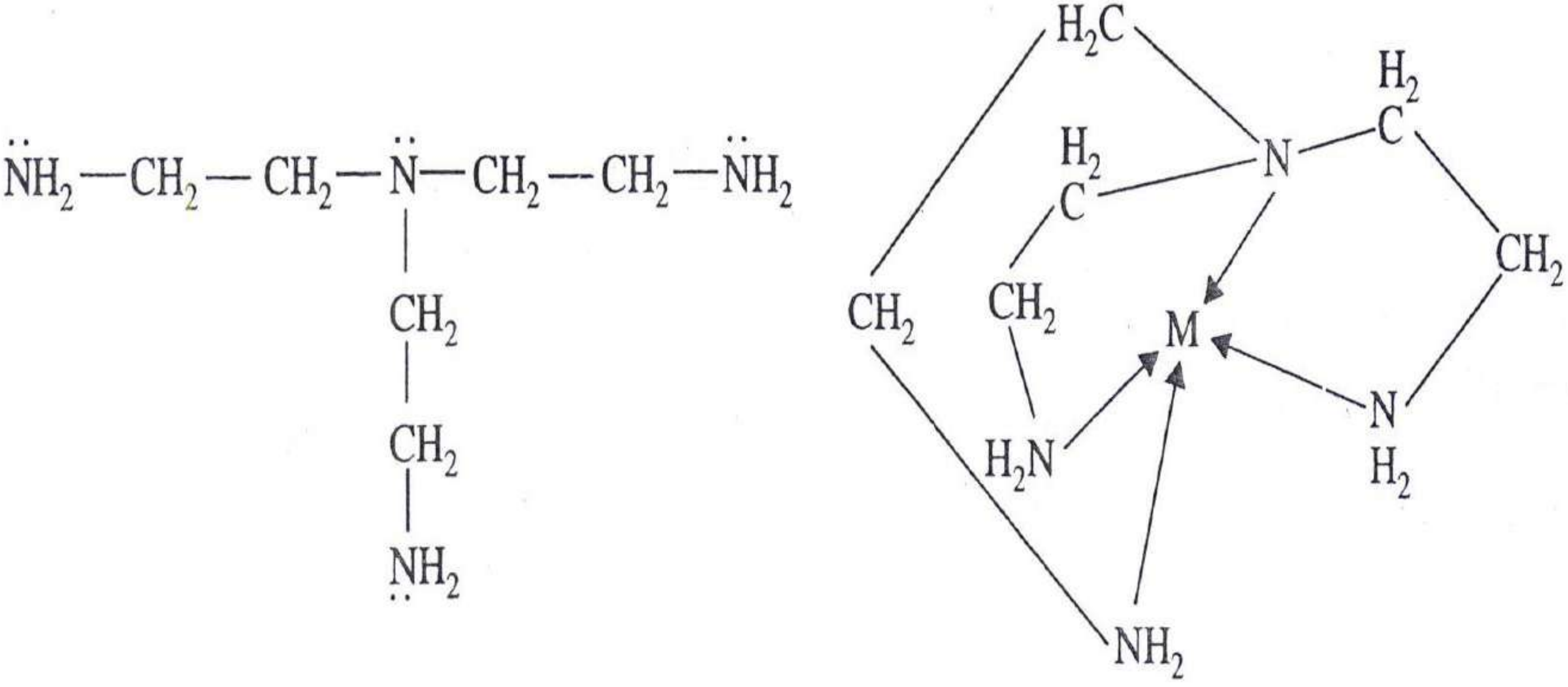


Fig. 1.29. (*a*) Structure of triethylene tetramine (trien) molecule (*b*) Chelated complex formed by triethylene tetramine molecule with the metallic atom, M.

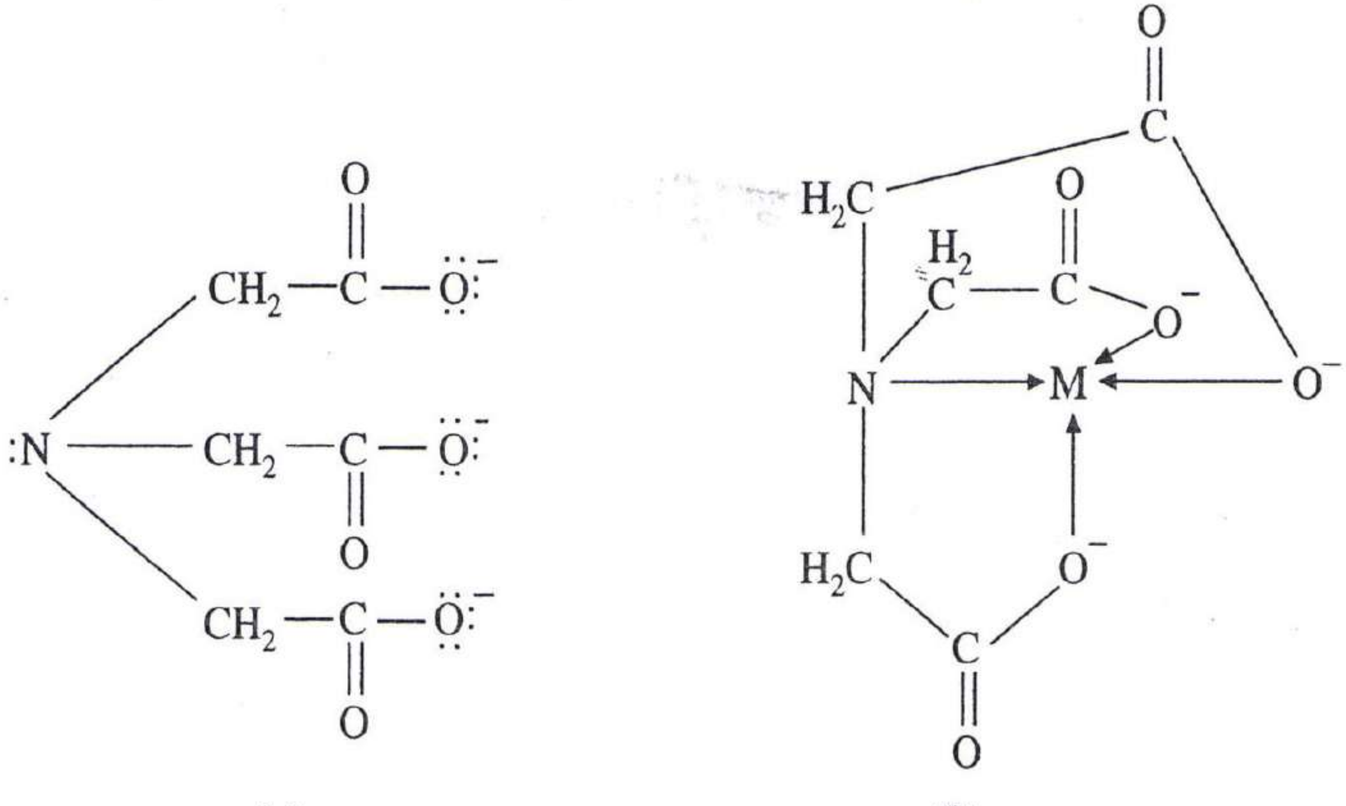
2. Triaminotriethylamine (tren), $N(CH_2—CH_2—NH_2)_3$. Its structure is given at (*a*) of Fig. 1.30. This structure shows that it has four N-atoms as its donor atoms. The attachment of this ligand to the central metal atom, M in its complexes takes place through its four N-atoms, resulting in the formation of chelated complex having three 5-membered rings as shown at (*b*) of Fig. 1.30.



(*a*) (*b*)

Fig. 1.30. (*a*) Structure of triaminotriethylamine (tren), $N(CH_2—CH_2—NH_2)_3$ (*b*) Structure of the chelated complex formed by the attachment of triaminotriethylamine molecule with metallic atom, M.

3. Nitrilotriacetato ion (nta^{-3} or NTA^{-3}). The structure of this ion is given at (*a*) of Fig. 1.31. This structure shows that this ligand is a tribasic tetradentate ligand. The coordination of this ligand to the metal ion takes place through N-atom (neutral donor atom) and three negatively-charged O-atoms (acidic donor atoms) of COO^- groups. This type of coordination gives rise to the formation of a chelate having three 5-membered rings as shown at (*b*) of Fig. 1.31.



(*a*) (*b*)

Fig. 1.31. (*a*) Structure of nitrilotriacetato ion (nta^{-3} or NTA^{-3}) (*b*) Structure of the chelated complex formed by nta^{-3} ion.

Examples of pentadentate ligands

Important examples are given below:

1. Tetraethylene pentamine (tetraen). The structure of this molecule is shown at (*a*) of Fig. 1.32. This structure shows that it has five N-atoms as its donor atoms (neutral donor atoms). Thus this ligand coordinates to the metal atom through these five N-atoms and forms four 5-membered rings as shown at (*b*) of Fig. 1.32.

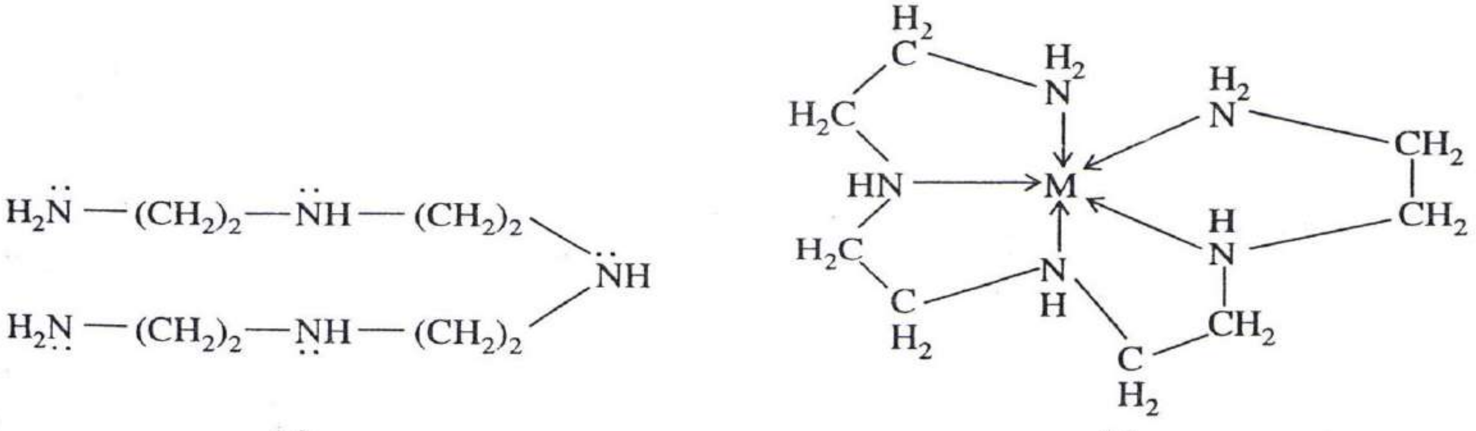


Fig. 1.32. (*a*) Structure of tetraethylene pentamine (tetraen) (*b*) Structure of the chelated complex formed by tetraethylene pentamine with metallic atom, M.

2. Ethylene diamine triacetate ion. It is an anionic ligand and its structure is shown at (*a*) of Fig. 1.33. This structure shows that it has three negative charges and five donor atoms *viz* two N-atoms (numbered as 1 and 2) and three negatively-charged O-atoms (numbered as 3, 4 and 5). Its coordination to the metal atom occurs through two N-atoms (neutral donor atoms) and three negatively-charged O-atoms (acidic donor atoms) of COO^- groups, forming four 5-membered rings as shown at (*b*) of Fig. 1.33.

Example of hexadentate ligand

Ethylene diamine tetracetate ion ($edta^{-4}$ or $EDTA^{-4}$ or Y^{-4}) is an important example of hexadentate ligand. It structure is given in Fig. 1.34.

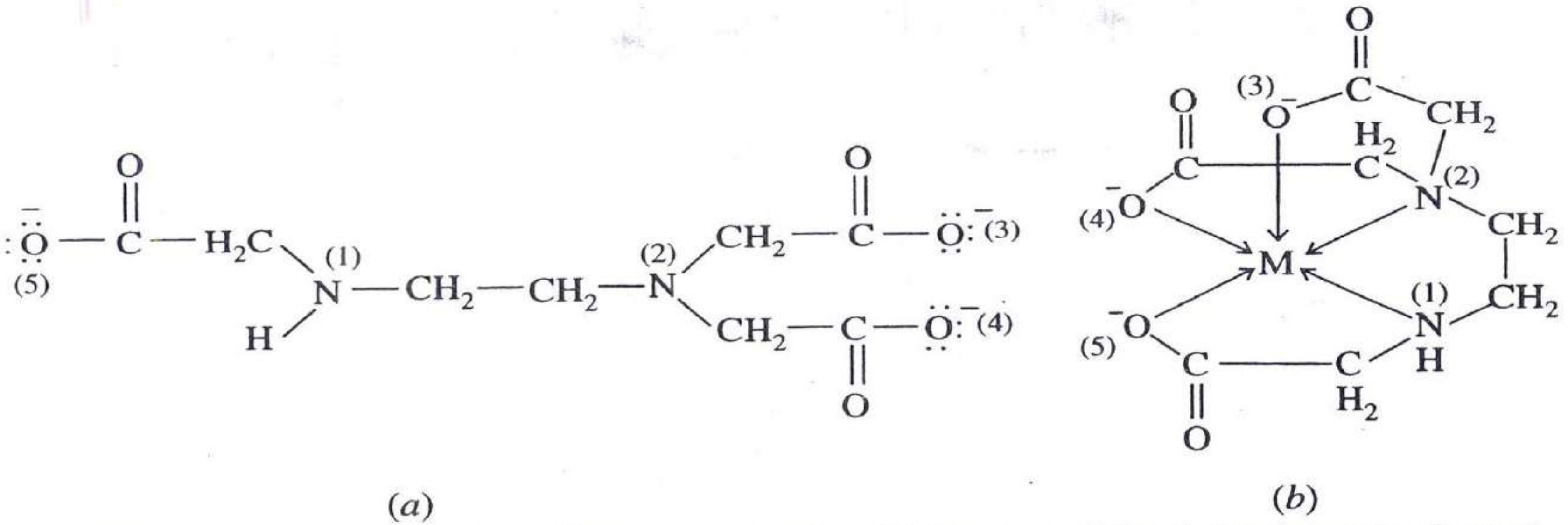


Fig. 1.33. (*a*) Structure of ethylene diamine triacetate ion (*b*) Structure of the chelated complex formed by ethylene diamine triacetate ion with metallic atom, M.

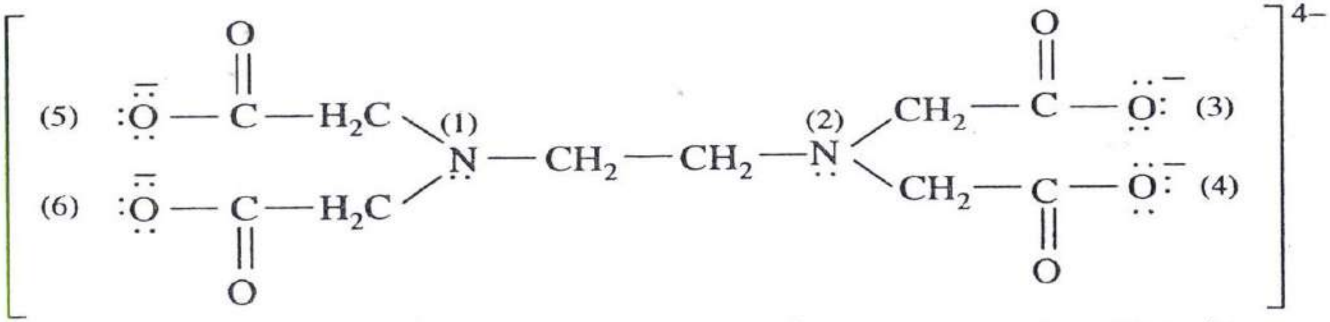


Fig. 1.34. Structure of ethylene diamine tetracetate ion (edta^{4-} or EDTA^{4-})

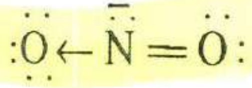
The structure shows that it has two neutral N-atoms (numbered as 1 and 2) and four negatively-charged O-atoms (numbered as 3, 4, 5 and 6) as its donor atoms. Thus it is tetrabasic hexadentate ligand. The co-ordination of this ligand to the metal atom takes place thorugh two N-atoms and four O-atoms, forming five 6-membered rings as is evident from the structure of *d* and *l*-forms of [Co^{3+}(EDTA)]$^-$ ion given in Figures 4.33 and 4.34 on page 91of chapter 4 (See *optical isomerism exhibited by octahedral complexes containing polydentate ligands*).

Ambidentate Ligands and Linkage Isomerism

There are many ligands which have two or more different donor atoms in their structure. Such ligands can coordinate to the metal atom through any of their donor atoms and hence are given different names corresponding to the nature of donor atoms linked to the metal atom. Such ligands are called **ambidentate** or **ambident ligands.** When an ambidentate ligand having two different donor atoms coordinates to the metal atom through either of its two donor atoms, two different complex compounds are obtained. These compounds are different because they have different structure. Such compounds are called **linkage isomers** and the phenomenon is called **linkage isomerism**. Linkage isomerism arises due to the tendency of the ambidentate ligand to link to the metal atom in different ways through its two different donor atoms. The less stable form of a pair of linkage isomers often reverts to the more stable form. The less stable form is likely to exist at low temperature and with those metal ions which are known to form kinetically inert complexes (*e.g.*, Co^{2+}, Pt^{2+}, Pd^{2+} etc.).

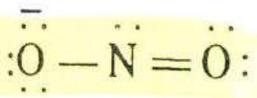
Examples of some ambidentate ligands and the pair of linkage isomers given by them

1. NO_2^- ion. We know that this ion can have any of the following two structures.



$:\overset{..}{\underset{..}{O}}\leftarrow\overset{-}{\overset{..}{N}}=\overset{..}{O}:$

Structure (I) (Nitro group)

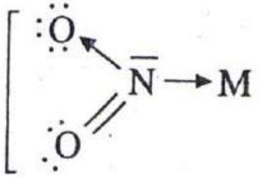


$:\overset{-}{\overset{..}{\underset{..}{O}}}-\overset{..}{N}=\overset{..}{O}:$

Structure (II) (Nitrito group)

In structure (I) N-atom is negatively-charged and contains one unshared pair of electrons while in structure (II), one O-atom is negatively-charged and this O-atom contains three unshared pairs of electrons. Thus when NO_2^- ion acts as a monodentate ligand, it may be linked to the central metal atom either through the lone pair of electrons on negatively-charged N atom of structure (I) or through the lone pair of electrons on negatively-charged on O-atom of structure (II). Thus:

(*a*) When NO_2^- ion gets coordinated to the metal atom through a lone pair of electrons on $\bar{\mathrm{N}}$



or $\mathrm{OO\bar{N}} \rightarrow \mathrm{M}$ or $\mathrm{O_2\bar{N}} \rightarrow \mathrm{M}$], it is called nitro ligand and is written as NO_2^-. The complexes containing nitro ligand are called **nitro complexes.** For example $[Co^{3+}(NH_3)_5(NO_2)]Cl_2$ (yellow brown) is called pentammine nitro cobalt (III) chloride, since the coordination of Co^{3+} ion to NO_2^- ion occurs through N-atom.

(*b*) When NO_2^- ion gets coordinated to the metal atom through a lone a pair of electrons on $\bar{\mathrm{O}}$ $[\mathrm{M} \leftarrow \overset{\bar{\cdot\cdot}}{\underset{\cdot\cdot}{\mathrm{O}}} - \overset{\cdot\cdot}{\mathrm{N}} = \overset{\cdot\cdot}{\mathrm{O}}:$ *or* $\mathrm{M} \leftarrow \bar{\mathrm{O}}\mathrm{NO}]$, it is called **nitrito ligand** which is written as $\mathrm{ON\bar{O}}$. The complexes containing nitrito ligand are called **nitrito complexes.** For example $[Co^{3+}(NH_3)_5(ONO]Cl_2$ (red) is called pentammine nitrito cobalt (III) chloride, because the coordination of NO_2^- ion to Co^{3+} ion takes place through O-atom.

Sometimes ambidentate ligands are distinguished by putting the symbol of the atom through which the coordination of the ligand to the central metal atom takes place. For example $[Co^{3+}(NH_3)_5(NO_2)]Cl_2$ (yellow-brown) is called pentammine nitrito (N) cobalt (III) chloride and $[Co^{3+}(NH_3)_5(ONO)]Cl_2$ (red) is called *pentammine nitrito* (O) *cobalt* (III) *chloride.*

Both nitro and nitrito complex compounds mentioned above are called **linkage isomers** and the isomerism shown by them is called **linkage isomerism.**

Another example of a pair of linkage isomers is furnished by *diammine bis (pyridine) dinitro cobalt* (III) *nitrate*, $[Co^{3+}(NH_3)_2(py)_2(NO_2)_2]NO_3$ and *diammine bis (pyridine) dinitrito cobalt* (III) *nitrate*, $[Co^{3+}(NH_3)_2(py)_2(ONO)_2]NO_3$.

It has been found that nitro (NO_2^-) is a stronger ligand than the nitrite (ONO^-). Linkage isomers can be identified by infra-red spectroscopy.

2. SCN⁻ ion. We know that this ion can be represented by any of the following two structures:

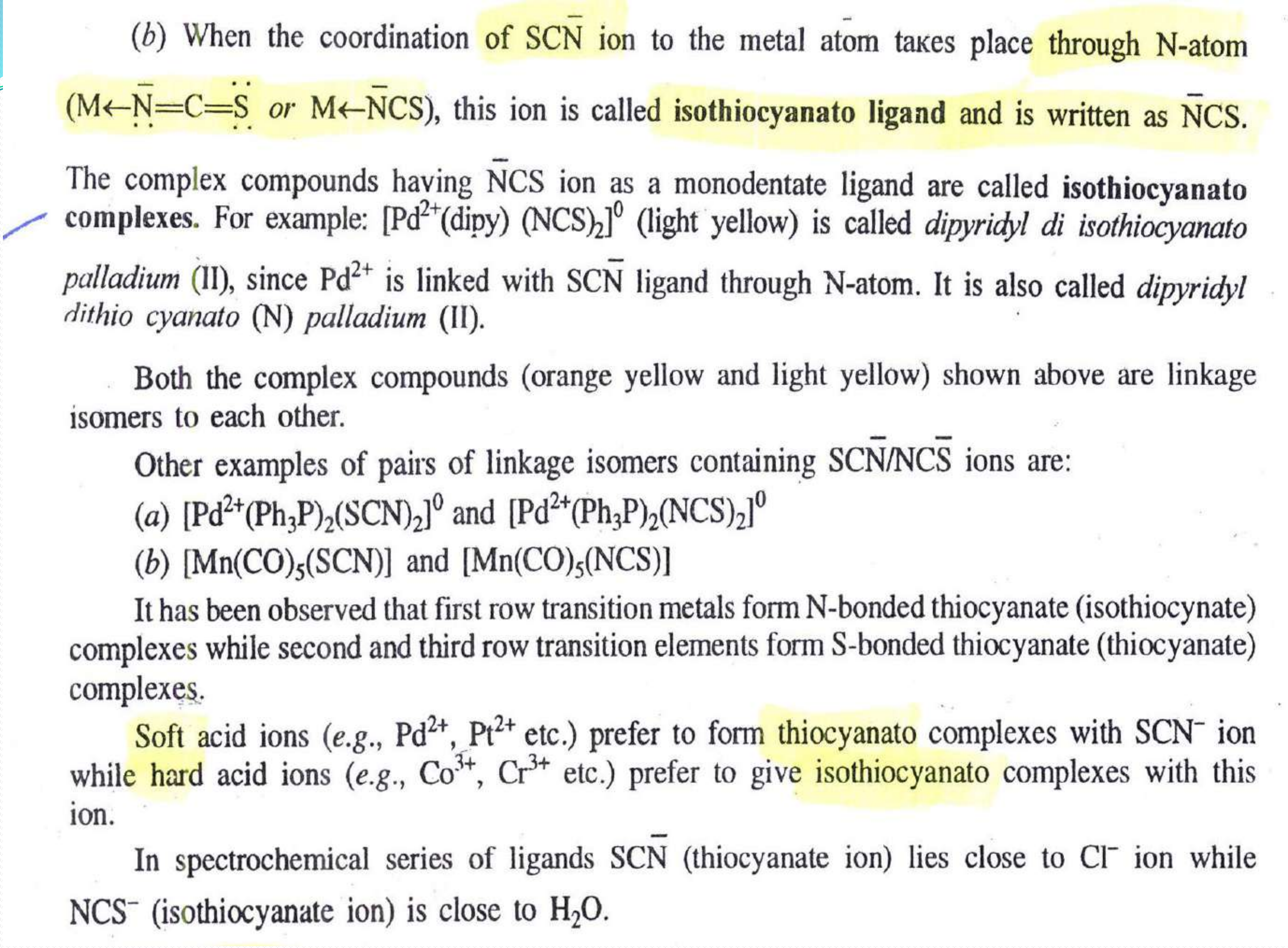
$$:\underset{\cdot\cdot}{\overset{-\cdot}{S}}{-}C\equiv N: \qquad\qquad :\overset{\cdot\cdot}{S}{=}C{=}\overset{-\cdot}{N}:$$

Structure (I)
(Thio cyanato group)

Structure (II)
(Iso-thiocyanato group)

Structures given above show that when SCN⁻ ion acts as a monodentate ligand , it may be coordinated to the central metal atom either through the lone pair of electrons on $\bar{S}$ atom [Structure (I)] or through the lone pair of electrons on N⁻ atom [Structure (II)]. Thus:

(*a*) When SCN⁻ ion gets coordinated to the metal atom through the lone pair on negatively-charged S-atom [$M\leftarrow\underset{\cdot\cdot}{\overset{-\cdot}{S}}{-}C\equiv N:$ *or* $M\leftarrow\bar{S}CN$], it is called **thiocyanato ligand** and is written as $\bar{S}CN$. The complexes containing thiocyanato ligand are called **thiocyanato complexes.** For example $[Pd^{2+}(dipy)(SCN)_2]^0$ (orange yellow) is called *dipyridyl dithiocyanato palladium* (II), since the coordination of $SC\bar{N}$ ligand to Pd^{2+} ion takes place through S-atom. This compound is also called *dipyridyl dithiocyanato* (S) *palladium* (II).



(*b*) When the coordination of $\mathrm{SC\bar{N}}$ ion to the metal atom takes place through N-atom ($\mathrm{M \leftarrow \underset{\cdot\cdot}{\bar{N}} = C = \underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}}$ *or* $\mathrm{M \leftarrow \bar{N}CS}$), this ion is called **isothiocyanato ligand** and is written as $\mathrm{\bar{N}CS}$.

The complex compounds having $\mathrm{\bar{N}CS}$ ion as a monodentate ligand are called **isothiocyanato complexes.** For example: $[\mathrm{Pd}^{2+}(\mathrm{dipy})(\mathrm{NCS})_2]^0$ (light yellow) is called *dipyridyl di isothiocyanato palladium* (II), since Pd^{2+} is linked with $\mathrm{SC\bar{N}}$ ligand through N-atom. It is also called *dipyridyl dithio cyanato* (N) *palladium* (II).

Both the complex compounds (orange yellow and light yellow) shown above are linkage isomers to each other.

Other examples of pairs of linkage isomers containing $\mathrm{SC\bar{N}}/\mathrm{NC\bar{S}}$ ions are:

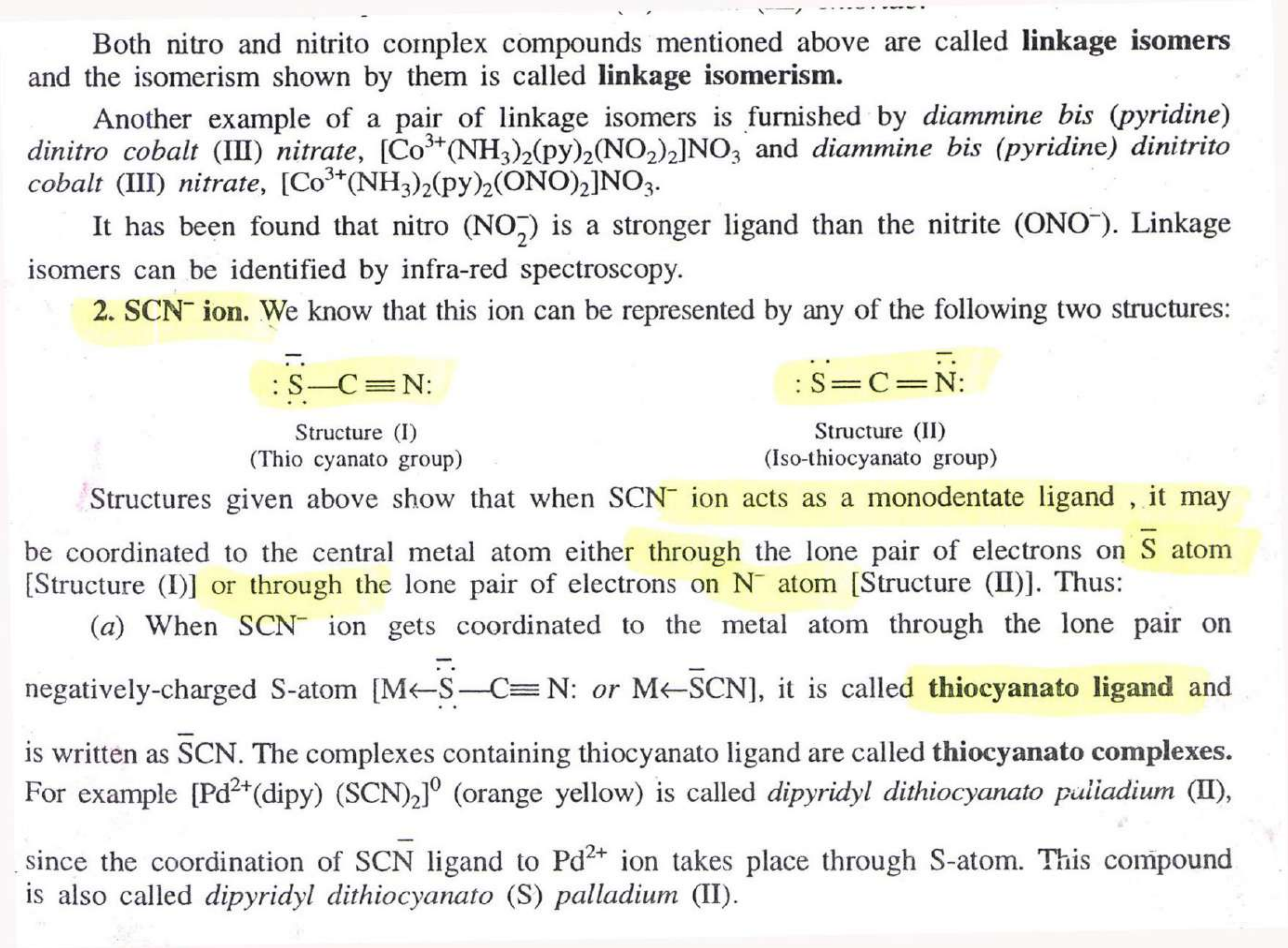
(*a*) $[\mathrm{Pd}^{2+}(\mathrm{Ph_3P})_2(\mathrm{SCN})_2]^0$ and $[\mathrm{Pd}^{2+}(\mathrm{Ph_3P})_2(\mathrm{NCS})_2]^0$

(*b*) $[\mathrm{Mn(CO)_5(SCN)}]$ and $[\mathrm{Mn(CO)_5(NCS)}]$

It has been observed that first row transition metals form N-bonded thiocyanate (isothiocynate) complexes while second and third row transition elements form S-bonded thiocyanate (thiocyanate) complexes.

Soft acid ions (*e.g.*, Pd^{2+}, Pt^{2+} etc.) prefer to form thiocyanato complexes with SCN^- ion while hard acid ions (*e.g.*, Co^{3+}, Cr^{3+} etc.) prefer to give isothiocyanato complexes with this ion.

In spectrochemical series of ligands $\mathrm{SC\bar{N}}$ (thiocyanate ion) lies close to Cl^- ion while NCS^- (isothiocyanate ion) is close to H_2O.



Both nitro and nitrito complex compounds mentioned above are called **linkage isomers** and the isomerism shown by them is called **linkage isomerism.**

Another example of a pair of linkage isomers is furnished by *diammine bis (pyridine) dinitro cobalt* (III) *nitrate*, $[Co^{3+}(NH_3)_2(py)_2(NO_2)_2]NO_3$ and *diammine bis (pyridine) dinitrito cobalt* (III) *nitrate*, $[Co^{3+}(NH_3)_2(py)_2(ONO)_2]NO_3$.

It has been found that nitro (NO_2^-) is a stronger ligand than the nitrite (ONO^-). Linkage isomers can be identified by infra-red spectroscopy.

2. SCN^- ion. We know that this ion can be represented by any of the following two structures:

$$:\overset{-}{\underset{..}{\overset{..}{S}}}-C\equiv N: \qquad\qquad :\overset{..}{S}=C=\overset{-}{\overset{..}{N}}:$$

Structure (I)
(Thio cyanato group)

Structure (II)
(Iso-thiocyanato group)

Structures given above show that when SCN^- ion acts as a monodentate ligand , it may be coordinated to the central metal atom either through the lone pair of electrons on $\overset{-}{S}$ atom [Structure (I)] or through the lone pair of electrons on N^- atom [Structure (II)]. Thus:

(*a*) When SCN^- ion gets coordinated to the metal atom through the lone pair on negatively-charged S-atom $[M\leftarrow\overset{-}{\underset{..}{\overset{..}{S}}}-C\equiv N:$ *or* $M\leftarrow\overset{-}{S}CN]$, it is called **thiocyanato ligand** and is written as $\overset{-}{S}CN$. The complexes containing thiocyanato ligand are called **thiocyanato complexes.** For example $[Pd^{2+}(dipy)(SCN)_2]^0$ (orange yellow) is called *dipyridyl dithiocyanato palladium* (II), since the coordination of $SC\overset{-}{N}$ ligand to Pd^{2+} ion takes place through S-atom. This compound is also called *dipyridyl dithiocyanato* (S) *palladium* (II).

be linked to the central metal atom either through the lone pair of electrons on O^- [Structure (I)] or through the lone pair of electrons on S^- [Structure (II)]. The complex compounds in which $S_2O_3^{2-}$ ion is linked to the metal atom through O-atom are called *thiosulphate-O complex compounds* ($M—O—S_2O_2$) while those in which $S_2O_3^{2-}$ ion is attached to the metal through S-atom are called *thiosulphate-S complex compounds* ($M—S—SO_3$). Both these complexes are linkage isomers to each other.

Examples: (*a*) $H_4[CN)_5Co^{3+}—O—S_2O_2]$ (yellow) (O-bonded form) and $H_4[(CN)_5\ Co^{3+}—S—SO_3]$ (red) (S-bonded form) are linkage isomers to each other. O-bonded form is decomposed by H_2O to give sulphur and H_2SO_3 while S-bonded form gives H_2S and H_2SO_4.

$$H_4[(CN)_5Co^{3+}—O—S_2O_2] + H_2O \longrightarrow H_2[Co^{3+}(CN)_5\ (H_2O)] + S + H_2SO_3$$
$$H_4[(CN)_5Co^{3+}—S—SO_3] + 2H_2O \longrightarrow H_2[Co^{3+}(CN)_5\ (H_2O)] + H_2S + H_2SO_4$$

(*b*) $[(NH_3)_5Co^{3+}—O—S_2O_2]^+$ (O-bonded form) and $[(NH_3)_5Co^{3+}—S—SO_3]^+$ (S-bonded form) are linkage isomers.

Bridging Ligands and Bridged Complexes

Although the ligands like N_2 or $:N{\equiv}N:$ (dinitrogen), $NH_2—NH_2$ or N_2H_4 (hydrazine), OH^- (hydroxo), NH_2^- (amido or amino), NH^{2-} (imido), Cl^-, F^-, O^{2-}(oxo), O_2^{2-} or $:\overset{-}{\underset{..}{\ddot{O}}}—\overset{-}{\underset{..}{\ddot{O}}}:$ (peroxo), O_2^- or $:\ddot{O} \overset{...}{—} \ddot{O}:^-$ (superoxo), SO_4^{2-}, NO_2^- , CO etc. are monodentate ligands, they also act as bidendate ligands when they are attached with two separate metals atoms, making a bridge between them. Such ligands are called *bridging ligands* and the complexes thus formed are called *bridged* (or *polynuclear* or *multinuclear*) *complexes.* Each bridging ligand makes two σ-bonds with two metal atoms. A bridging ligand must have at least two lone pairs of electrons which the ligand uses to get coordinated to two metal atoms. The polynuclear complex may be *dinuclear, trinuclear, tetranuclear* etc.

Nomenclature of bridging ligands

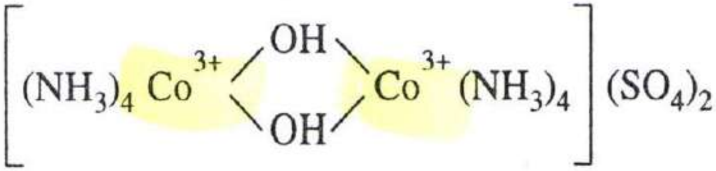
While naming the bridging ligands, the prefex μ is used before the name of each of the bridging ligands. For two similar bridging ligands *di*–μ or μ–*di* is used [Also see "*Nomenclature of Coordination Compounds*" discussed in chapter 2].

Bridged complexes of Co(III)

Co (III) forms a number of bridged complexes. These complexes are of the following types:

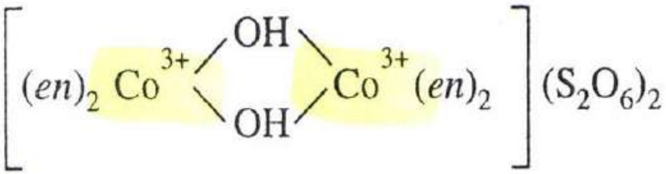
1. Bridged complexes containing hydroxo ions (OH^-) as bridging ligands. Examples of such complexes are (*i*), (*ii*), (*iii*) and (*iv*) given below in Fig. 1.35.

(*i*)



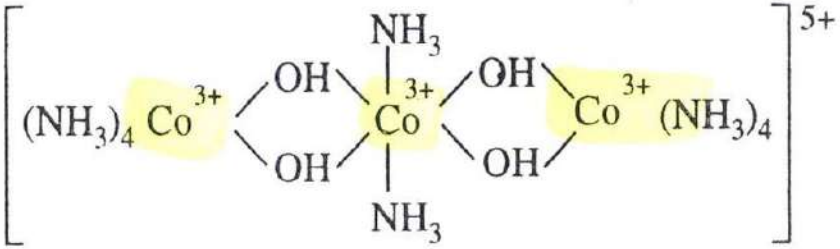
Octammine μ-dihydroxo dicobalt (III) sulphate

(*ii*)



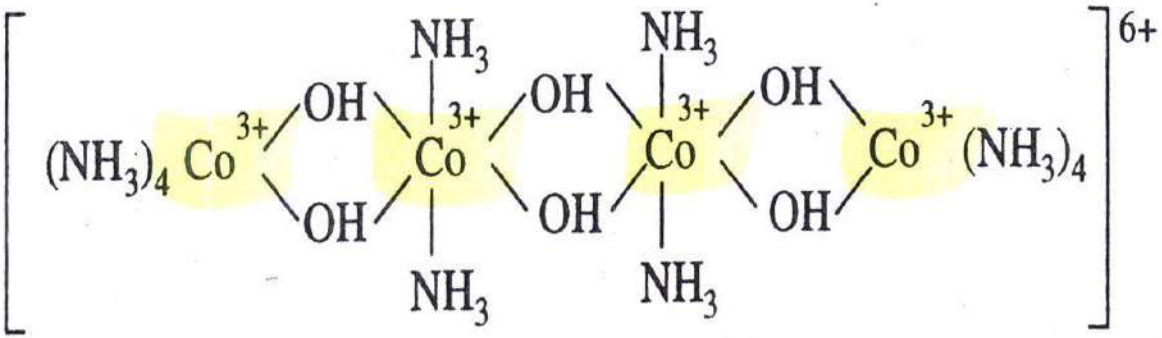
Tetrakis-(ethylenediamine) μ-dihydroxo dicobalt (III) dithionate

(*iii*)



Tetra- μ-hydroxo decammine tricobalt (III) ion

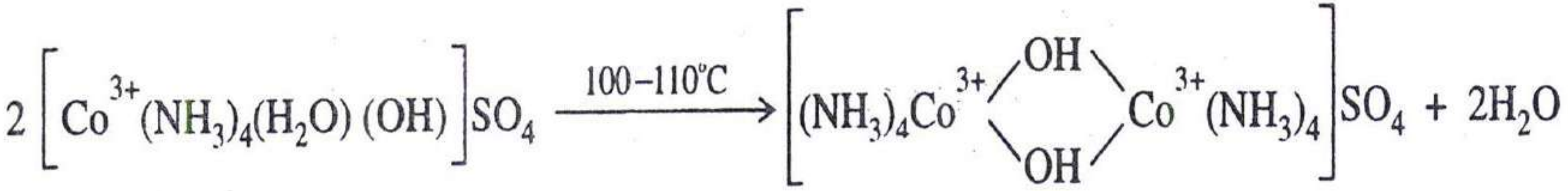
(*iv*)

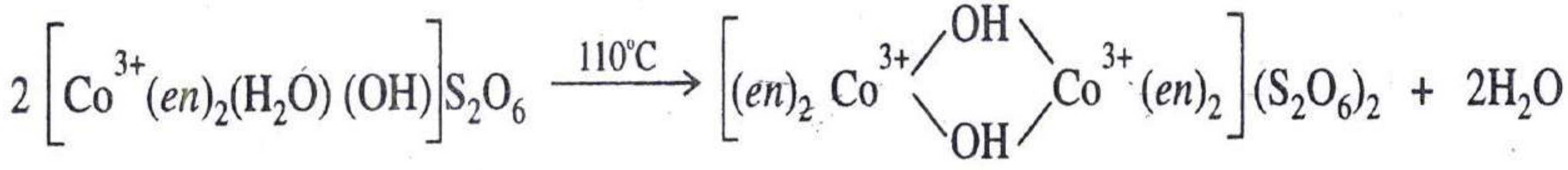


Dodeca ammine hexa-μ-hydroxo tetra cobalt (III) ion

Fig. 1.35. Examples of hydroxy-bridged complexes of Co (III) containing similar terminal ligands.

Complexes (*i*) and (*ii*) are binuclear complexes, complex (*iii*) is a trinuclear complex while complex (*iv*) is a tetranuclear complex. (*i*) and (*ii*) are obtained by the hydrolytic reactions of Co (III) compound in solution.





Complex (*iii*) is obtained by the treatment of $[Co^{3+}(NH_3)_4(H_2O)Cl]SO_4$ with cold alkali. Structures of complexes (*i*) (*ii*), (*iii*) and (*iv*) shown in Fig. 1.35 are given in Figures 1.36, 1.37, 1.38 and 1.39 respectively.

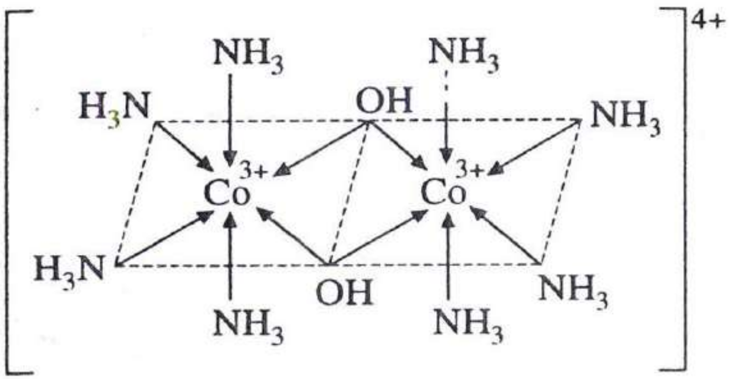


Fig. 1.36. Structure of octammine μ-dihydroxo dicobalt (III) ion.

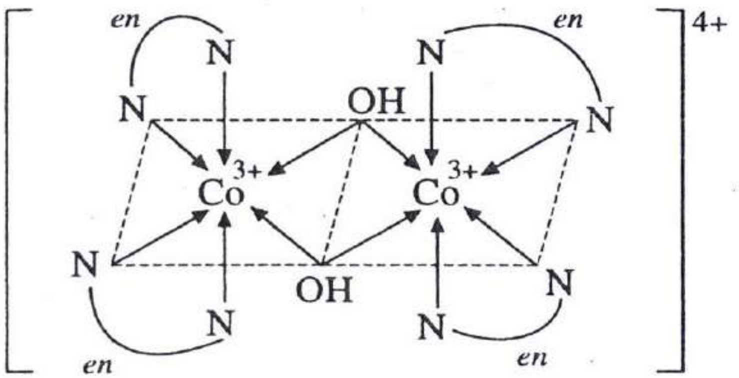


Fig. 1.37. Structure of tetrakis-(ethylene diamine) μ-dihydroxo dicobalt (III) ion.

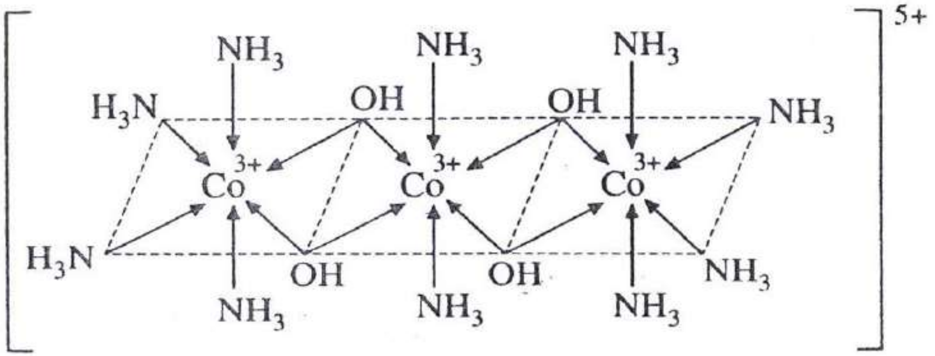
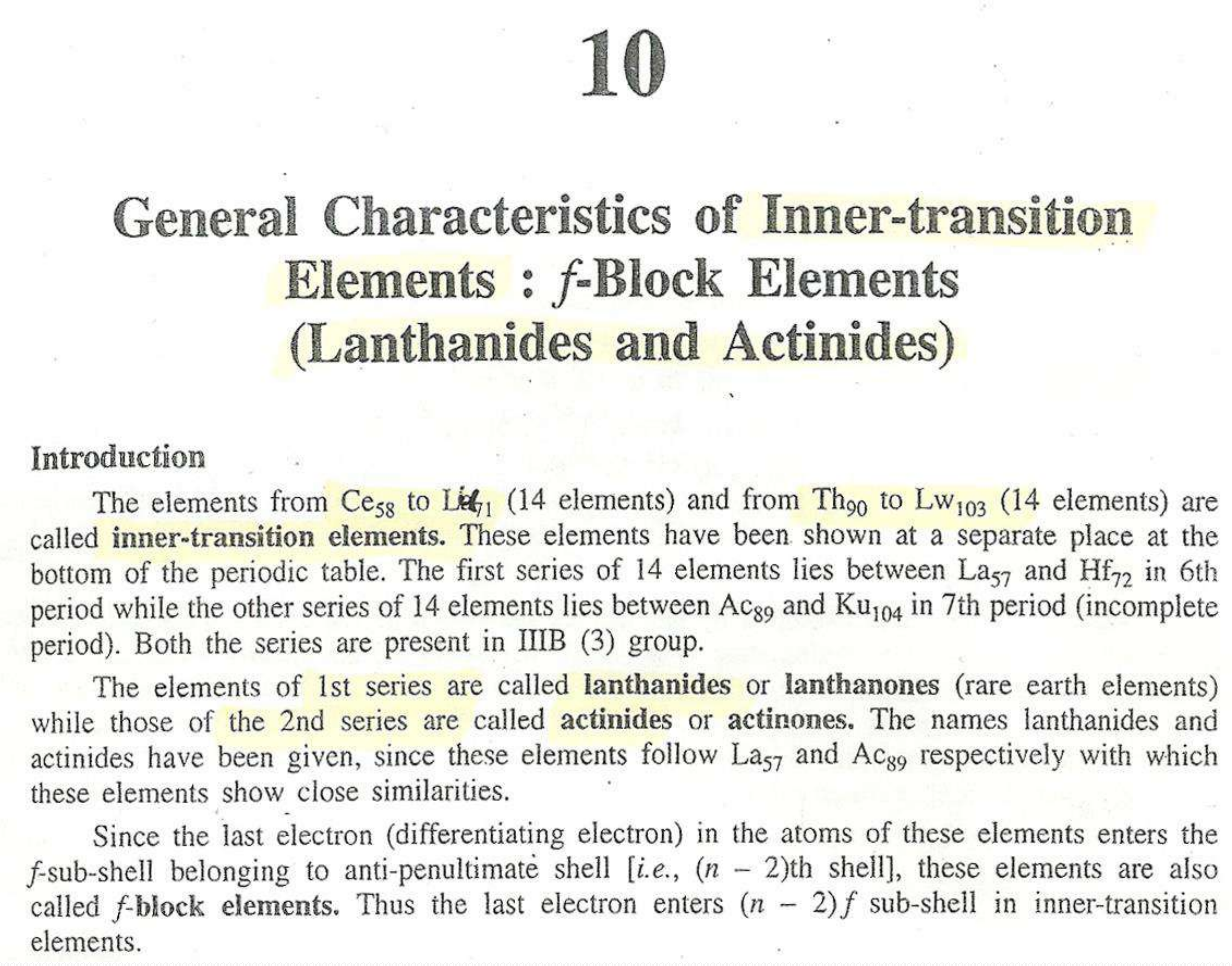


Fig. 1.38. Structure of μ-tetrahydroxo-decammine tricoblat (III) ion.

So far we have discussed hydroxy-bridged polynuclear complexes of Co(III) which contain similar terminal ligands. Co(III), however, also forms hydroxy-bridged binuclear complexes in



10

General Characteristics of Inner-transition Elements : *f*-Block Elements (Lanthanides and Actinides)

Introduction

The elements from Ce_{58} to Lu_{71} (14 elements) and from Th_{90} to Lw_{103} (14 elements) are called **inner-transition elements.** These elements have been shown at a separate place at the bottom of the periodic table. The first series of 14 elements lies between La_{57} and Hf_{72} in 6th period while the other series of 14 elements lies between Ac_{89} and Ku_{104} in 7th period (incomplete period). Both the series are present in IIIB (3) group.

The elements of 1st series are called **lanthanides** or **lanthanones** (rare earth elements) while those of the 2nd series are called **actinides** or **actinones.** The names lanthanides and actinides have been given, since these elements follow La_{57} and Ac_{89} respectively with which these elements show close similarities.

Since the last electron (differentiating electron) in the atoms of these elements enters the *f*-sub-shell belonging to anti-penultimate shell [*i.e.*, $(n-2)$th shell], these elements are also called ***f*-block elements.** Thus the last electron enters $(n-2)f$ sub-shell in inner-transition elements.

Since lanthanides are present in 6th period ($n = 6$) of the periodic table, the last electron in these elements goes to $(6 - 2)f$ or $4f$ sub-shell. Thus lanthanides are also called **4*f* block elements,** *i.e., lanthanides can be defined as those elements in which the last electron goes to 4f sub-shell.*

Similarly, since actinides are present in 7th period ($n = 7$) of the periodic table, the last electron in these elements goes to $(7 - 2)f$ or $5f$ sub-shell. Thus actinides are also called **5*f*-block elements**, *i.e., actinides are those elements in which the last electron enters 5f sub-shell.*

Valence-shell electronic configuration of the atoms of *f*-block elements can be represented as $(n - 2)f^{0-14}. (n - 1)d^{0-2}. ns^2$ which shows that in these elements the outermost three shells are partially-filled while the remaining inner shells are completely-filled.

Now we shall discuss lanthanides (4*f*-block elements) and actinides (5*f*-block elements) under separate sections.

Lanthanides: 4*f*-Block Elements

As already said, the 14 elements *viz.* Ce_{58} to Lu_{71} are called lanthanides.

General characteristics of lanthanides

The following are important properteis of lanthanides.

1. Electronic configurations

We know that the electronic configuration of La_{57} which is followed by 14 lanthanides is $[Xe]_{54}\,4f^0\,5d^1\,6s^2$ in which $5d$ sub-shell is singly-filled and $4f$ sub-shell is vacant. This configuration shows that as we move in the series of 14 lanthanides (Ce_{58} to Lu_{71}), the additional electron should occupy the vacant $4f$ orbitals and $5d$ orbitals should remain singly-filled, *i.e.*, the expected configurations of the atoms of lanthanides should be those in which $5d$ orbitals are singly-filled and $4f$ orbitals are progressively filled up with electrons. In other words, we can say that the expected configuration of the atoms of lanthanides should be $[Xe]_{54}\,4f^{1-14}\,5d^1\,6s^2$. But, since the energies of $5d$ and $4f$ orbitals are closely similar, in all the lanthanides, excepting Gd_{64} and Lu_{71}, $5d^1$ electron gets shifted to 4f orbitals and hence $5d$ orbitals remain vacant. In Gd_{64}, the shifting of $5d^1$ electron to $4f$ orbitals does not take place, since this type of shifting gives unstable configuration *viz.* $[Xe]_{54}\,5f^8 5d^0 6s^2$ to Gd_{64}. In Lu_{71} the shifting of $5d^1$ electron to $4f$ orbitals is also not possible because $4f$ orbitals are already filled to their maximum capacity of 14 electrons.

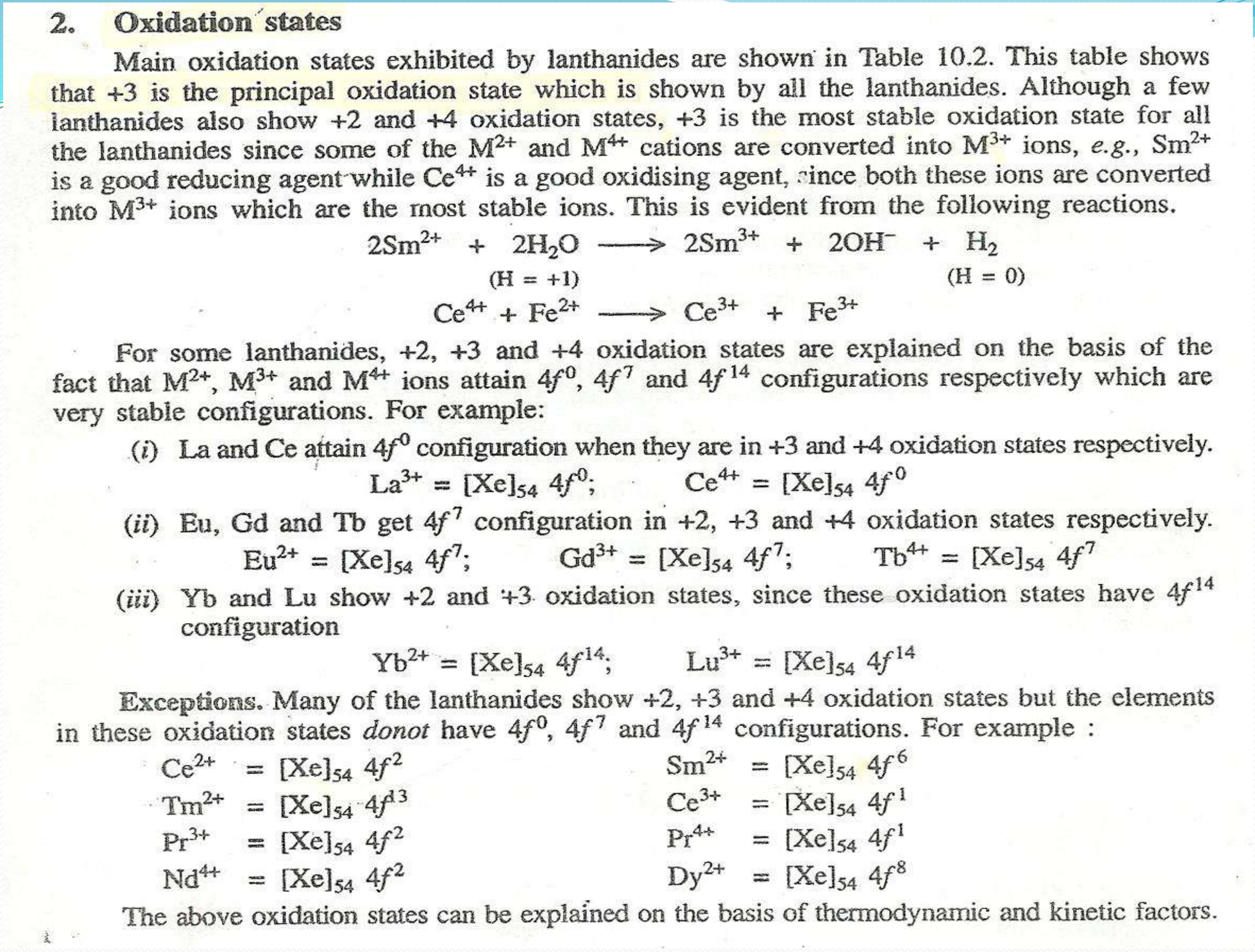
Observed as well as expected configurations are given in Table 10.1. Observed configurations show that the complete and valence configurations can be written as :

Complete configuration : 2, 8, 18, 20 to 32, 8 or 9, 2

or 2, 8, 18, $4s^2p^6d^{10}f^{2-14}$, $5s^2p^6d^{0-1}$, $6s^2$

or $[Xe]_{54}\,4f^{2-14}\,5d^{0-1}6s^2$

Valence-shell configuration : $4f^{2-14}\,5d^{0-1}\,6s^2$.



2. Oxidation states

Main oxidation states exhibited by lanthanides are shown in Table 10.2. This table shows that +3 is the principal oxidation state which is shown by all the lanthanides. Although a few lanthanides also show +2 and +4 oxidation states, +3 is the most stable oxidation state for all the lanthanides since some of the M^{2+} and M^{4+} cations are converted into M^{3+} ions, *e.g.*, Sm^{2+} is a good reducing agent while Ce^{4+} is a good oxidising agent, since both these ions are converted into M^{3+} ions which are the most stable ions. This is evident from the following reactions.

$$2Sm^{2+} + \underset{(H = +1)}{2H_2O} \longrightarrow 2Sm^{3+} + 2OH^- + \underset{(H = 0)}{H_2}$$

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

For some lanthanides, +2, +3 and +4 oxidation states are explained on the basis of the fact that M^{2+}, M^{3+} and M^{4+} ions attain $4f^0$, $4f^7$ and $4f^{14}$ configurations respectively which are very stable configurations. For example:

(*i*) La and Ce attain $4f^0$ configuration when they are in +3 and +4 oxidation states respectively.

$$La^{3+} = [Xe]_{54}\ 4f^0; \qquad Ce^{4+} = [Xe]_{54}\ 4f^0$$

(*ii*) Eu, Gd and Tb get $4f^7$ configuration in +2, +3 and +4 oxidation states respectively.

$$Eu^{2+} = [Xe]_{54}\ 4f^7; \qquad Gd^{3+} = [Xe]_{54}\ 4f^7; \qquad Tb^{4+} = [Xe]_{54}\ 4f^7$$

(*iii*) Yb and Lu show +2 and +3 oxidation states, since these oxidation states have $4f^{14}$ configuration

$$Yb^{2+} = [Xe]_{54}\ 4f^{14}; \qquad Lu^{3+} = [Xe]_{54}\ 4f^{14}$$

Exceptions. Many of the lanthanides show +2, +3 and +4 oxidation states but the elements in these oxidation states *donot* have $4f^0$, $4f^7$ and $4f^{14}$ configurations. For example :

$Ce^{2+} = [Xe]_{54}\ 4f^2$ $\qquad$ $Sm^{2+} = [Xe]_{54}\ 4f^6$

$Tm^{2+} = [Xe]_{54}\ 4f^{13}$ $\qquad$ $Ce^{3+} = [Xe]_{54}\ 4f^1$

$Pr^{3+} = [Xe]_{54}\ 4f^2$ $\qquad$ $Pr^{4+} = [Xe]_{54}\ 4f^1$

$Nd^{4+} = [Xe]_{54}\ 4f^2$ $\qquad$ $Dy^{2+} = [Xe]_{54}\ 4f^8$

The above oxidation states can be explained on the basis of thermodynamic and kinetic factors.

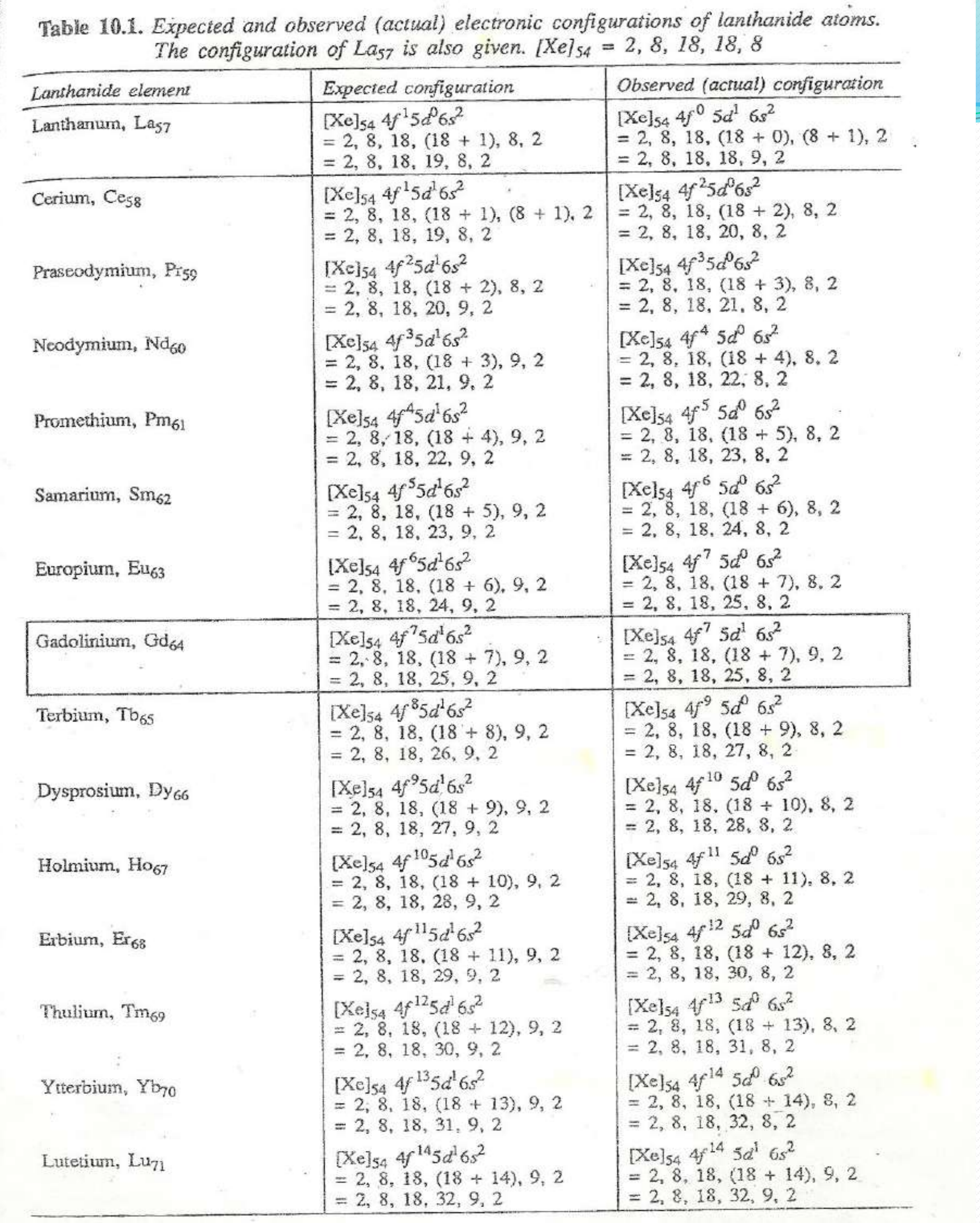
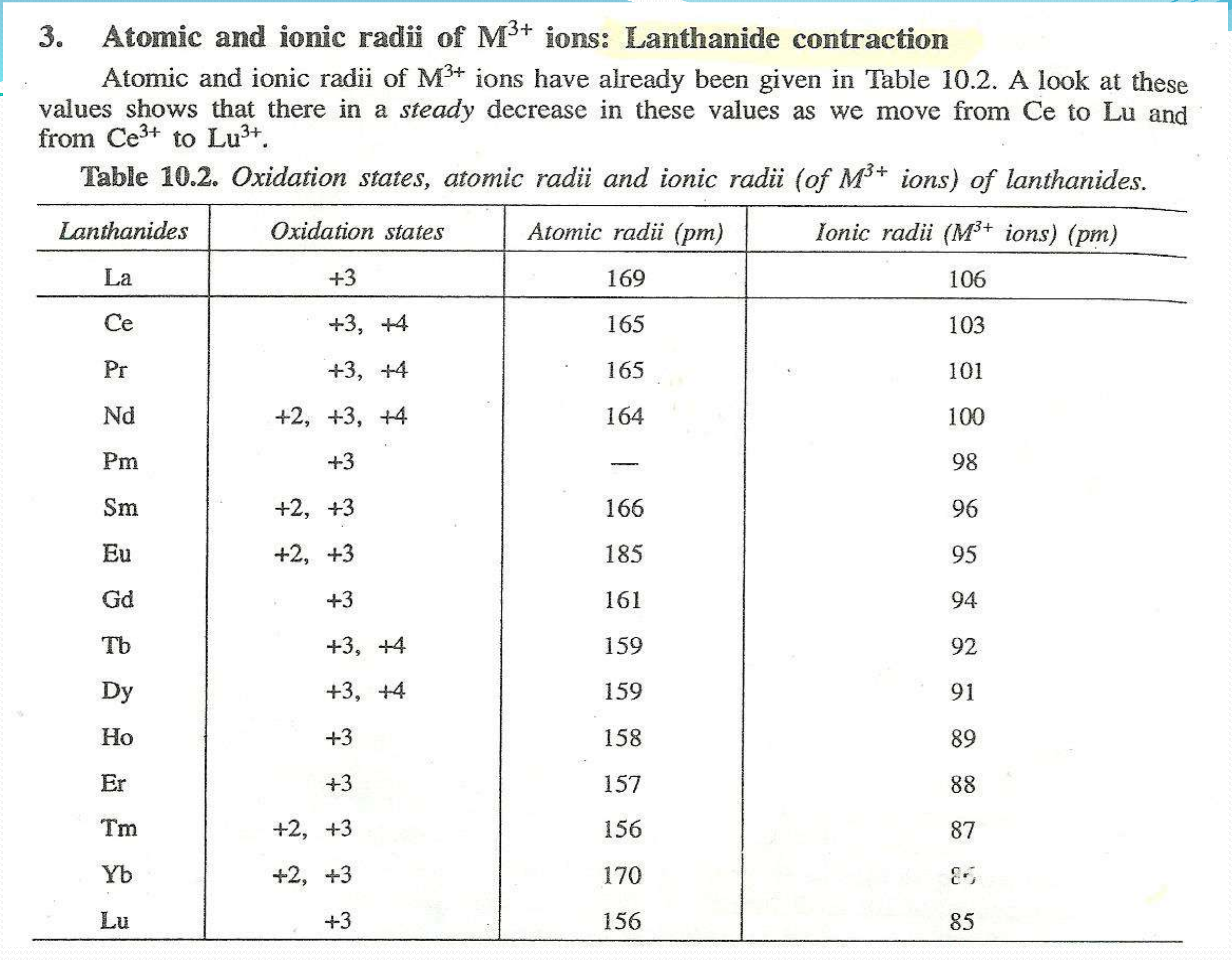


Table 10.1. *Expected and observed (actual) electronic configurations of lanthanide atoms. The configuration of* La_{57} *is also given.* $[Xe]_{54}$ = 2, 8, 18, 18, 8

Lanthanide element	*Expected configuration*	*Observed (actual) configuration*
Lanthanum, La_{57}	$[Xe]_{54}\,4f^{1}5d^{0}6s^{2}$ = 2, 8, 18, (18 + 1), 8, 2 = 2, 8, 18, 19, 8, 2	$[Xe]_{54}\,4f^{0}\,5d^{1}\,6s^{2}$ = 2, 8, 18, (18 + 0), (8 + 1), 2 = 2, 8, 18, 18, 9, 2
Cerium, Ce_{58}	$[Xe]_{54}\,4f^{1}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 1), (8 + 1), 2 = 2, 8, 18, 19, 8, 2	$[Xe]_{54}\,4f^{2}5d^{0}6s^{2}$ = 2, 8, 18, (18 + 2), 8, 2 = 2, 8, 18, 20, 8, 2
Praseodymium, Pr_{59}	$[Xe]_{54}\,4f^{2}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 2), 8, 2 = 2, 8, 18, 20, 9, 2	$[Xe]_{54}\,4f^{3}5d^{0}6s^{2}$ = 2, 8, 18, (18 + 3), 8, 2 = 2, 8, 18, 21, 8, 2
Neodymium, Nd_{60}	$[Xe]_{54}\,4f^{3}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 3), 9, 2 = 2, 8, 18, 21, 9, 2	$[Xe]_{54}\,4f^{4}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 4), 8, 2 = 2, 8, 18, 22, 8, 2
Promethium, Pm_{61}	$[Xe]_{54}\,4f^{4}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 4), 9, 2 = 2, 8, 18, 22, 9, 2	$[Xe]_{54}\,4f^{5}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 5), 8, 2 = 2, 8, 18, 23, 8, 2
Samarium, Sm_{62}	$[Xe]_{54}\,4f^{5}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 5), 9, 2 = 2, 8, 18, 23, 9, 2	$[Xe]_{54}\,4f^{6}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 6), 8, 2 = 2, 8, 18, 24, 8, 2
Europium, Eu_{63}	$[Xe]_{54}\,4f^{6}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 6), 9, 2 = 2, 8, 18, 24, 9, 2	$[Xe]_{54}\,4f^{7}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 7), 8, 2 = 2, 8, 18, 25, 8, 2
Gadolinium, Gd_{64}	$[Xe]_{54}\,4f^{7}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 7), 9, 2 = 2, 8, 18, 25, 9, 2	$[Xe]_{54}\,4f^{7}\,5d^{1}\,6s^{2}$ = 2, 8, 18, (18 + 7), 9, 2 = 2, 8, 18, 25, 8, 2
Terbium, Tb_{65}	$[Xe]_{54}\,4f^{8}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 8), 9, 2 = 2, 8, 18, 26, 9, 2	$[Xe]_{54}\,4f^{9}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 9), 8, 2 = 2, 8, 18, 27, 8, 2
Dysprosium, Dy_{66}	$[Xe]_{54}\,4f^{9}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 9), 9, 2 = 2, 8, 18, 27, 9, 2	$[Xe]_{54}\,4f^{10}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 10), 8, 2 = 2, 8, 18, 28, 8, 2
Holmium, Ho_{67}	$[Xe]_{54}\,4f^{10}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 10), 9, 2 = 2, 8, 18, 28, 9, 2	$[Xe]_{54}\,4f^{11}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 11), 8, 2 = 2, 8, 18, 29, 8, 2
Erbium, Er_{68}	$[Xe]_{54}\,4f^{11}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 11), 9, 2 = 2, 8, 18, 29, 9, 2	$[Xe]_{54}\,4f^{12}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 12), 8, 2 = 2, 8, 18, 30, 8, 2
Thulium, Tm_{69}	$[Xe]_{54}\,4f^{12}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 12), 9, 2 = 2, 8, 18, 30, 9, 2	$[Xe]_{54}\,4f^{13}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 13), 8, 2 = 2, 8, 18, 31, 8, 2
Ytterbium, Yb_{70}	$[Xe]_{54}\,4f^{13}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 13), 9, 2 = 2, 8, 18, 31, 9, 2	$[Xe]_{54}\,4f^{14}\,5d^{0}\,6s^{2}$ = 2, 8, 18, (18 + 14), 8, 2 = 2, 8, 18, 32, 8, 2
Lutetium, Lu_{71}	$[Xe]_{54}\,4f^{14}5d^{1}6s^{2}$ = 2, 8, 18, (18 + 14), 9, 2 = 2, 8, 18, 32, 9, 2	$[Xe]_{54}\,4f^{14}\,5d^{1}\,6s^{2}$ = 2, 8, 18, (18 + 14), 9, 2 = 2, 8, 18, 32, 9, 2



3. Atomic and ionic radii of M^{3+} ions: Lanthanide contraction

Atomic and ionic radii of M^{3+} ions have already been given in Table 10.2. A look at these values shows that there in a *steady* decrease in these values as we move from Ce to Lu and from Ce^{3+} to Lu^{3+}.

Table 10.2. *Oxidation states, atomic radii and ionic radii (of M^{3+} ions) of lanthanides.*

Lanthanides	*Oxidation states*	*Atomic radii (pm)*	*Ionic radii (M^{3+} ions) (pm)*
La	+3	169	106
Ce	+3, +4	165	103
Pr	+3, +4	165	101
Nd	+2, +3, +4	164	100
Pm	+3	—	98
Sm	+2, +3	166	96
Eu	+2, +3	185	95
Gd	+3	161	94
Tb	+3, +4	159	92
Dy	+3, +4	159	91
Ho	+3	158	89
Er	+3	157	88
Tm	+2, +3	156	87
Yb	+2, +3	170	86
Lu	+3	156	85

The steady decrease in the atomic and ionic radii (M^{3+} ions) of lanthanide elements with increasing atomic number is called **lanthanide contraction.**

When we say that there is a steady decrease in the values of atomic and ionic radii, this means that the decrease is *very small.* For example on moving from Ce to Lu the atomic radii decrease from 165 pm to 156 pm and the decrease is only equal to 165 – 156 = 9 pm. Similarly, the ionic radii decrease from 103 to 85 on moving from Ce^{3+} to Lu^{3+} and the decrease in only equal to 103 – 85 = 18 pm. Thus we see that although the atomic number or nuclear charge increases by +14 units which is a large number, the decrease in atomic and ionic radii is only equal to 9 pm and 18 pm respectively. This decrease in atomic and ionic radii is very small as compared to that found in the elements of other groups and periods.

It may be seen from the table that although the atomic radii show some irregularities (*e.g.*, the atomic radii of Eu and Yb are abnormally high), the ionic radii of M^{3+} ions contract steadily.

Cause of lanthanide contraction

We know that as we proceed from one element to the next one in lanthamide series, the nuclear charge (*i.e.*, atomic number) increases by +1 at each next element. Thus as we move from Ce to Lu, the attraction between the nucleus and the outermost shell electron increases gradually at each step. It is also known that as we move from Ce to Lu, the addition of extra electron takes place to 4*f* orbitals. Since 4*f* orbitals have very diffused shape, the electrons in these orbitals are not able to shield (decrease) effectively the attraction of the nucleus for the electrons in the outer-most shell as the atomic number of lanthanides increases. Thus it is only due to the gradual increase in the nuclear charge (*i.e.*, increase in the attraction between the nucleus and the outer-most shell electrons) that the size of the lanthanide atoms and M^{3+} ions decreases gradually with atomic number. The above discussion shows that it is due to the poor shielding effect of 4*f* electrons and gradual increase in the nuclear charge that the lanthanide contraction takes place among lanthanides.

Consequences of lanthanide contraction

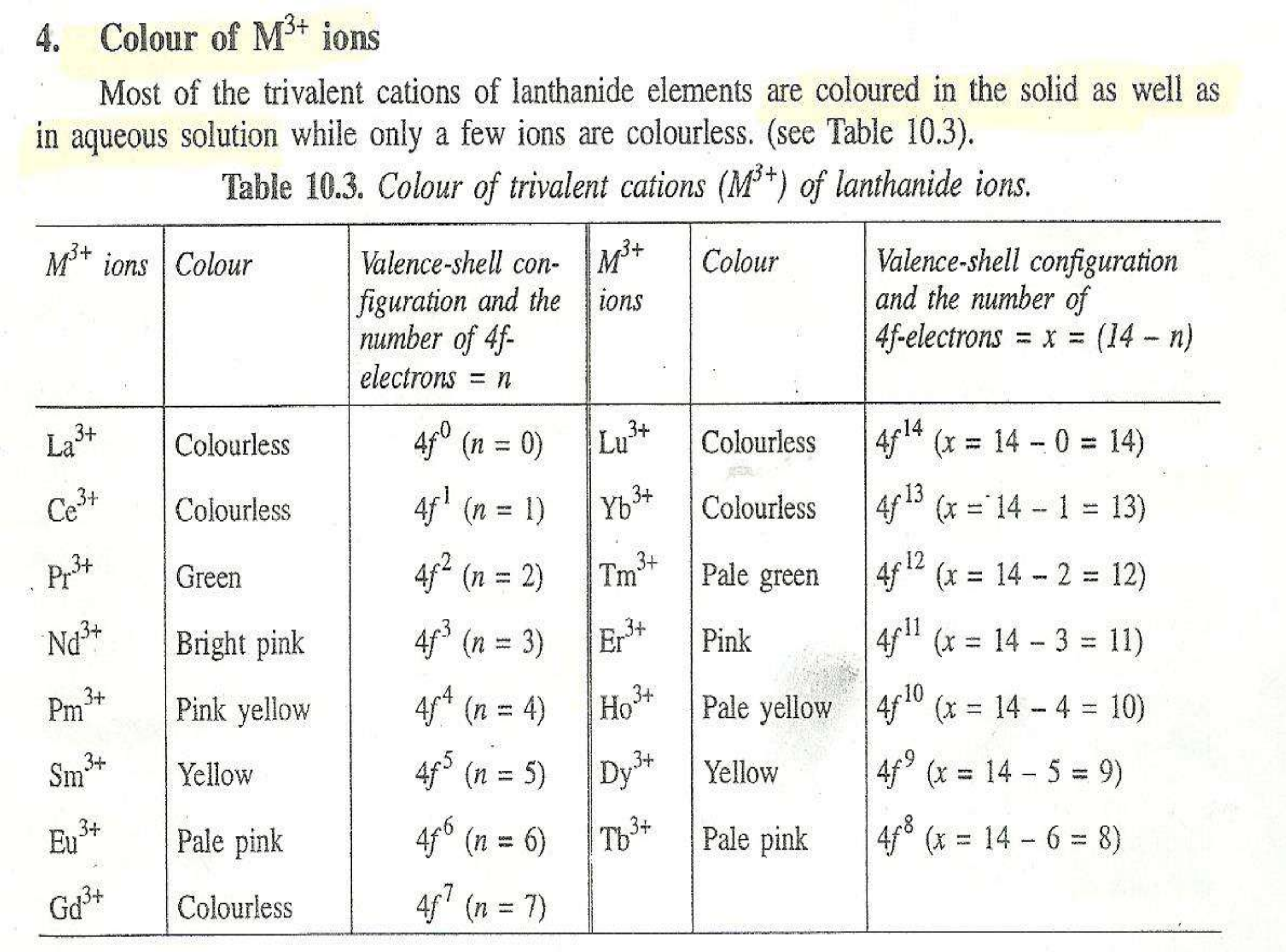
Lanthanide contraction plays an important role in determining the chemistry of lanthanides and heavier transition series elements. Some, important consequences of lanthanide contraction are discussed below :

(*a*) **Basic character of lanthanide hydroxides, $M(OH)_3$.** Due to lanthanide contraction, the size of +3 lanthanide ions (M^{3+} ions) decreases regularly with increase in atomic number. As a result of this decrease in size, the covalent character between M^{3+} ion and OH^- ions increases from $La(OH)_3$ to $Lu(OH)_3$. (*Fajan's rules*). Therefore, the basic character of the hydroxides decreases with increase in atomic number. Consequently, $La(OH)_3$ is most basic while $Lu(OH)_3$ is the least basic.

(*b*) **Similarities among lanthanides.** Because of very small change in the radii of lanthanides, their chemical properties are quite similar. It is due to their similar properties that the lanthanides cannot be separated from each other in pure state. Recently, methods based on repeated fractional crystallisation or ion exchange techniques, which take the advantage of slight differences in their properties like solubility, complex ion formation, hydration etc. arising from very slight size differences of their trivalent ions, have been used.

(*c*) **Comparison between the densities of the elements of 1st, 2nd and 3rd transition series.** See "*Atomic Volumes and Densities*" discussed in the chapter of "*General Characteristics of a d-Block Elements*" (Chapter 6).

(*d*) **Resemblance between the atomic radii of the elements of 2nd and 3rd transition series.** See "*Atomic Radii*" discussed in the chapter of "*General characteristics of d-blcok Elements*". (Chapter 6).



4. Colour of M^{3+} ions

Most of the trivalent cations of lanthanide elements are coloured in the solid as well as in aqueous solution while only a few ions are colourless. (see Table 10.3).

Table 10.3. *Colour of trivalent cations (M^{3+}) of lanthanide ions.*

M^{3+} ions	*Colour*	*Valence-shell configuration and the number of 4f-electrons = n*	*M^{3+} ions*	*Colour*	*Valence-shell configuration and the number of 4f-electrons = x = (14 – n)*
La^{3+}	Colourless	$4f^0$ $(n = 0)$	Lu^{3+}	Colourless	$4f^{14}$ $(x = 14 - 0 = 14)$
Ce^{3+}	Colourless	$4f^1$ $(n = 1)$	Yb^{3+}	Colourless	$4f^{13}$ $(x = 14 - 1 = 13)$
Pr^{3+}	Green	$4f^2$ $(n = 2)$	Tm^{3+}	Pale green	$4f^{12}$ $(x = 14 - 2 = 12)$
Nd^{3+}	Bright pink	$4f^3$ $(n = 3)$	Er^{3+}	Pink	$4f^{11}$ $(x = 14 - 3 = 11)$
Pm^{3+}	Pink yellow	$4f^4$ $(n = 4)$	Ho^{3+}	Pale yellow	$4f^{10}$ $(x = 14 - 4 = 10)$
Sm^{3+}	Yellow	$4f^5$ $(n = 5)$	Dy^{3+}	Yellow	$4f^9$ $(x = 14 - 5 = 9)$
Eu^{3+}	Pale pink	$4f^6$ $(n = 6)$	Tb^{3+}	Pale pink	$4f^8$ $(x = 14 - 6 = 8)$
Gd^{3+}	Colourless	$4f^7$ $(n = 7)$			

It may be seen from the table that the colour depends on the number of electrons present in $4f$ orbitals. The ion having n electrons in $4f$ orbitals has the same colour as the ion which has $(14 - n)$ electrons in $4f$ orbitals. For example La^{3+} $(4f^0)$ which has no electron in its $4f$ orbitals $(n = 0)$ is colourless and Lu^{3+} ion $(4f^{14})$ which has $(14 - 0) = 14$ electrons in $4f$ orbitals is also colourless. Similarly Pr^{3+} ion $(4f^2)$ which has two electrons in its $4f$ orbitals $(n = 2)$ and Tm^{3+} ion $(4f^{12})$ which has $(14 - 2) = 12$ electrons in its $4f$ orbitals have the same colour (green). (See Fig. 10.1)

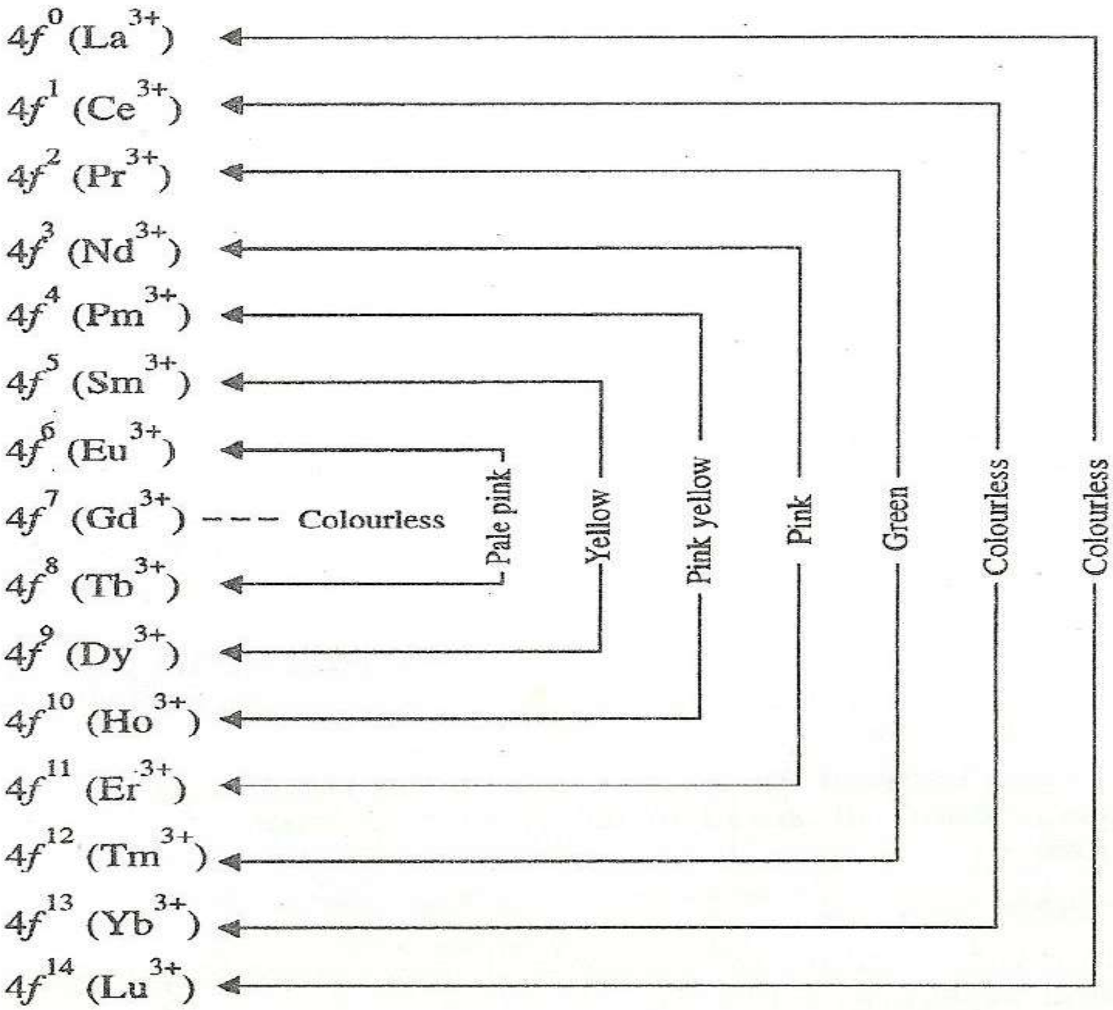
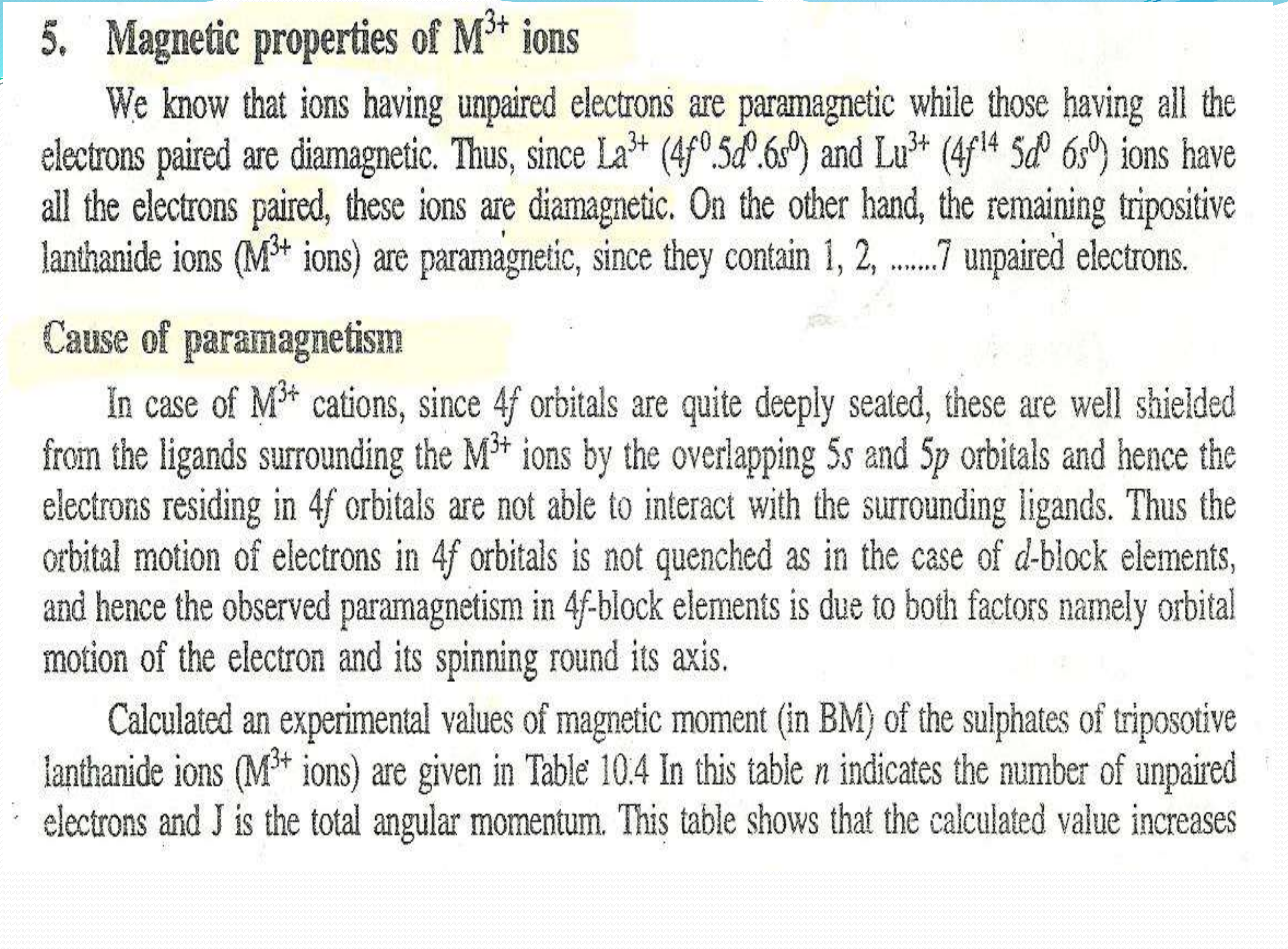


Fig. 10.1. Colour of tripositive lanthanide cations (M^{3+} ions).



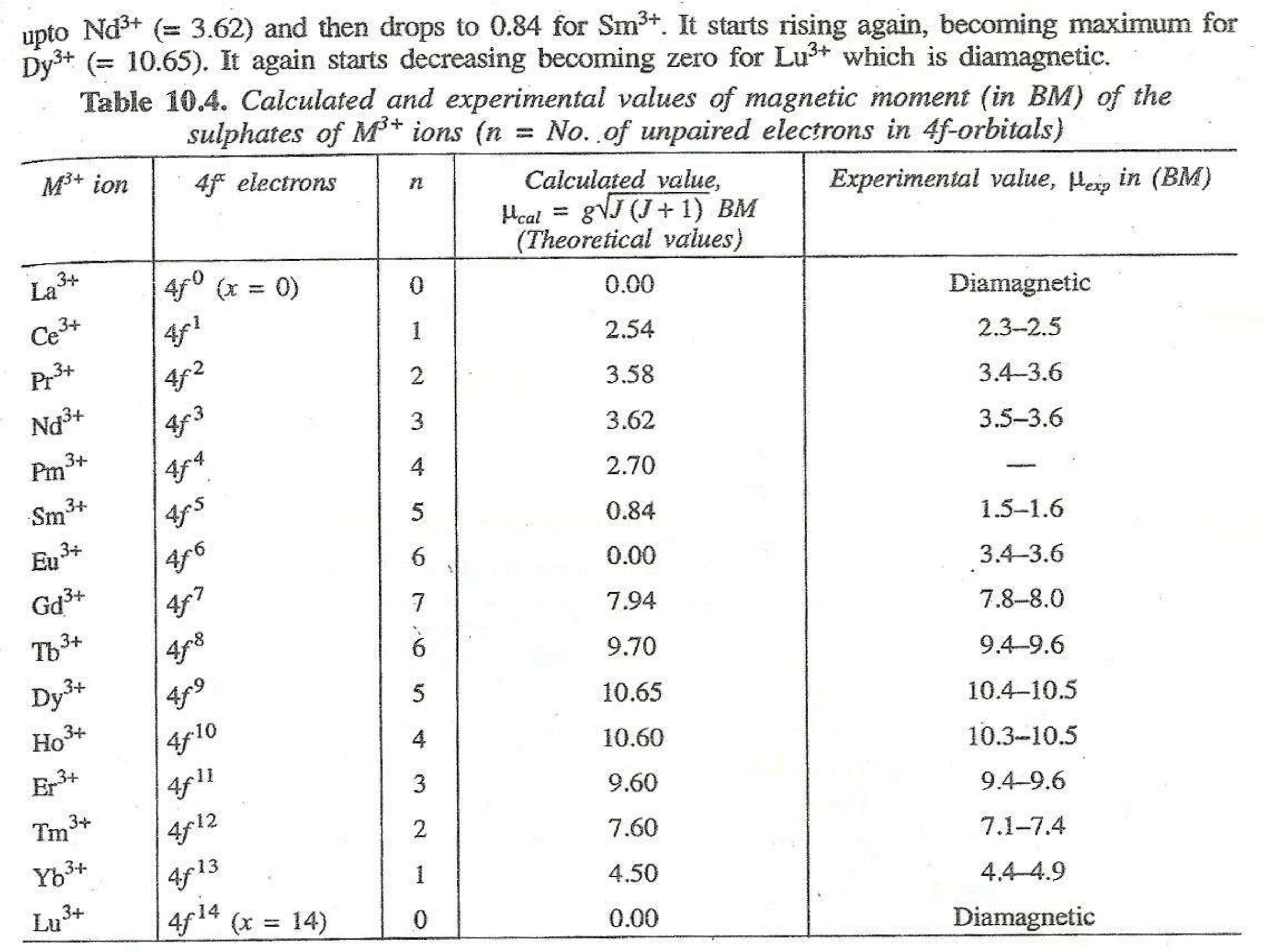
5. Magnetic properties of M^{3+} ions

We know that ions having unpaired electrons are paramagnetic while those having all the electrons paired are diamagnetic. Thus, since La^{3+} ($4f^0.5d^0.6s^0$) and Lu^{3+} ($4f^{14}\ 5d^0\ 6s^0$) ions have all the electrons paired, these ions are diamagnetic. On the other hand, the remaining tripositive lanthanide ions (M^{3+} ions) are paramagnetic, since they contain 1, 2, ...7 unpaired electrons.

Cause of paramagnetism

In case of M^{3+} cations, since 4*f* orbitals are quite deeply seated, these are well shielded from the ligands surrounding the M^{3+} ions by the overlapping 5*s* and 5*p* orbitals and hence the electrons residing in 4*f* orbitals are not able to interact with the surrounding ligands. Thus the orbital motion of electrons in 4*f* orbitals is not quenched as in the case of *d*-block elements, and hence the observed paramagnetism in 4*f*-block elements is due to both factors namely orbital motion of the electron and its spinning round its axis.

Calculated an experimental values of magnetic moment (in BM) of the sulphates of triposotive lanthanide ions (M^{3+} ions) are given in Table 10.4 In this table *n* indicates the number of unpaired electrons and J is the total angular momentum. This table shows that the calculated value increases



upto Nd^{3+} (= 3.62) and then drops to 0.84 for Sm^{3+}. It starts rising again, becoming maximum for Dy^{3+} (= 10.65). It again starts decreasing becoming zero for Lu^{3+} which is diamagnetic.

Table 10.4. *Calculated and experimental values of magnetic moment (in BM) of the sulphates of M^{3+} ions (n = No. of unpaired electrons in 4f-orbitals)*

M^{3+} *ion*	$4f^x$ *electrons*	n	*Calculated value,* $\mu_{cal} = g\sqrt{J(J+1)}$ *BM* *(Theoretical values)*	*Experimental value,* μ_{exp} *in (BM)*
La^{3+}	$4f^0$ ($x = 0$)	0	0.00	Diamagnetic
Ce^{3+}	$4f^1$	1	2.54	2.3–2.5
Pr^{3+}	$4f^2$	2	3.58	3.4–3.6
Nd^{3+}	$4f^3$	3	3.62	3.5–3.6
Pm^{3+}	$4f^4$	4	2.70	—
Sm^{3+}	$4f^5$	5	0.84	1.5–1.6
Eu^{3+}	$4f^6$	6	0.00	3.4–3.6
Gd^{3+}	$4f^7$	7	7.94	7.8–8.0
Tb^{3+}	$4f^8$	6	9.70	9.4–9.6
Dy^{3+}	$4f^9$	5	10.65	10.4–10.5
Ho^{3+}	$4f^{10}$	4	10.60	10.3–10.5
Er^{3+}	$4f^{11}$	3	9.60	9.4–9.6
Tm^{3+}	$4f^{12}$	2	7.60	7.1–7.4
Yb^{3+}	$4f^{13}$	1	4.50	4.4–4.9
Lu^{3+}	$4f^{14}$ ($x = 14$)	0	0.00	Diamagnetic

6. Physical properties

All the lanthanides are soft, malleable and ductile, and have low tensile strength. They are not good conductors of heat and electricity. In general, the atomic volumes and densities of these elements increase with the increase in atomic number.

7. Chemical reactivity of lanthanides

All the lanthanides are almost equally chemical reactive. Their similar chemical reactivity is due to the fact that since 4*f* electrons in lanthanides are very effectively shielded from the interaction with other elements by the overlapping 5*s*, 5*p* and 6*s* electrons (5*d* orbitals donot contain any electron), these elements have very little difference in their chemical reactivity. It is because of similarity in their chemical reactivity that lanthanides occur together in nature and hence it is difficult to separate these elements from each other.

Lanthanides are generally more reactive them *d*-block elements.

8. Formation of compounds

(*a*) Many lanthanides react with carbon to form salt-like carbides and with H_2 to give salt- like hydrides. Lanthanides react with air or O_2 and S to form sesquioxides (M_2O_3) and sulphides (M_2S_3) respectively. Cerium gives CeO_2. Ytterbium, however, resists the action of air even at 1000°C due to the formation of a protective coating of its oxide. M_2O_3 oxides react with H_2O to form in soluble hydroxides, $M(OH)_3$. Oxides react with CO_2 to give carbonates, $M_2(CO_3)_3$.

All the lanthanides react with H_2O slowly in cold but rapidly on heating and liberate H_2 and form $M(OH)_3$.

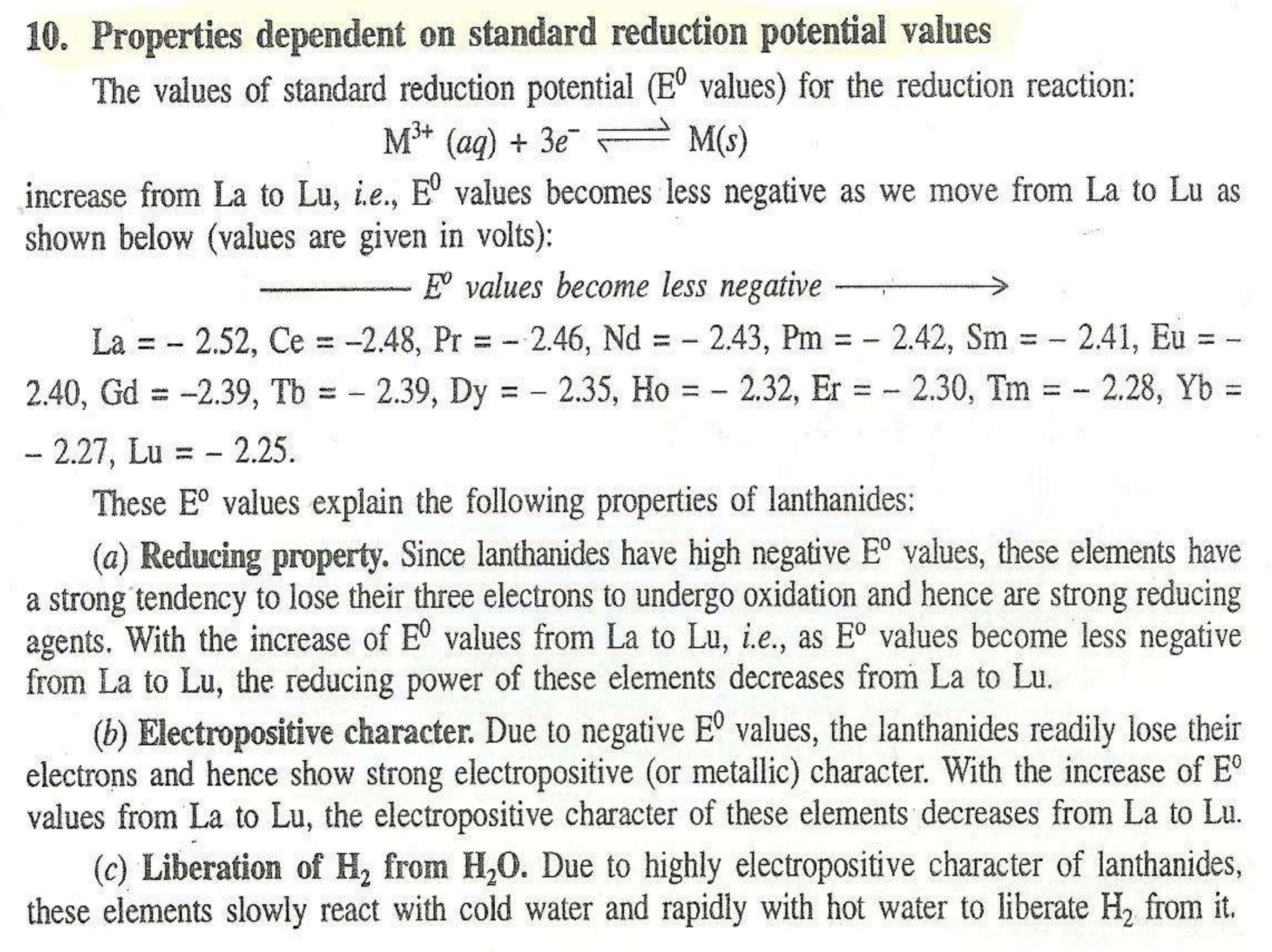
(*b*) Lanthanide compounds are generally ionic, coloured and show paramagnetism. Fluorides, oxides, hydroxides, carbonates, phosphates, chromates and oxalates of lanthanides are largely soluble in water. On the other hand, the halides other than fluorides, nitrates, acetates, perchlorates and salts of oxy acids of lanthanides follow the pattern of solubility of the salts of group 2 elements. However, lanthanide sulphates are soluble in water.

All hydroxides, $M(OH)_3$ are ionic and basic in nature. These are stronger bases than $Al(OH)_3$, but weaker than $Ca(OH)_2$. Due to lanthanide contraction, the basicity of the hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. Thus $La(OH)_3$ is the strongest base and $Lu(OH)_3$ is the weakest base.

Hydrides react with CO_2 to form $M_2(CO_3)_3$.

9. Formation of complexes

Although tripositive lanthanide cations have a high charge equal to +3 on them, yet their size is so large that their charge-to-radius ratio becomes so small that these ions have very poor tendency to form complexes. Common ligands with which M^{3+} ions form stable complexes are: (*i*) *chelating oxygen containing ligands* like EDTA citric acid, oxalic acid, acetylacetone, (*ii*) *nitrogen containing ligands* like ethylenediamine, NCS etc.



10. Properties dependent on standard reduction potential values

The values of standard reduction potential (E^0 values) for the reduction reaction:

$$M^{3+}\,(aq) + 3e^- \rightleftharpoons M(s)$$

increase from La to Lu, *i.e.*, E^0 values becomes less negative as we move from La to Lu as shown below (values are given in volts):

$$\xrightarrow{\hspace{3em} E^0 \text{ values become less negative} \hspace{3em}}$$

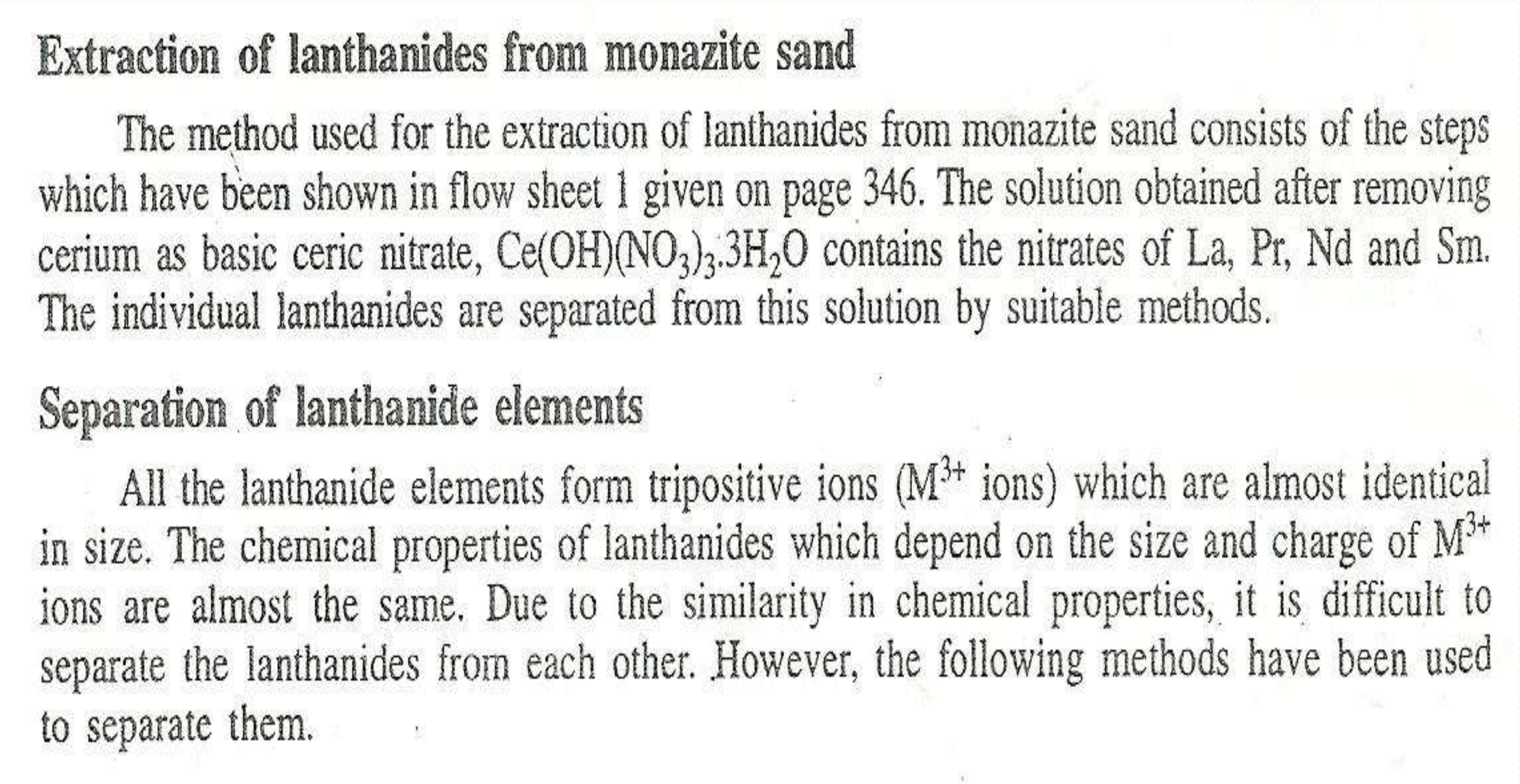
La = – 2.52, Ce = –2.48, Pr = – 2.46, Nd = – 2.43, Pm = – 2.42, Sm = – 2.41, Eu = – 2.40, Gd = –2.39, Tb = – 2.39, Dy = – 2.35, Ho = – 2.32, Er = – 2.30, Tm = – 2.28, Yb = – 2.27, Lu = – 2.25.

These E^o values explain the following properties of lanthanides:

(*a*) **Reducing property.** Since lanthanides have high negative E^o values, these elements have a strong tendency to lose their three electrons to undergo oxidation and hence are strong reducing agents. With the increase of E^0 values from La to Lu, *i.e.*, as E^o values become less negative from La to Lu, the reducing power of these elements decreases from La to Lu.

(*b*) **Electropositive character.** Due to negative E^0 values, the lanthanides readily lose their electrons and hence show strong electropositive (or metallic) character. With the increase of E^0 values from La to Lu, the electropositive character of these elements decreases from La to Lu.

(*c*) **Liberation of H_2 from H_2O.** Due to highly electropositive character of lanthanides, these elements slowly react with cold water and rapidly with hot water to liberate H_2 from it.

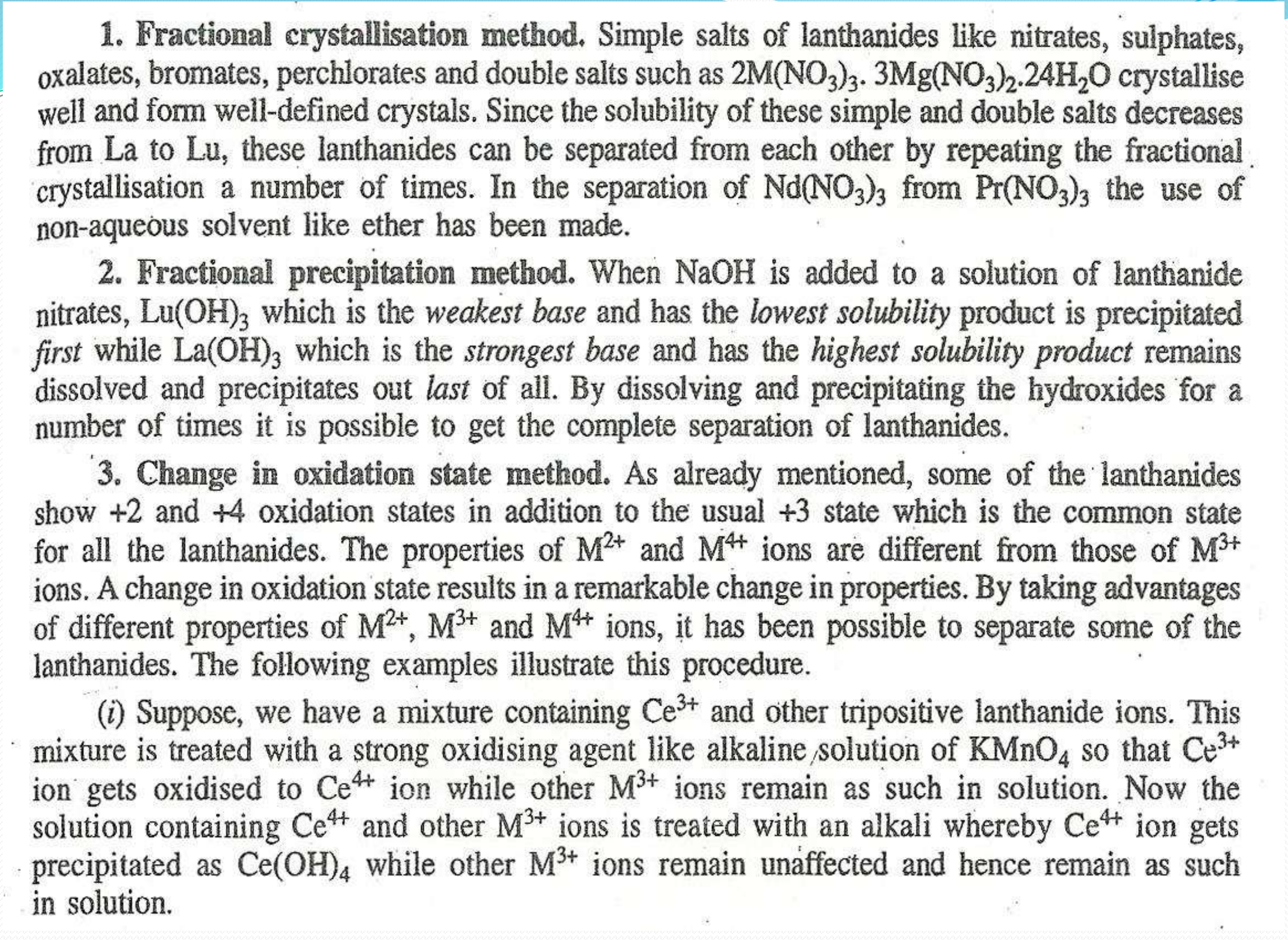


Extraction of lanthanides from monazite sand

The method used for the extraction of lanthanides from monazite sand consists of the steps which have been shown in flow sheet 1 given on page 346. The solution obtained after removing cerium as basic ceric nitrate, $Ce(OH)(NO_3)_3.3H_2O$ contains the nitrates of La, Pr, Nd and Sm. The individual lanthanides are separated from this solution by suitable methods.

Separation of lanthanide elements

All the lanthanide elements form tripositive ions (M^{3+} ions) which are almost identical in size. The chemical properties of lanthanides which depend on the size and charge of M^{3+} ions are almost the same. Due to the similarity in chemical properties, it is difficult to separate the lanthanides from each other. However, the following methods have been used to separate them.

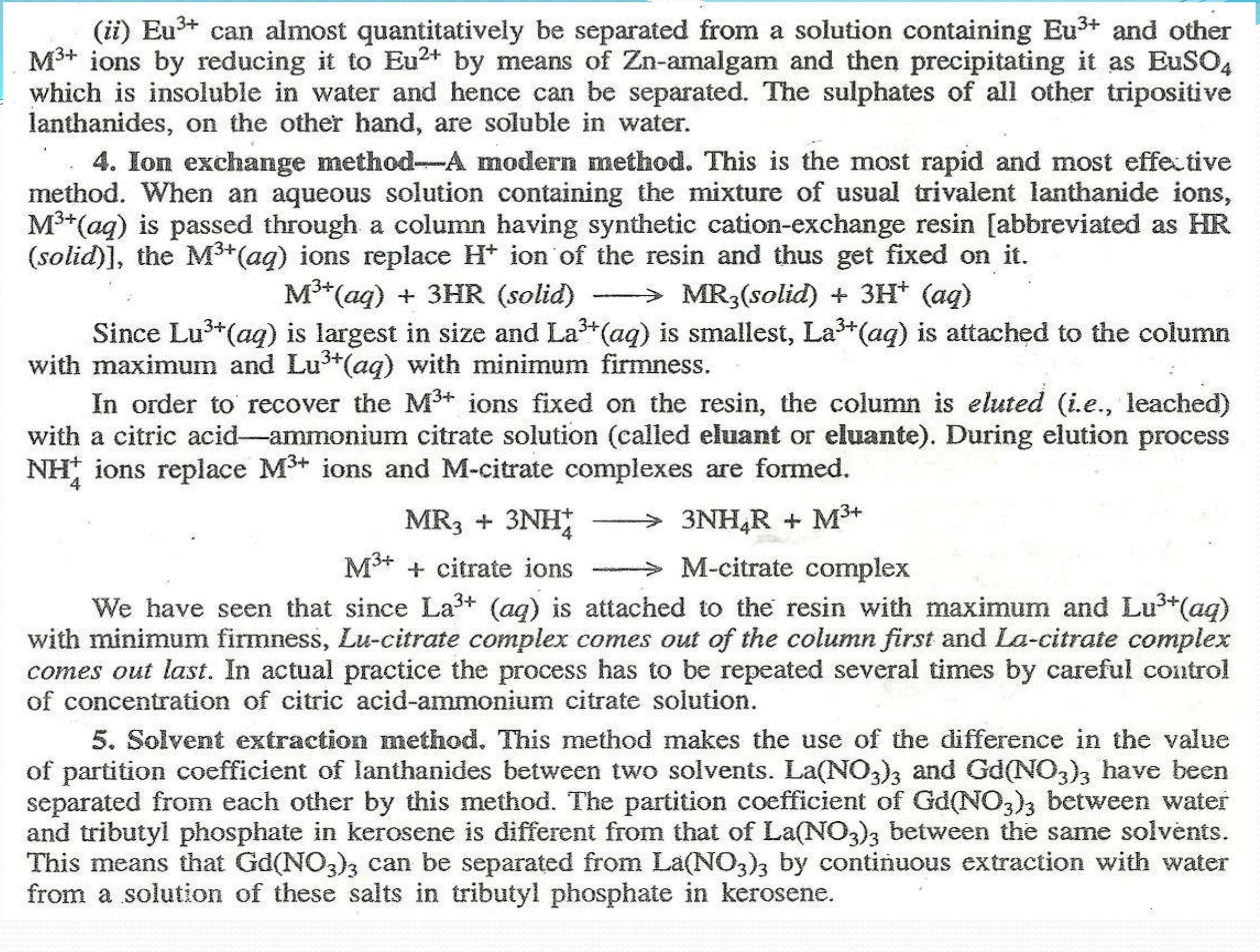


1. Fractional crystallisation method. Simple salts of lanthanides like nitrates, sulphates, oxalates, bromates, perchlorates and double salts such as $2M(NO_3)_3 . 3Mg(NO_3)_2 . 24H_2O$ crystallise well and form well-defined crystals. Since the solubility of these simple and double salts decreases from La to Lu, these lanthanides can be separated from each other by repeating the fractional crystallisation a number of times. In the separation of $Nd(NO_3)_3$ from $Pr(NO_3)_3$ the use of non-aqueous solvent like ether has been made.

2. Fractional precipitation method. When NaOH is added to a solution of lanthanide nitrates, $Lu(OH)_3$ which is the *weakest base* and has the *lowest solubility* product is precipitated *first* while $La(OH)_3$ which is the *strongest base* and has the *highest solubility product* remains dissolved and precipitates out *last* of all. By dissolving and precipitating the hydroxides for a number of times it is possible to get the complete separation of lanthanides.

3. Change in oxidation state method. As already mentioned, some of the lanthanides show +2 and +4 oxidation states in addition to the usual +3 state which is the common state for all the lanthanides. The properties of M^{2+} and M^{4+} ions are different from those of M^{3+} ions. A change in oxidation state results in a remarkable change in properties. By taking advantages of different properties of M^{2+}, M^{3+} and M^{4+} ions, it has been possible to separate some of the lanthanides. The following examples illustrate this procedure.

(*i*) Suppose, we have a mixture containing Ce^{3+} and other tripositive lanthanide ions. This mixture is treated with a strong oxidising agent like alkaline solution of $KMnO_4$ so that Ce^{3+} ion gets oxidised to Ce^{4+} ion while other M^{3+} ions remain as such in solution. Now the solution containing Ce^{4+} and other M^{3+} ions is treated with an alkali whereby Ce^{4+} ion gets precipitated as $Ce(OH)_4$ while other M^{3+} ions remain unaffected and hence remain as such in solution.



(*ii*) Eu^{3+} can almost quantitatively be separated from a solution containing Eu^{3+} and other M^{3+} ions by reducing it to Eu^{2+} by means of Zn-amalgam and then precipitating it as $EuSO_4$ which is insoluble in water and hence can be separated. The sulphates of all other tripositive lanthanides, on the other hand, are soluble in water.

4. Ion exchange method—A modern method. This is the most rapid and most effective method. When an aqueous solution containing the mixture of usual trivalent lanthanide ions, $M^{3+}(aq)$ is passed through a column having synthetic cation-exchange resin [abbreviated as HR (*solid*)], the $M^{3+}(aq)$ ions replace H^+ ion of the resin and thus get fixed on it.

$$M^{3+}(aq) + 3HR\ (solid) \longrightarrow MR_3(solid) + 3H^+\ (aq)$$

Since $Lu^{3+}(aq)$ is largest in size and $La^{3+}(aq)$ is smallest, $La^{3+}(aq)$ is attached to the column with maximum and $Lu^{3+}(aq)$ with minimum firmness.

In order to recover the M^{3+} ions fixed on the resin, the column is *eluted* (*i.e.*, leached) with a citric acid—ammonium citrate solution (called **eluant** or **eluante**). During elution process NH_4^+ ions replace M^{3+} ions and M-citrate complexes are formed.

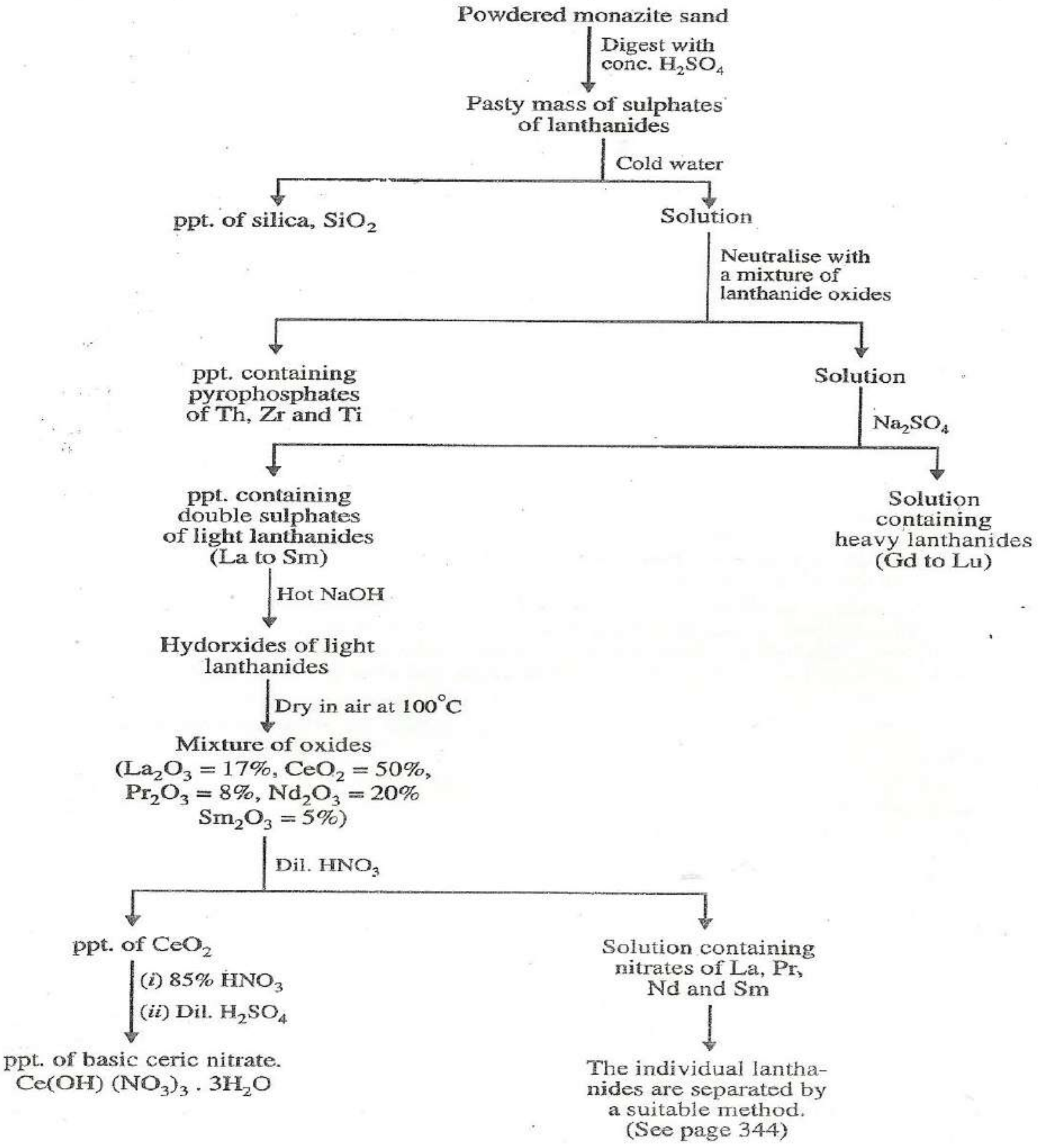
$$MR_3 + 3NH_4^+ \longrightarrow 3NH_4R + M^{3+}$$

$$M^{3+} + \text{citrate ions} \longrightarrow \text{M-citrate complex}$$

We have seen that since La^{3+} (*aq*) is attached to the resin with maximum and $Lu^{3+}(aq)$ with minimum firmness, *Lu-citrate complex comes out of the column first* and *La-citrate complex comes out last*. In actual practice the process has to be repeated several times by careful control of concentration of citric acid-ammonium citrate solution.

5. Solvent extraction method. This method makes the use of the difference in the value of partition coefficient of lanthanides between two solvents. $La(NO_3)_3$ and $Gd(NO_3)_3$ have been separated from each other by this method. The partition coefficient of $Gd(NO_3)_3$ between water and tributyl phosphate in kerosene is different from that of $La(NO_3)_3$ between the same solvents. This means that $Gd(NO_3)_3$ can be separated from $La(NO_3)_3$ by continuous extraction with water from a solution of these salts in tributyl phosphate in kerosene.

Flow sheet 1. *Extraction of lanthanides from monazite sand.*



Powdered monazite sand

Digest with conc. H_2SO_4

Pasty mass of sulphates of lanthanides

Cold water

ppt. of silica, SiO_2

Solution

Neutralise with a mixture of lanthanide oxides

ppt. containing pyrophosphates of Th, Zr and Ti

Solution

Na_2SO_4

ppt. containing double sulphates of light lanthanides (La to Sm)

Solution containing heavy lanthanides (Gd to Lu)

Hot NaOH

Hydorxides of light lanthanides

Dry in air at 100°C

Mixture of oxides
($La_2O_3 = 17\%$, $CeO_2 = 50\%$,
$Pr_2O_3 = 8\%$, $Nd_2O_3 = 20\%$
$Sm_2O_3 = 5\%$)

Dil. HNO_3

ppt. of CeO_2

(*i*) 85% HNO_3
(*ii*) Dil. H_2SO_4

ppt. of basic ceric nitrate. $Ce(OH)(NO_3)_3 \cdot 3H_2O$

Solution containing nitrates of La, Pr, Nd and Sm

The individual lanthanides are separated by a suitable method. (See page 344)

Production of lanthanide metals

The following methods may be used for this purpose:

1. Electrolysis of fused chlorides. This method is similar to that used in the metallurgy of Ca by the electrolysis of $CaCl_2$.

2. Reduction of anhydrous chlorides with Na. Lighter lanthanides such as La, Ce and Gd can easily be prepared by the reduction of their anhydrous chlorides with Na at 100°C.

$$LaCl_3 + 3Na \xrightarrow{100^\circ C} La + 3NaCl$$

3. Reduction of anhydrous fluorides and chlorides with Mg or Ca. Heavier lanthanides such as Lu are prepared when anhydrous fluorides and chlorides are reduced by Ca or Mg metals at a temperature above 1000°C, since the fluorides are less volatile than the chlorides and consequently the loss caused by evaporation in case of fluorides is small.

Uses of lanthanides and their compounds

(*i*) Certain alloys of the lanthanide elements, known as *misch metals* containing predominantly 30–35% of Ce together with smaller quantities of other light lanthanides are used as reducing agents in metalllurgical operations. Mg-alloys containing about 30% misch metal and 1% Zr are used for making parts of jet engine.

(*ii*) La, Ce, Pr, Nd mixed with steel are used in cigarette lighters, toys, flame throwing tanks.

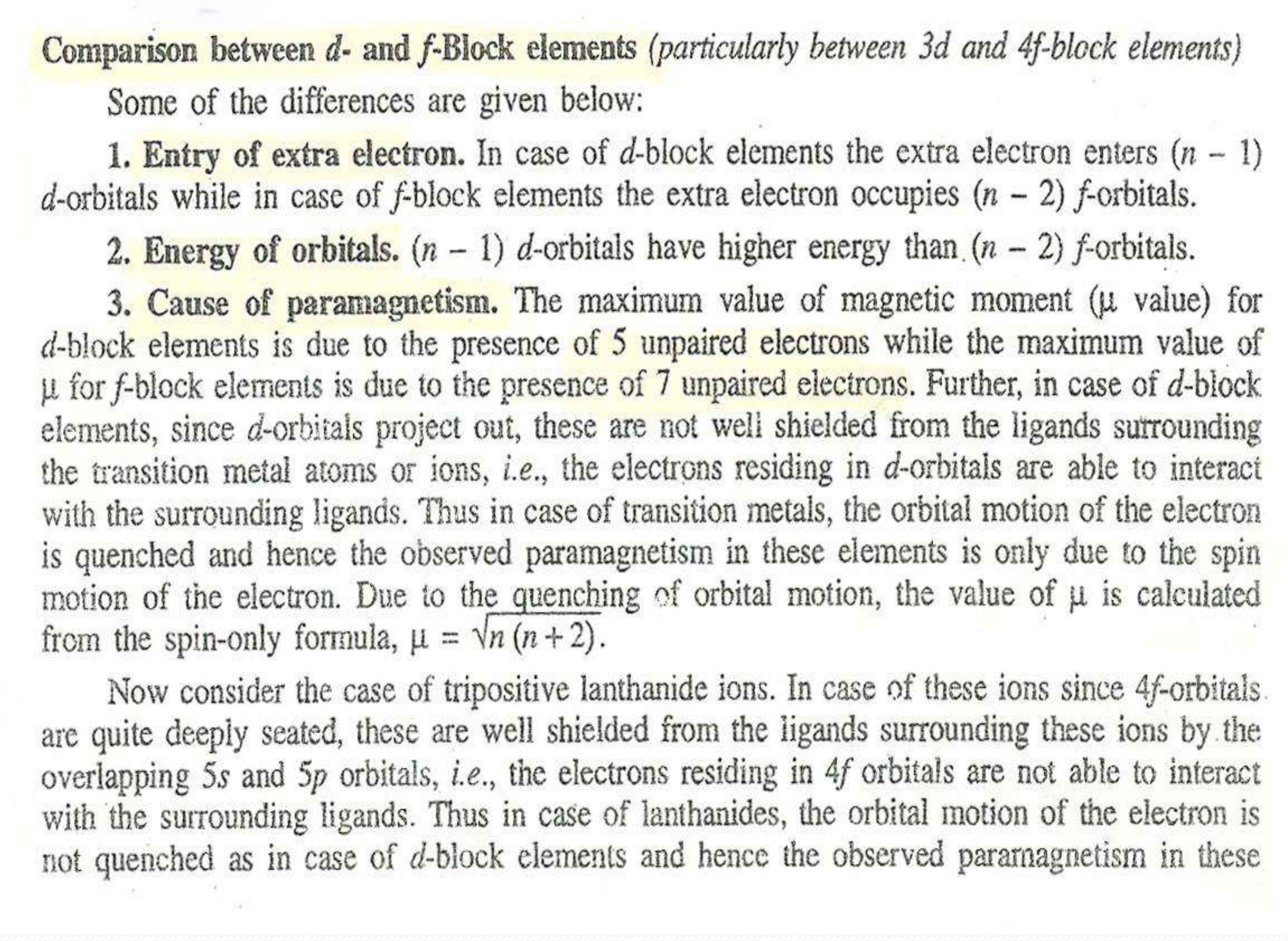
(*iii*) Nd_2O_3 and Pr_2O_3 are used as colouring agents for glass and in the production of standard filters. Lanthanum oxides are used for polishing glass. Ceria (CeO_2) is used in gas mantles.

(*iv*) Cerium phosphate is used as a catalyst in petroleum cracking.

(*v*) Cerium salts are used in analysis, dyeing cotton, lead accumulators, medicines etc.

(*vi*) Lanthanide compounds are used as good catalysts in a number of reactions like hydrogenation, dehydrogenation, oxidation and cracking of petroleum.

(*vii*) Lanthanide compounds are filled into arc carbon electrodes to give more brilliant light.



Comparison between *d*- and *f*-Block elements *(particularly between 3d and 4f-block elements)*

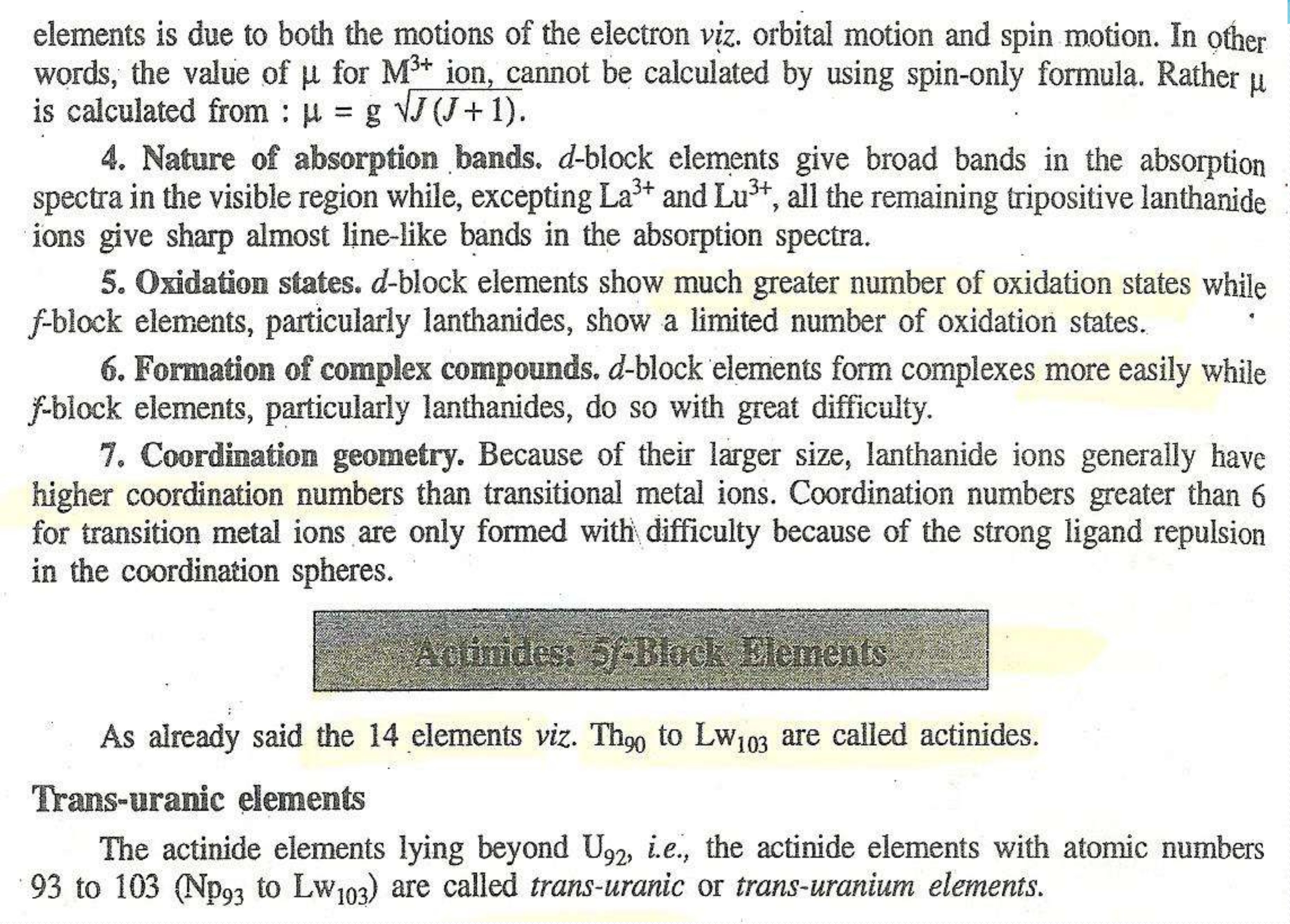
Some of the differences are given below:

1. Entry of extra electron. In case of *d*-block elements the extra electron enters (n – 1) *d*-orbitals while in case of *f*-block elements the extra electron occupies (n – 2) *f*-orbitals.

2. Energy of orbitals. (n – 1) *d*-orbitals have higher energy than (n – 2) *f*-orbitals.

3. Cause of paramagnetism. The maximum value of magnetic moment (μ value) for *d*-block elements is due to the presence of 5 unpaired electrons while the maximum value of μ for *f*-block elements is due to the presence of 7 unpaired electrons. Further, in case of *d*-block elements, since *d*-orbitals project out, these are not well shielded from the ligands surrounding the transition metal atoms or ions, *i.e.*, the electrons residing in *d*-orbitals are able to interact with the surrounding ligands. Thus in case of transition metals, the orbital motion of the electron is quenched and hence the observed paramagnetism in these elements is only due to the spin motion of the electron. Due to the quenching of orbital motion, the value of μ is calculated from the spin-only formula, $\mu = \sqrt{n\,(n+2)}$.

Now consider the case of tripositive lanthanide ions. In case of these ions since 4*f*-orbitals are quite deeply seated, these are well shielded from the ligands surrounding these ions by the overlapping 5*s* and 5*p* orbitals, *i.e.*, the electrons residing in 4*f* orbitals are not able to interact with the surrounding ligands. Thus in case of lanthanides, the orbital motion of the electron is not quenched as in case of *d*-block elements and hence the observed paramagnetism in these


elements is due to both the motions of the electron *viz.* orbital motion and spin motion. In other words, the value of μ for M^{3+} ion, cannot be calculated by using spin-only formula. Rather μ is calculated from : $\mu = g\sqrt{J(J+1)}$.

4. Nature of absorption bands. *d*-block elements give broad bands in the absorption spectra in the visible region while, excepting La^{3+} and Lu^{3+}, all the remaining tripositive lanthanide ions give sharp almost line-like bands in the absorption spectra.

5. Oxidation states. *d*-block elements show much greater number of oxidation states while *f*-block elements, particularly lanthanides, show a limited number of oxidation states.

6. Formation of complex compounds. *d*-block elements form complexes more easily while *f*-block elements, particularly lanthanides, do so with great difficulty.

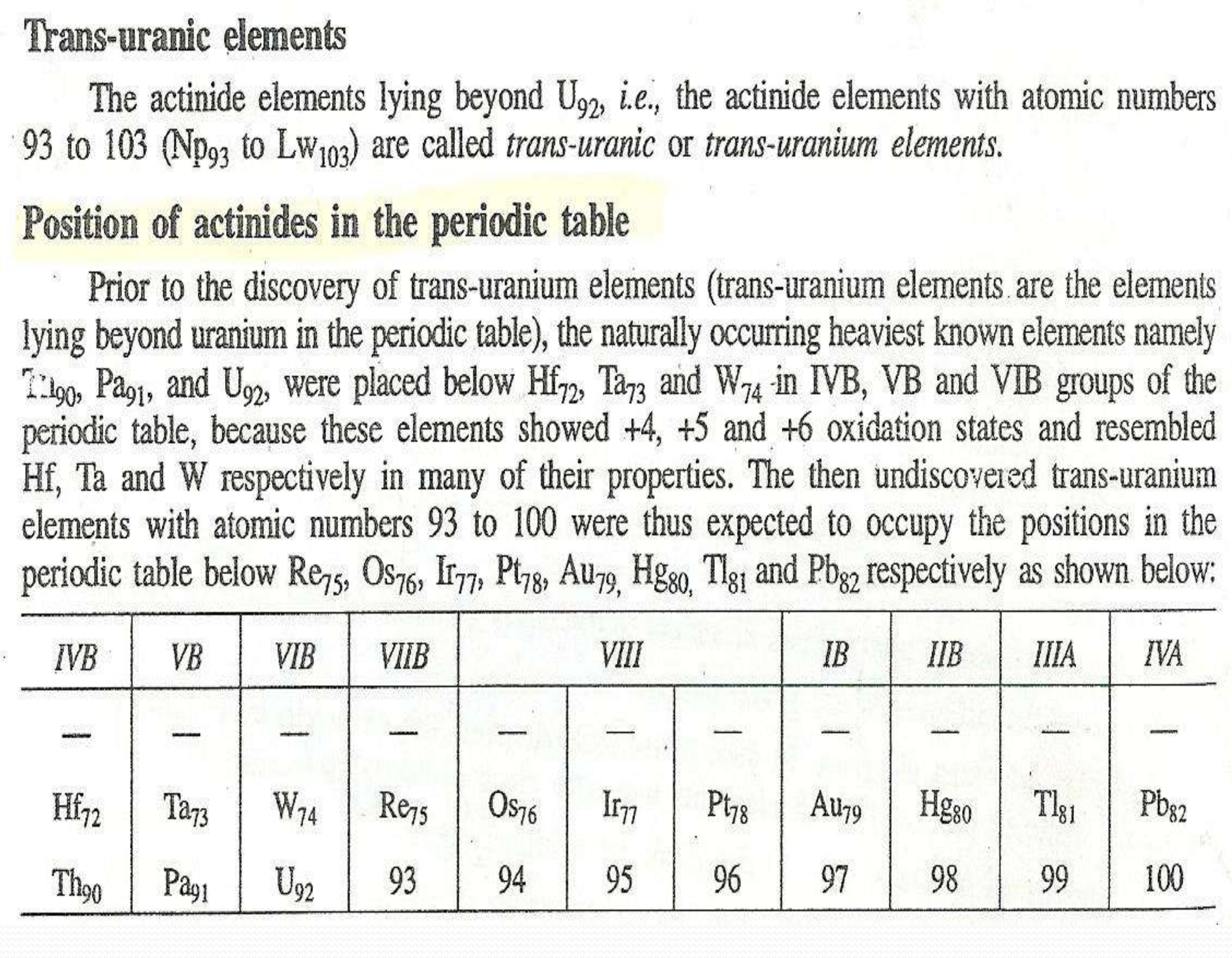
7. Coordination geometry. Because of their larger size, lanthanide ions generally have higher coordination numbers than transitional metal ions. Coordination numbers greater than 6 for transition metal ions are only formed with difficulty because of the strong ligand repulsion in the coordination spheres.

Actinides: 5*f*-Block Elements

As already said the 14 elements *viz.* Th_{90} to Lw_{103} are called actinides.

Trans-uranic elements

The actinide elements lying beyond U_{92}, *i.e.*, the actinide elements with atomic numbers 93 to 103 (Np_{93} to Lw_{103}) are called *trans-uranic* or *trans-uranium elements*.



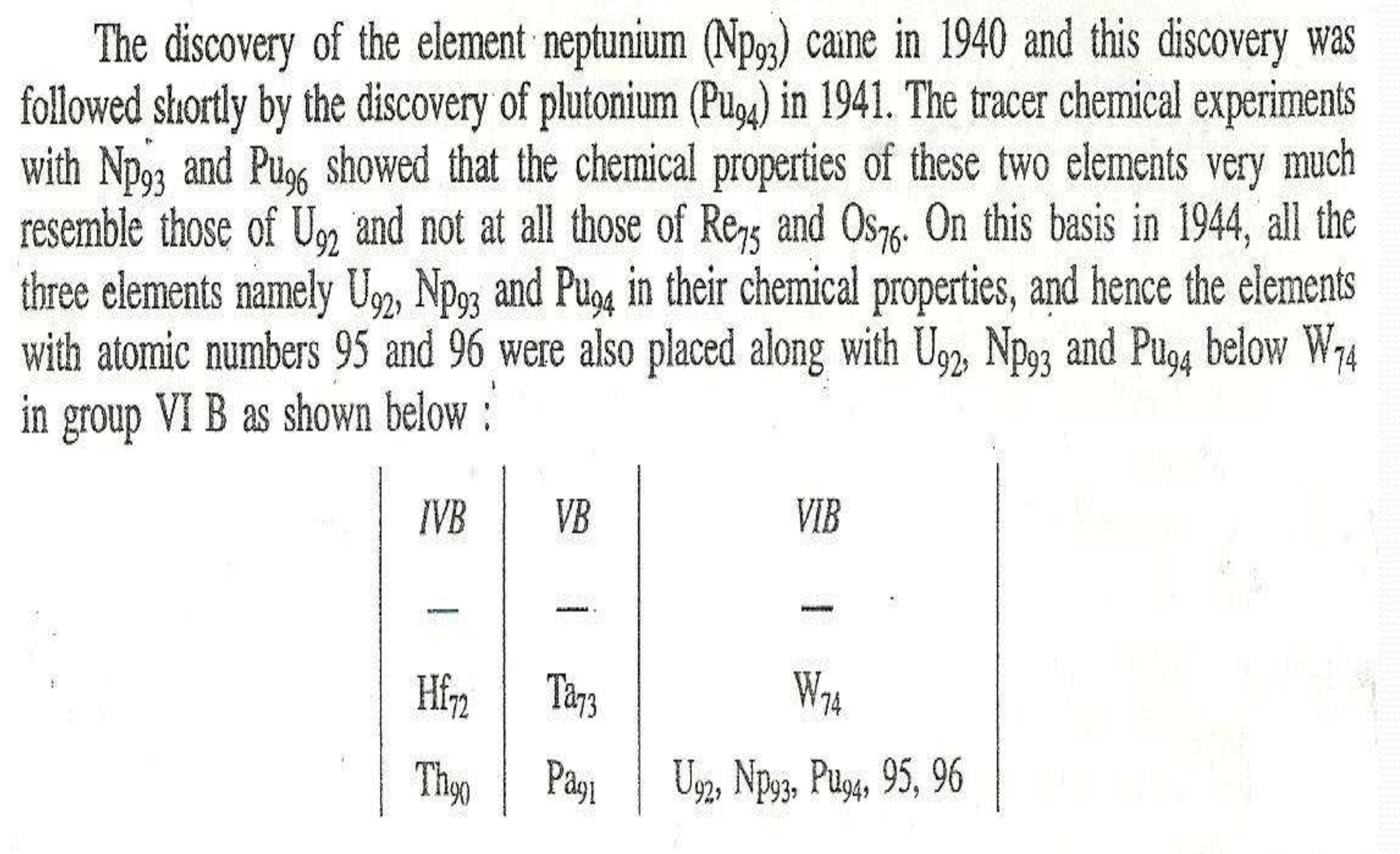
Trans-uranic elements

The actinide elements lying beyond U_{92}, *i.e.*, the actinide elements with atomic numbers 93 to 103 (Np_{93} to Lw_{103}) are called *trans-uranic* or *trans-uranium elements.*

Position of actinides in the periodic table

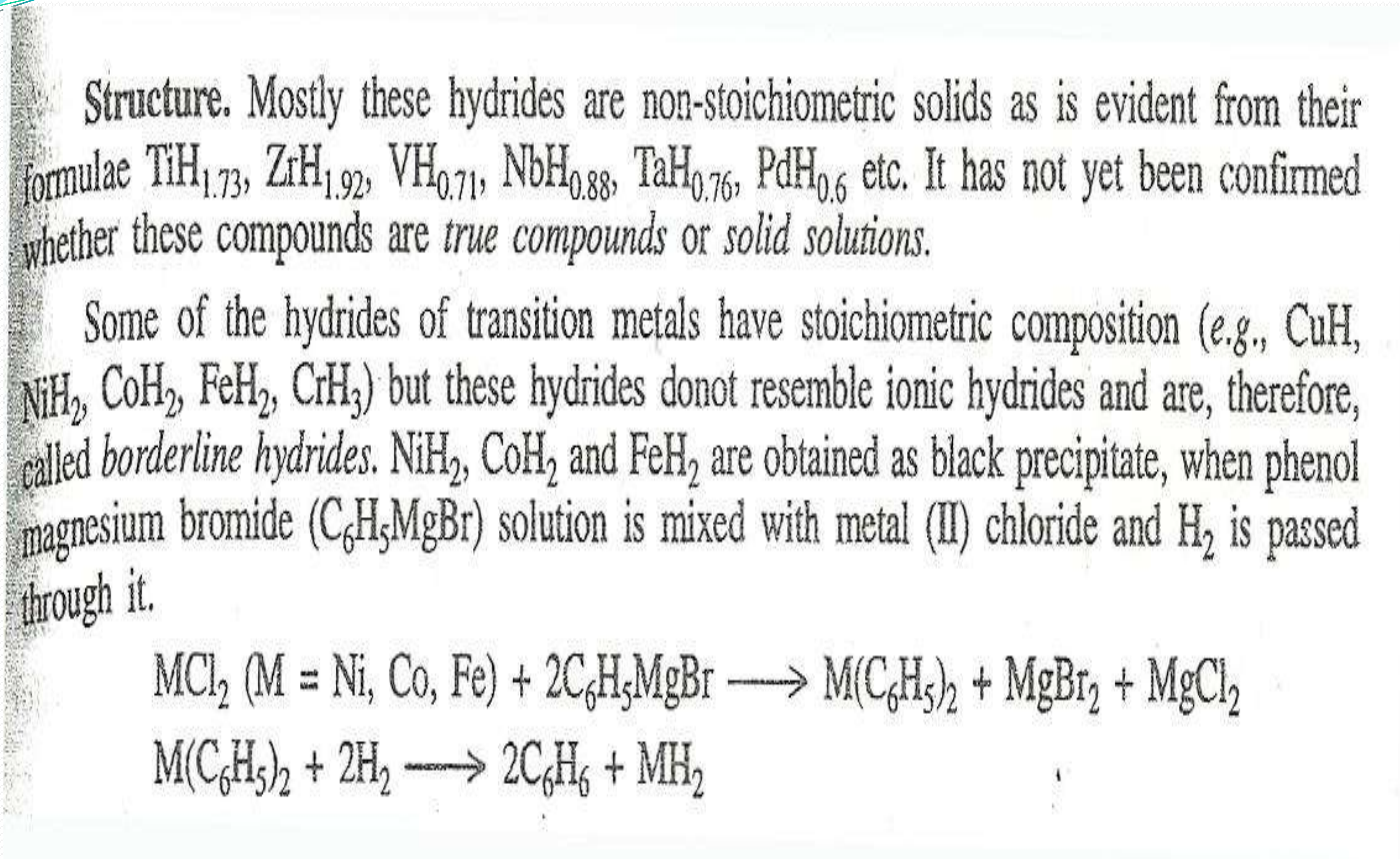
Prior to the discovery of trans-uranium elements (trans-uranium elements are the elements lying beyond uranium in the periodic table), the naturally occurring heaviest known elements namely Th_{90}, Pa_{91}, and U_{92}, were placed below Hf_{72}, Ta_{73} and W_{74} in IVB, VB and VIB groups of the periodic table, because these elements showed +4, +5 and +6 oxidation states and resembled Hf, Ta and W respectively in many of their properties. The then undiscovered trans-uranium elements with atomic numbers 93 to 100 were thus expected to occupy the positions in the periodic table below Re_{75}, Os_{76}, Ir_{77}, Pt_{78}, Au_{79}, Hg_{80}, Tl_{81} and Pb_{82} respectively as shown below:

IVB	*VB*	*VIB*	*VIIB*	*VIII*			*IB*	*IIB*	*IIIA*	*IVA*
—	—	—	—	—	—	—	—	—	—	—
Hf_{72}	Ta_{73}	W_{74}	Re_{75}	Os_{76}	Ir_{77}	Pt_{78}	Au_{79}	Hg_{80}	Tl_{81}	Pb_{82}
Th_{90}	Pa_{91}	U_{92}	93	94	95	96	97	98	99	100



The discovery of the element neptunium (Np_{93}) came in 1940 and this discovery was followed shortly by the discovery of plutonium (Pu_{94}) in 1941. The tracer chemical experiments with Np_{93} and Pu_{96} showed that the chemical properties of these two elements very much resemble those of U_{92} and not at all those of Re_{75} and Os_{76}. On this basis in 1944, all the three elements namely U_{92}, Np_{93} and Pu_{94} in their chemical properties, and hence the elements with atomic numbers 95 and 96 were also placed along with U_{92}, Np_{93} and Pu_{94} below W_{74} in group VI B as shown below :

IVB	*VB*	*VIB*
—	—	—
Hf_{72}	Ta_{73}	W_{74}
Th_{90}	Pa_{91}	U_{92}, Np_{93}, Pu_{94}, 95, 96



Structure. Mostly these hydrides are non-stoichiometric solids as is evident from their formulae $TiH_{1.73}$, $ZrH_{1.92}$, $VH_{0.71}$, $NbH_{0.88}$, $TaH_{0.76}$, $PdH_{0.6}$ etc. It has not yet been confirmed whether these compounds are *true compounds* or *solid solutions*.

Some of the hydrides of transition metals have stoichiometric composition (*e.g.*, CuH, NiH_2, CoH_2, FeH_2, CrH_3) but these hydrides donot resemble ionic hydrides and are, therefore, called *borderline hydrides*. NiH_2, CoH_2 and FeH_2 are obtained as black precipitate, when phenol magnesium bromide (C_6H_5MgBr) solution is mixed with metal (II) chloride and H_2 is passed through it.

$$MCl_2\ (M = Ni, Co, Fe) + 2C_6H_5MgBr \longrightarrow M(C_6H_5)_2 + MgBr_2 + MgCl_2$$

$$M(C_6H_5)_2 + 2H_2 \longrightarrow 2C_6H_6 + MH_2$$

B. Interstitial or metallic carbides

These carbides are also called *refractory carbides*. These carbides are formed by those transition metals whose atomic radii (metallic radii for coordination number 12) are generally greater than 1.3 Å ($R_M > 1.3$ Å), since the radius ratio namely R_C/R_M must be either 1 : 0.41 or 1 : 0.59 to permit C-atoms to enter into the octahedral holes (also called cavities, interstices or interstitial positions) of the cubic close packing of the metallic lattice without distorting it. The radius of the metals Ti, Zr, Hf (Group IV B); V, Nb, Ta (Group V B); Mo and W (Group VI B) is greater than 1.3 Å and hence these metals give the interstitial carbides which are of two types *viz.* MC type (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W) and MC_2 type (M = V, Mo, W).

Preparation. Interstitial carbides are prepared:

(*i*) *by direct combination of the metal with carbon.* In this method powdered metal is heated with powdered carbon at high temperature. Carbides obtained by this method are purified and made compact by sintering them in vacuum or in an atmosphere of inert gases.

(*ii*) *by reducing the metallic oxide with carbon in an electric furnace at about 2000°C.* This method has been used for the preparation of TiC, ZrC, HfC, VC, NbC, TaC, WC.

$$TiO_2 + 3C \longrightarrow TiC + 2CO$$

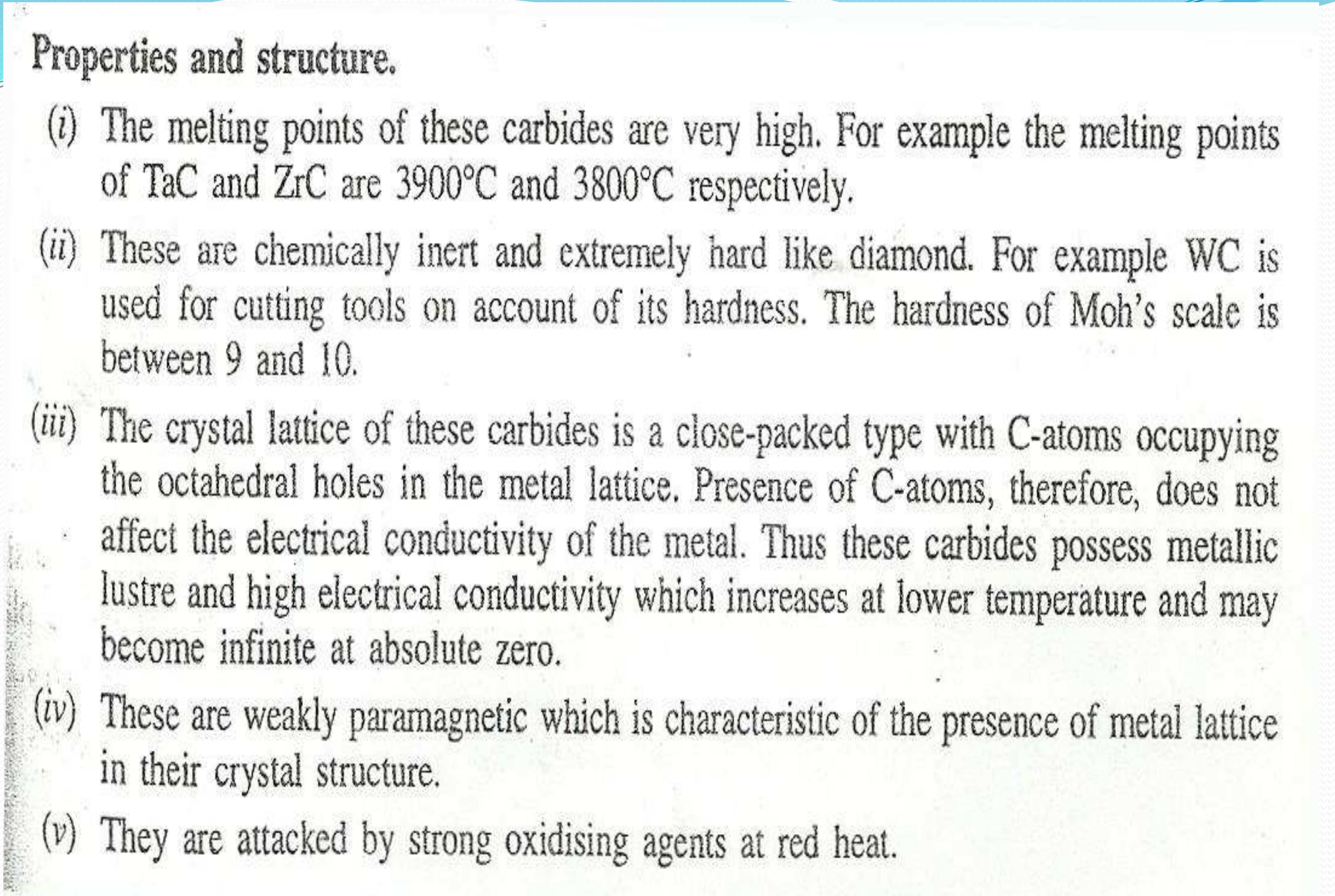
$$WO_3 + 4C \longrightarrow WC + 3CO$$

$$MoO_3 + 4C \longrightarrow MoC + 3CO$$

(*iii*) *by heating the metal in an atmosphere of CH_4 at different temperatures.* HfC, MoC, TaC, WC etc. carbides have been prepared by this method, *e.g.*,

$$Hf + CH_4 \longrightarrow HfC + 2H_2$$

$$Mo + CH_4 \longrightarrow MoC + 2H_2$$



Properties and structure.

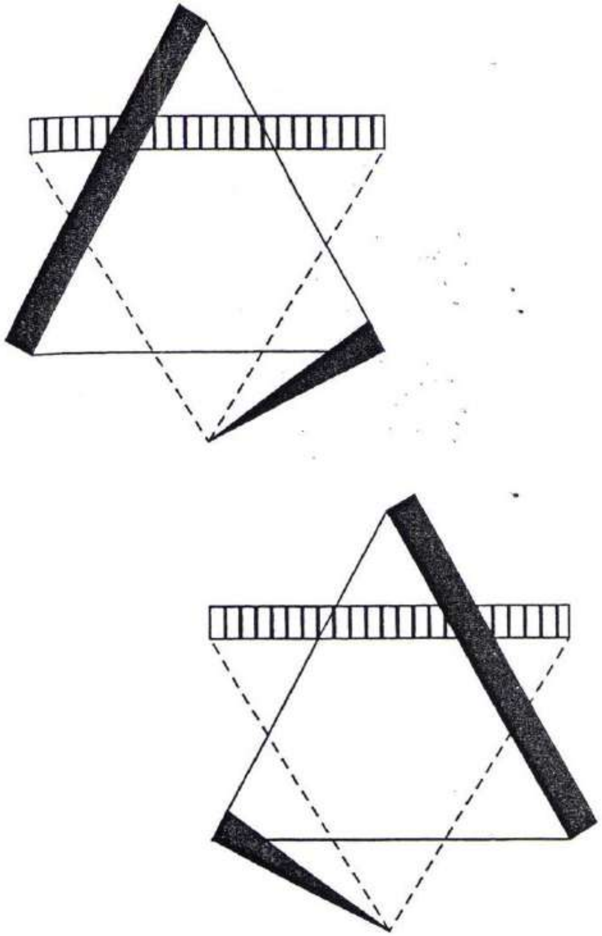
(*i*) The melting points of these carbides are very high. For example the melting points of TaC and ZrC are 3900°C and 3800°C respectively.

(*ii*) These are chemically inert and extremely hard like diamond. For example WC is used for cutting tools on account of its hardness. The hardness of Moh's scale is between 9 and 10.

(*iii*) The crystal lattice of these carbides is a close-packed type with C-atoms occupying the octahedral holes in the metal lattice. Presence of C-atoms, therefore, does not affect the electrical conductivity of the metal. Thus these carbides possess metallic lustre and high electrical conductivity which increases at lower temperature and may become infinite at absolute zero.

(*iv*) These are weakly paramagnetic which is characteristic of the presence of metal lattice in their crystal structure.

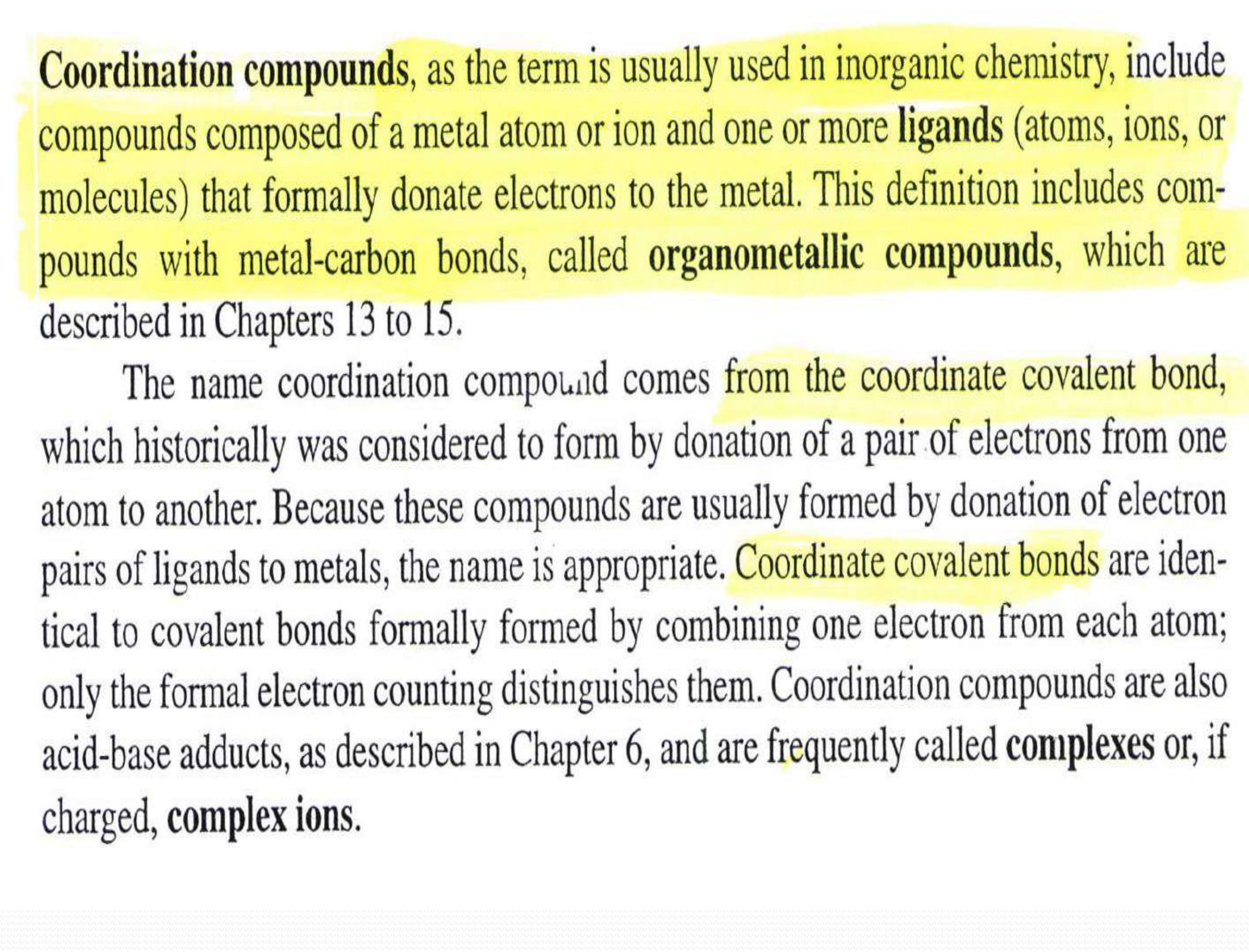
(*v*) They are attacked by strong oxidising agents at red heat.



CHAPTER

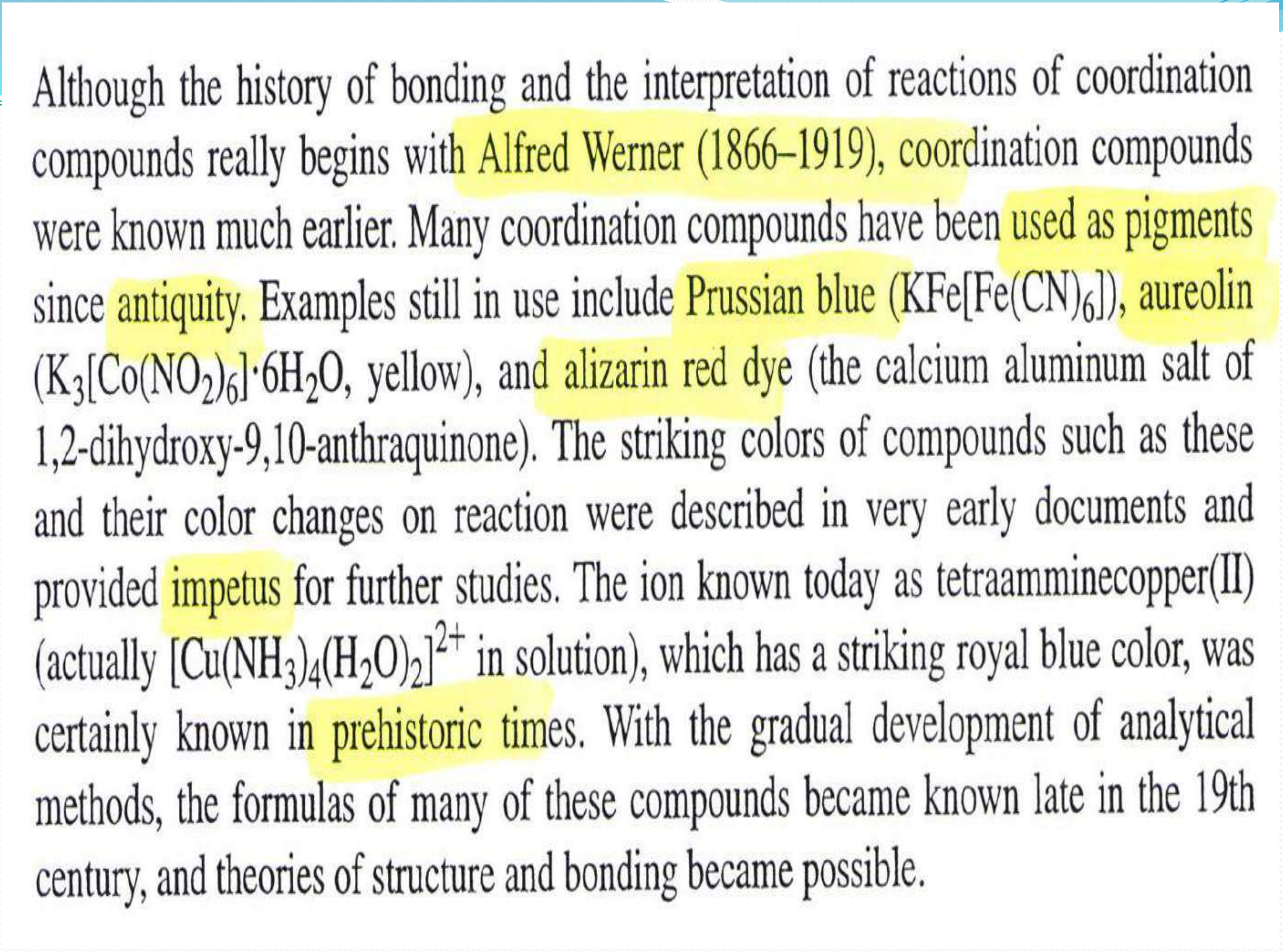
9

Coordination Chemistry I: Structures and Isomers

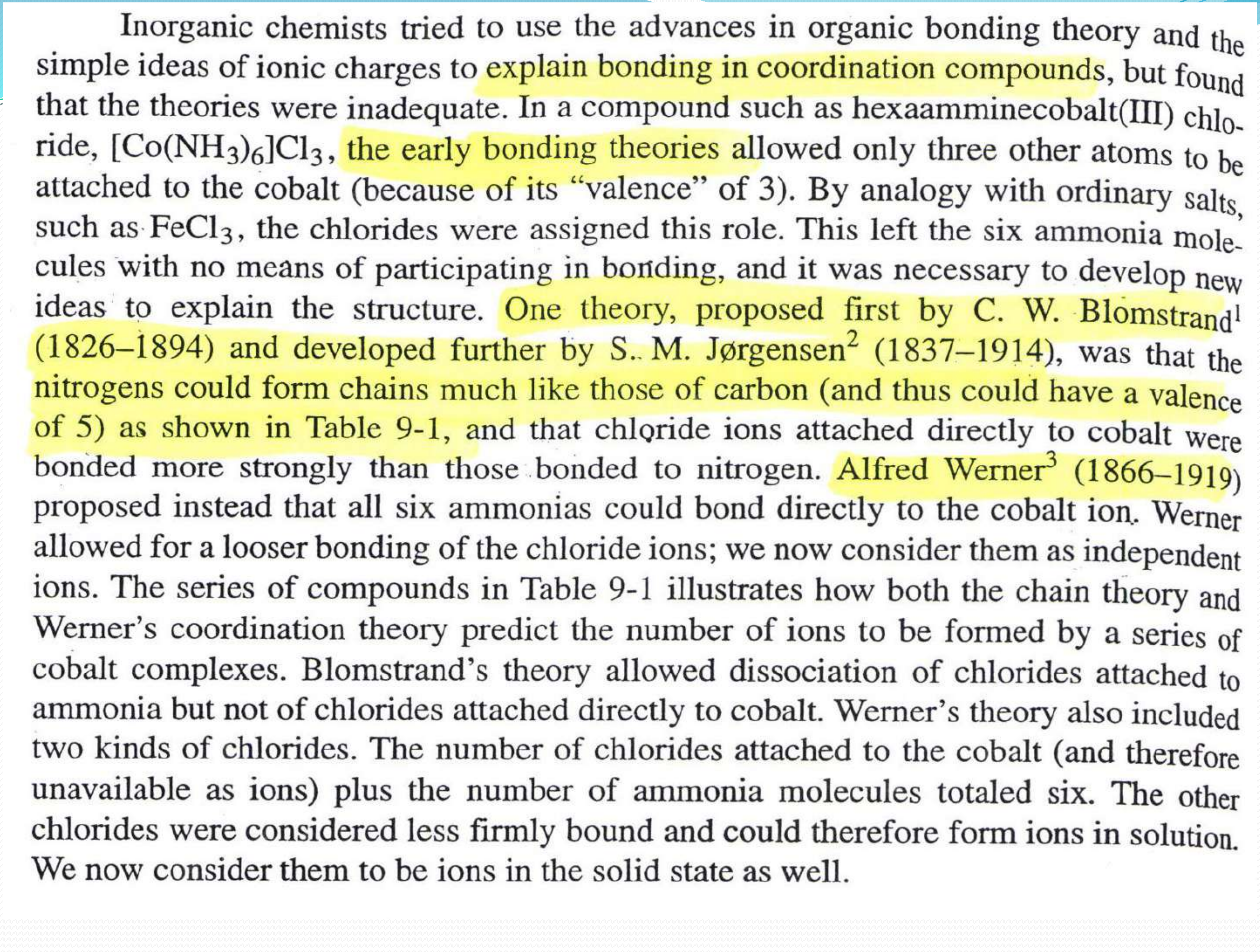


Coordination compounds, as the term is usually used in inorganic chemistry, include compounds composed of a metal atom or ion and one or more **ligands** (atoms, ions, or molecules) that formally donate electrons to the metal. This definition includes compounds with metal-carbon bonds, called **organometallic compounds**, which are described in Chapters 13 to 15.

The name coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. Because these compounds are usually formed by donation of electron pairs of ligands to metals, the name is appropriate. Coordinate covalent bonds are identical to covalent bonds formally formed by combining one electron from each atom; only the formal electron counting distinguishes them. Coordination compounds are also acid-base adducts, as described in Chapter 6, and are frequently called **complexes** or, if charged, **complex ions**.

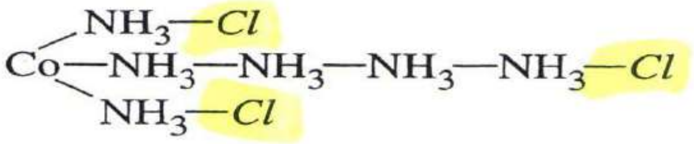
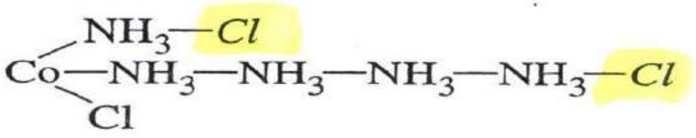
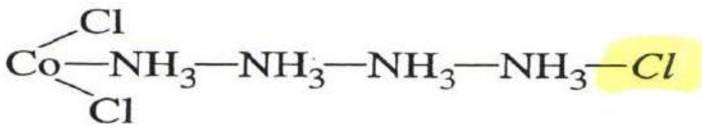
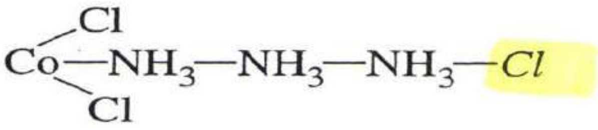


Although the history of bonding and the interpretation of reactions of coordination compounds really begins with Alfred Werner (1866–1919), coordination compounds were known much earlier. Many coordination compounds have been used as pigments since antiquity. Examples still in use include Prussian blue ($KFe[Fe(CN)_6]$), aureolin ($K_3[Co(NO_2)_6]\cdot 6H_2O$, yellow), and alizarin red dye (the calcium aluminum salt of 1,2-dihydroxy-9,10-anthraquinone). The striking colors of compounds such as these and their color changes on reaction were described in very early documents and provided impetus for further studies. The ion known today as tetraamminecopper(II) (actually $[Cu(NH_3)_4(H_2O)_2]^{2+}$ in solution), which has a striking royal blue color, was certainly known in prehistoric times. With the gradual development of analytical methods, the formulas of many of these compounds became known late in the 19th century, and theories of structure and bonding became possible.



Inorganic chemists tried to use the advances in organic bonding theory and the simple ideas of ionic charges to explain bonding in coordination compounds, but found that the theories were inadequate. In a compound such as hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, the early bonding theories allowed only three other atoms to be attached to the cobalt (because of its "valence" of 3). By analogy with ordinary salts, such as $FeCl_3$, the chlorides were assigned this role. This left the six ammonia molecules with no means of participating in bonding, and it was necessary to develop new ideas to explain the structure. One theory, proposed first by C. W. Blomstrand[1] (1826–1894) and developed further by S. M. Jørgensen[2] (1837–1914), was that the nitrogens could form chains much like those of carbon (and thus could have a valence of 5) as shown in Table 9-1, and that chloride ions attached directly to cobalt were bonded more strongly than those bonded to nitrogen. Alfred Werner[3] (1866–1919) proposed instead that all six ammonias could bond directly to the cobalt ion. Werner allowed for a looser bonding of the chloride ions; we now consider them as independent ions. The series of compounds in Table 9-1 illustrates how both the chain theory and Werner's coordination theory predict the number of ions to be formed by a series of cobalt complexes. Blomstrand's theory allowed dissociation of chlorides attached to ammonia but not of chlorides attached directly to cobalt. Werner's theory also included two kinds of chlorides. The number of chlorides attached to the cobalt (and therefore unavailable as ions) plus the number of ammonia molecules totaled six. The other chlorides were considered less firmly bound and could therefore form ions in solution. We now consider them to be ions in the solid state as well.

TABLE 9-1
Comparison of Blomstrand's Chain Theory and Werner's Coordination Theory

Werner Formula (Modern Form)	*Number of Ions Predicted*	*Blomstrand Chain Formula*	*Number of Ions Predicted*
$[Co(NH_3)_6]\mathit{Cl}_3$	4		4
$[Co(NH_3)_5Cl]\mathit{Cl}_2$	3		3
$[Co(NH_3)_4Cl_2]\mathit{Cl}$	2		2
$[Co(NH_3)_3Cl_3]$	0		2

NOTE: The italicized chlorides dissociate in solution, according to the two theories.

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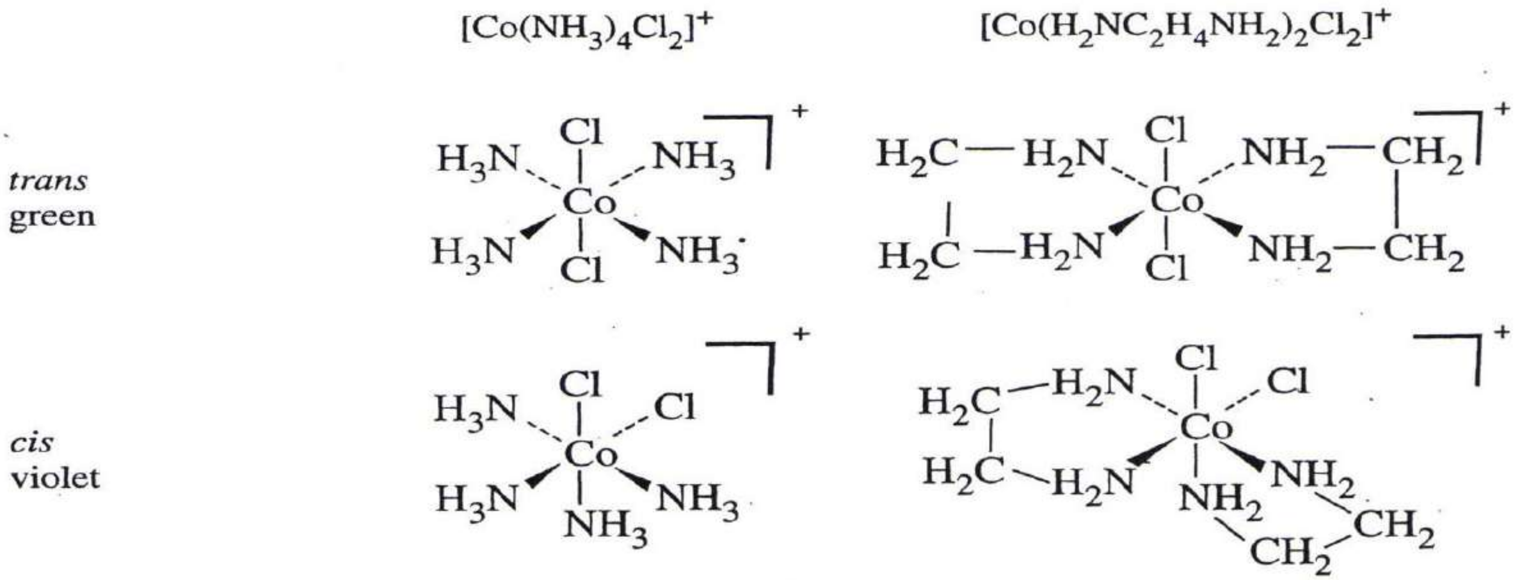
[1] C. W. Blomstrand, *Berichte*, **1871**, *4*, 40; translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 2*, Dover, New York, 1976, pp. 75–93.

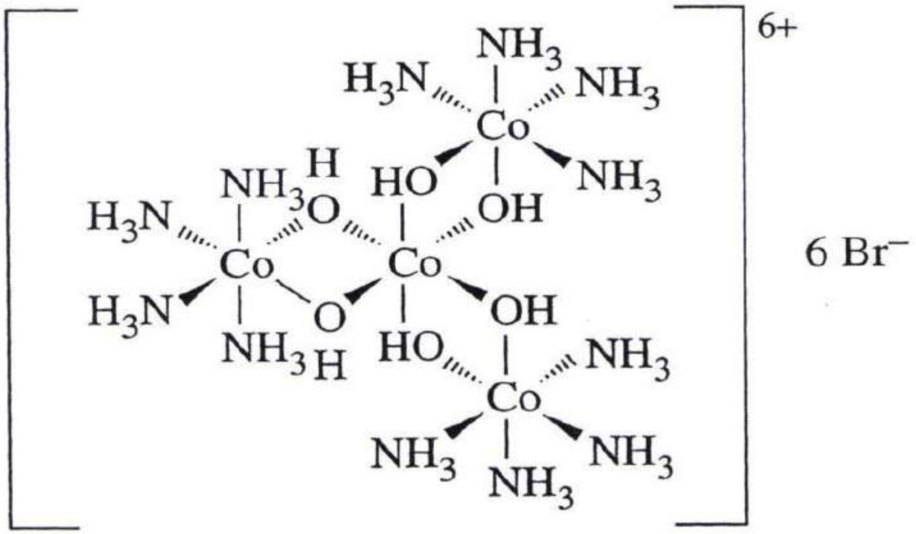
[2] S. M. Jørgensen, *Z. Anorg. Chem.*, **1899**, *19*, 109; translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 2*, pp. 94–164.

[3] A. Werner, *Z. Anorg. Chem.*, **1893**, *3*, 267; *Berichte*, **1907**, *40*, 4817; **1911**, *44*, 1887; **1914**, *47*, 3087; A. Werner and A. Miolati, *Z. Phys. Chem.*, **1893**, *12*, 35; **1894**, *14*, 506, all translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 1*, New York, 1968.



Except for the last compound in the table, the predictions match, and the ionic behavior does not distinguish between them. Even with the last compound, problems with purity and conductance measurements left some ambiguity. The argument between Jørgensen and Werner continued for many years, with each presenting data and explanations favoring his own position. This case illustrates some of the good features of such controversy. Werner was forced to develop his theory further and synthesize new compounds to test his ideas because Jørgensen defended the earlier theory so vigorously. Werner proposed an octahedral structure for compounds such as those in Table 9-1. He prepared and characterized many isomers, including both green and violet forms of $[Co(H_2NC_2H_4NH_2)_2Cl_2]^+$. He claimed that these compounds had the chlorides arranged ***trans*** (opposite each other) and ***cis*** (adjacent to each other) respectively, in an overall octahedral geometry, as in Figure 9-1. Jørgensen offered alternative isomeric structures but finally conceded defeat in 1907, when Werner succeeded in synthesizing the green *trans* and the violet *cis* isomers of $[Co(NH_3)_4Cl_2]^+$, for which there were no counterparts in the chain theory.

However, even synthesis of this compound and the later discovery of optically active coordination compounds did not completely convince all chemists, although such compounds could not be explained directly by the chain theory. It was argued that Werner's optically active compounds still contained carbon, and that their chirality could be due to the carbon atoms. Finally, Werner resolved the compound $[Co(Co(NH_3)_4(OH)_2)_3]Br_6$ (Figure 9-2), initially prepared by Jørgensen, into its two optically active forms, using *d*- and *l*-α-bromocamphor-π-sulfonate as the resolving agents. With this final proof of optical activity without carbon, the validity of Werner's theory was finally accepted. Pauling[4] extended the theory in terms of hybrid orbitals, and later theories[5] have adapted arguments first used for electronic structures of ions in crystals to coordination compounds.



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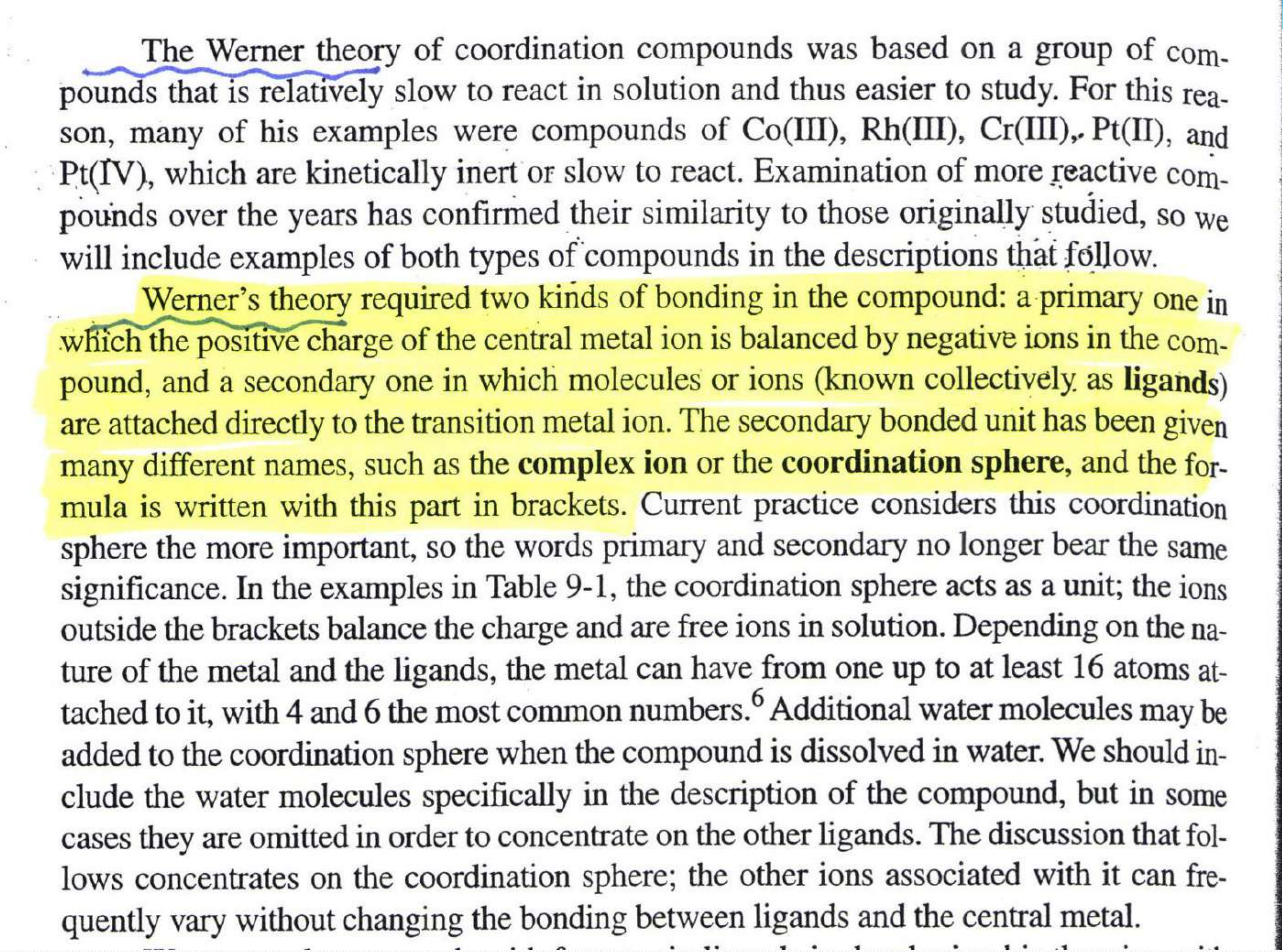
[4] L. Pauling, *J. Chem. Soc.*, **1948**, 1461; *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960, pp. 145–182.

[5] J. S. Griffith and L. E. Orgel, *Q. Rev. Chem. Soc.*, **1957**, *XI*, 381.



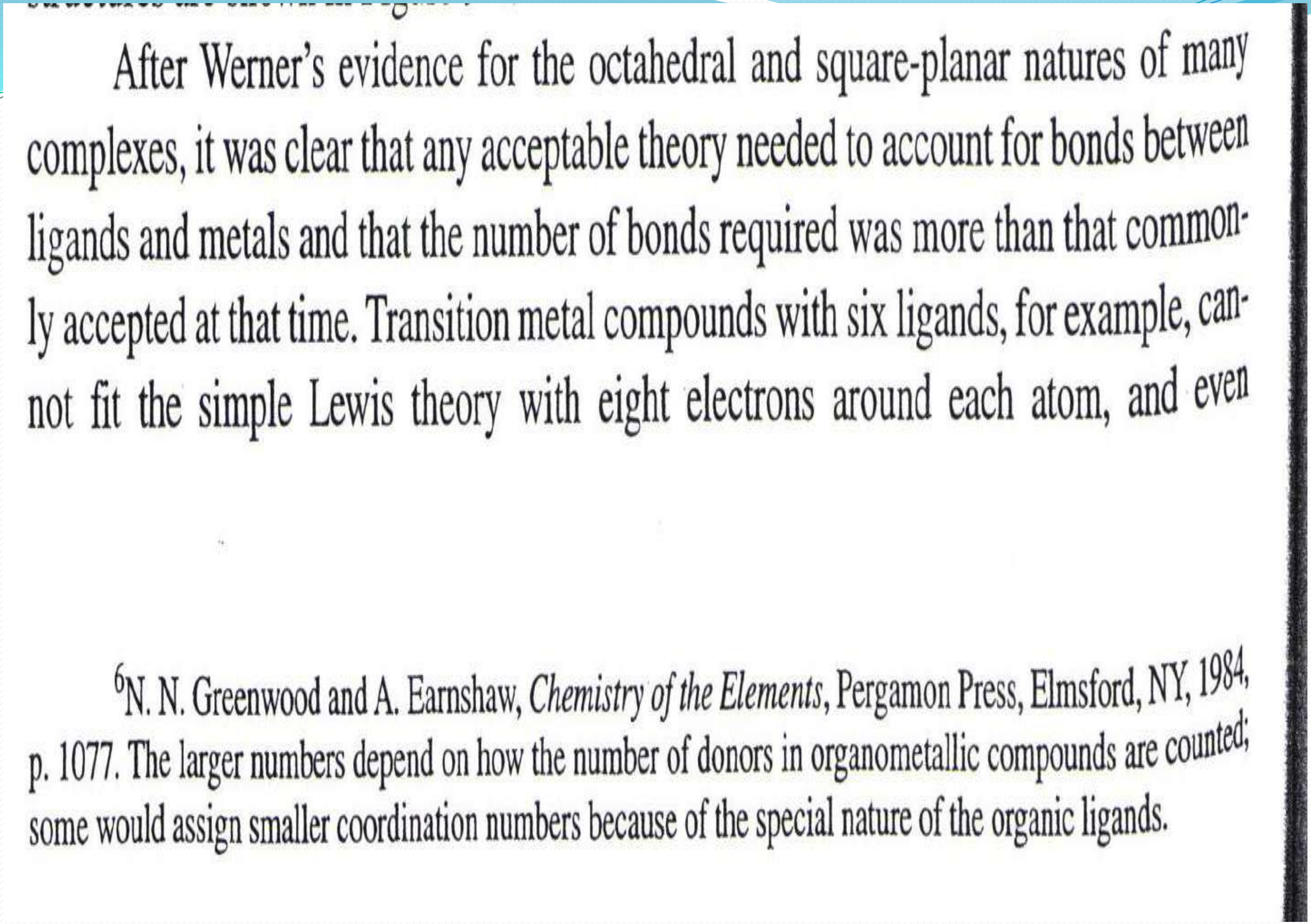
The Werner theory of coordination compounds was based on a group of compounds that is relatively slow to react in solution and thus easier to study. For this reason, many of his examples were compounds of Co(III), Rh(III), Cr(III), Pt(II), and Pt(IV), which are kinetically inert or slow to react. Examination of more reactive compounds over the years has confirmed their similarity to those originally studied, so we will include examples of both types of compounds in the descriptions that follow.

Werner's theory required two kinds of bonding in the compound: a primary one in which the positive charge of the central metal ion is balanced by negative ions in the compound, and a secondary one in which molecules or ions (known collectively as **ligands**) are attached directly to the transition metal ion. The secondary bonded unit has been given many different names, such as the **complex ion** or the **coordination sphere**, and the formula is written with this part in brackets. Current practice considers this coordination sphere the more important, so the words primary and secondary no longer bear the same significance. In the examples in Table 9-1, the coordination sphere acts as a unit; the ions outside the brackets balance the charge and are free ions in solution. Depending on the nature of the metal and the ligands, the metal can have from one up to at least 16 atoms attached to it, with 4 and 6 the most common numbers.[6] Additional water molecules may be added to the coordination sphere when the compound is dissolved in water. We should include the water molecules specifically in the description of the compound, but in some cases they are omitted in order to concentrate on the other ligands. The discussion that follows concentrates on the coordination sphere; the other ions associated with it can frequently vary without changing the bonding between ligands and the central metal.

Werner used compounds with four or six ligands in developing his theories, with the shapes of the coordination compounds established by the synthesis of isomers. For example, he was able to synthesize only two isomers of the $[Co(NH_3)_4Cl_2]^+$ ion. The possible structures with six ligands are octahedral, trigonal prismatic, trigonal antiprismatic, and hexagonal (either planar or pyramidal). Because there are two possible isomers for the octahedral shape and three for each of the others, as shown in Figure 9-3, Werner claimed that the structure was octahedral. Such an argument cannot be conclusive, because a missing isomer may simply be difficult to synthesize or isolate. However, later experiments confirmed the octahedral shape, with *cis* and *trans* isomers as shown in Figure 9-3.

Werner's synthesis and separation of optical isomers proved the octahedral shape conclusively, because none of the other six-coordinate geometries could have similar optical activity.

In a similar way, other experiments were consistent with square-planar Pt(II) compounds, with the four ligands at the corners of a square. Only two isomers are found for $[Pt(NH_3)_2Cl_2]$. Although the two could have had different shapes (tetrahedral and square-planar, for example), Werner assumed that they had the same overall shape and, because only one tetrahedral structure is possible for this compound, he argued that they must have square-planar shapes with *cis* and *trans* geometries. Again, his arguments were correct, although the evidence he presented could not be conclusive. The possible structures are shown in Figure 9-4.



After Werner's evidence for the octahedral and square-planar natures of many complexes, it was clear that any acceptable theory needed to account for bonds between ligands and metals and that the number of bonds required was more than that commonly accepted at that time. Transition metal compounds with six ligands, for example, cannot fit the simple Lewis theory with eight electrons around each atom, and even

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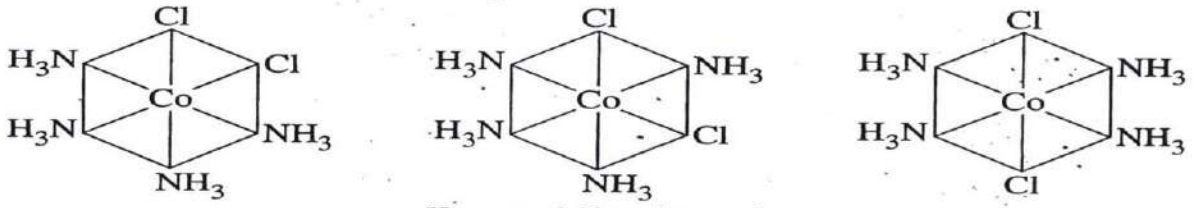
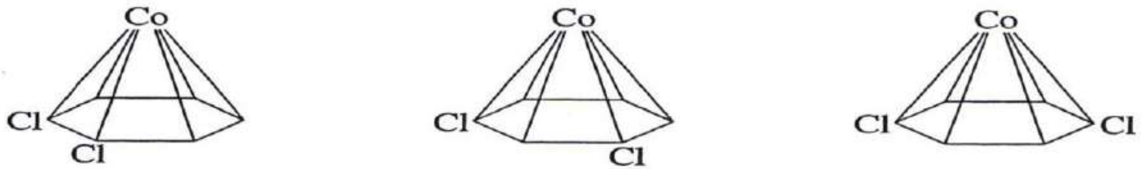
[6] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, p. 1077. The larger numbers depend on how the number of donors in organometallic compounds are counted; some would assign smaller coordination numbers because of the special nature of the organic ligands.

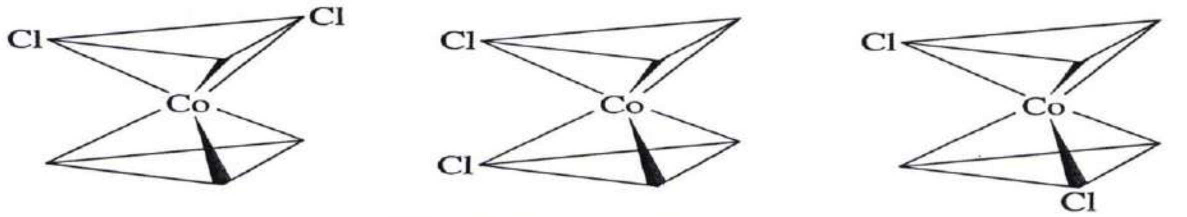
cis - and *trans* - Tetramminedichlorocobalt (III), $[Co(NH_3)_4Cl_2]^+$



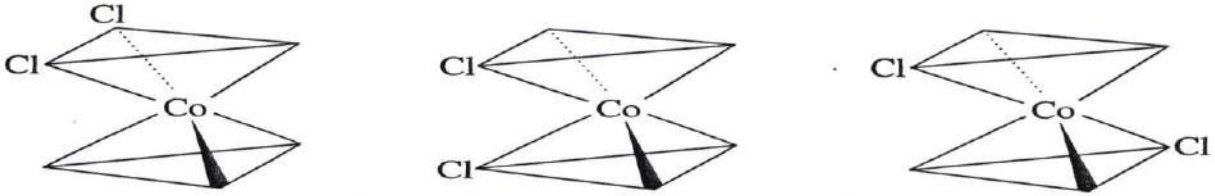
Hexagonal (three isomers)



Hexagonal pyramidal (three isomers)



Trigonal prismatic (three isomers)

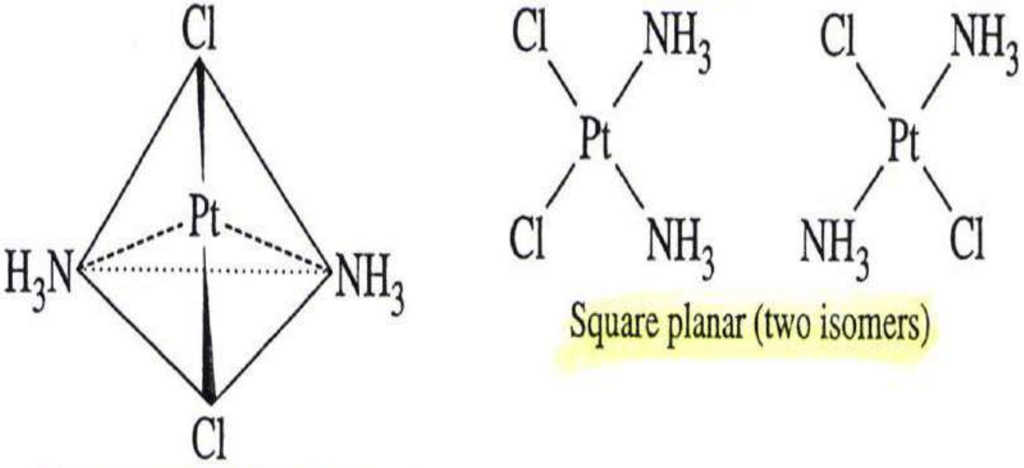


Trigonal antiprismatic (three isomers)

Octahedral (two isomers)

FIGURE 9-3 Possible Isomers for Hexacoordinate Complexes.

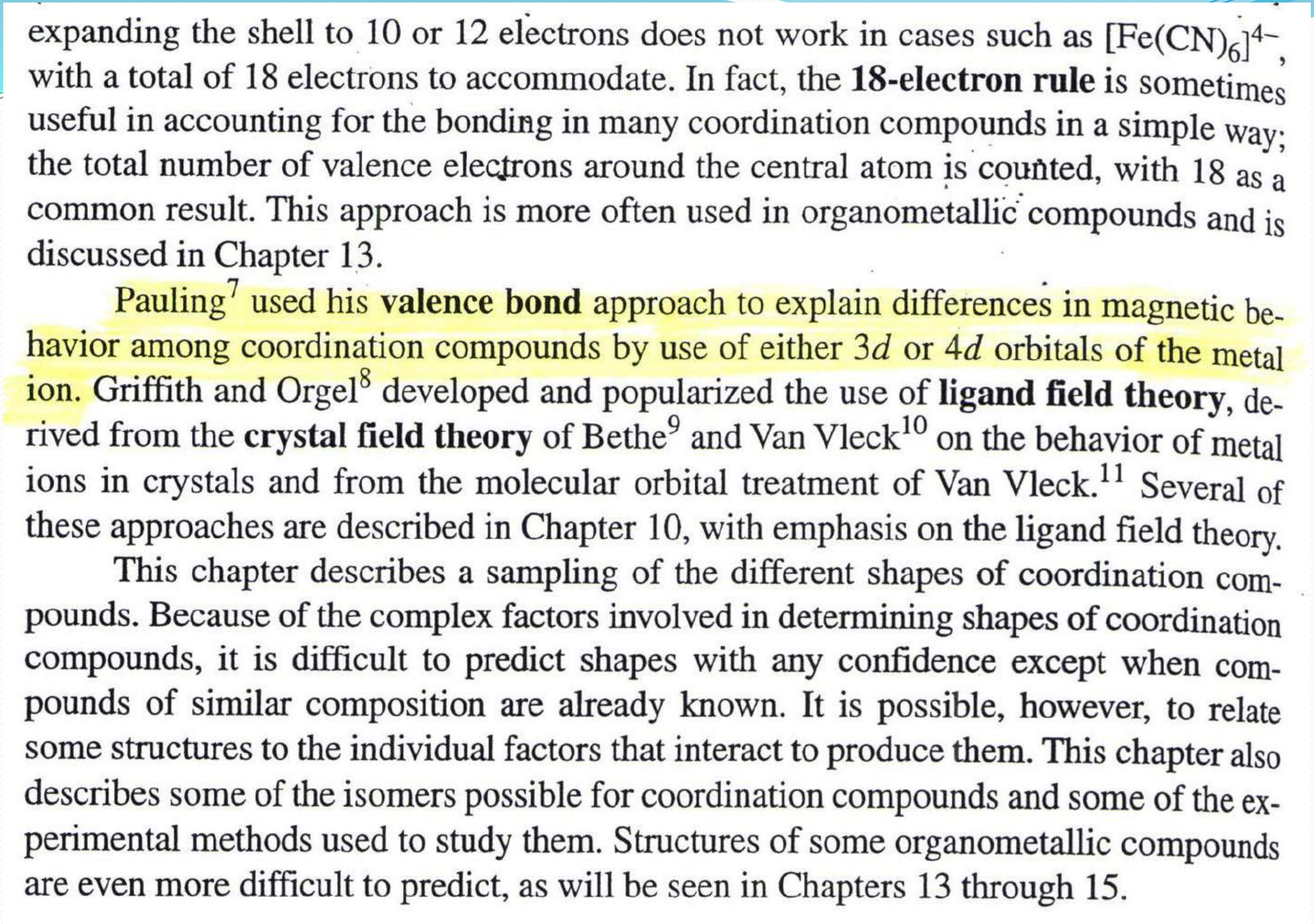
cis - and *trans* - Diamminedichloroplatinum (II), $[PtCl_2(NH_3)_2]$



Square planar (two isomers)

Tetrahedral (one isomer)

FIGURE 9-4 Possible Structures for Tetracoordinate Complexes.



expanding the shell to 10 or 12 electrons does not work in cases such as $[Fe(CN)_6]^{4-}$, with a total of 18 electrons to accommodate. In fact, the **18-electron rule** is sometimes useful in accounting for the bonding in many coordination compounds in a simple way; the total number of valence electrons around the central atom is counted, with 18 as a common result. This approach is more often used in organometallic compounds and is discussed in Chapter 13.

Pauling[7] used his **valence bond** approach to explain differences in magnetic behavior among coordination compounds by use of either 3*d* or 4*d* orbitals of the metal ion. Griffith and Orgel[8] developed and popularized the use of **ligand field theory**, derived from the **crystal field theory** of Bethe[9] and Van Vleck[10] on the behavior of metal ions in crystals and from the molecular orbital treatment of Van Vleck.[11] Several of these approaches are described in Chapter 10, with emphasis on the ligand field theory.

This chapter describes a sampling of the different shapes of coordination compounds. Because of the complex factors involved in determining shapes of coordination compounds, it is difficult to predict shapes with any confidence except when compounds of similar composition are already known. It is possible, however, to relate some structures to the individual factors that interact to produce them. This chapter also describes some of the isomers possible for coordination compounds and some of the experimental methods used to study them. Structures of some organometallic compounds are even more difficult to predict, as will be seen in Chapters 13 through 15.

As in any field of study, careful attention to nomenclature is required. The rules for names and formulas of coordination compounds are given here, with examples to show their use, but we need to be aware of changes in nomenclature with time. In many cases, the notation used by those who first prepared a compound is retained and expanded; in other cases, conflicting rules for names are proposed by different people and only after some time is a standard established. The literature naturally includes papers using all the possible names, and sometimes careful research is necessary to interpret those names that had relatively short lifetimes.

Following are the major rules required to name the compounds in this text and those found in the general literature. Reference to more complete sources may be needed to determine the names of other compounds.[12]

Organic (and some inorganic) ligands are frequently named with older trivial names rather than with IUPAC (International Union of Pure and Applied Chemistry) names. The IUPAC names are more correct, but trivial names and abbreviations are still commonly used. Tables 9-2, 9-3, and 9-4 list some of the common ligands. Ligands with two or more points of attachment to metal atoms are called **chelating ligands**, and the compounds are called **chelates** (pronounced key-lates), a name derived from the

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[7] Pauling, *The Nature of the Chemical Bond*, pp. 145–182.

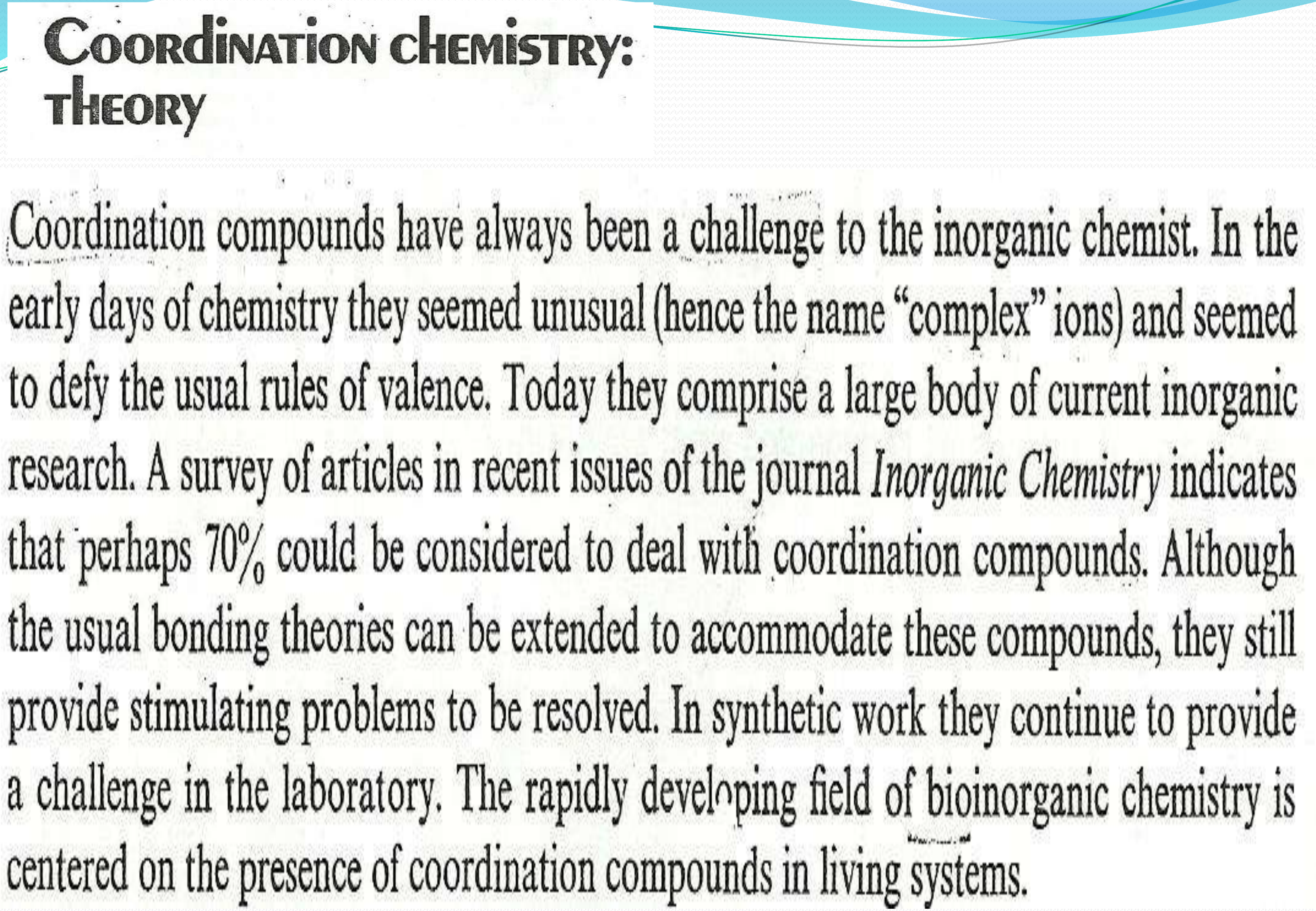
[8] Griffith and Orgel, *op. cit.*; L. E. Orgel, *An Introduction to Transition-Metal Chemistry*, Methuen, London, 1960.

[9] H. Bethe, *Ann. Phys.*, **1929**, *3*, 133.

[10] J. H. Van Vleck, *Phys. Rev.*, **1932**, *41*, 208.

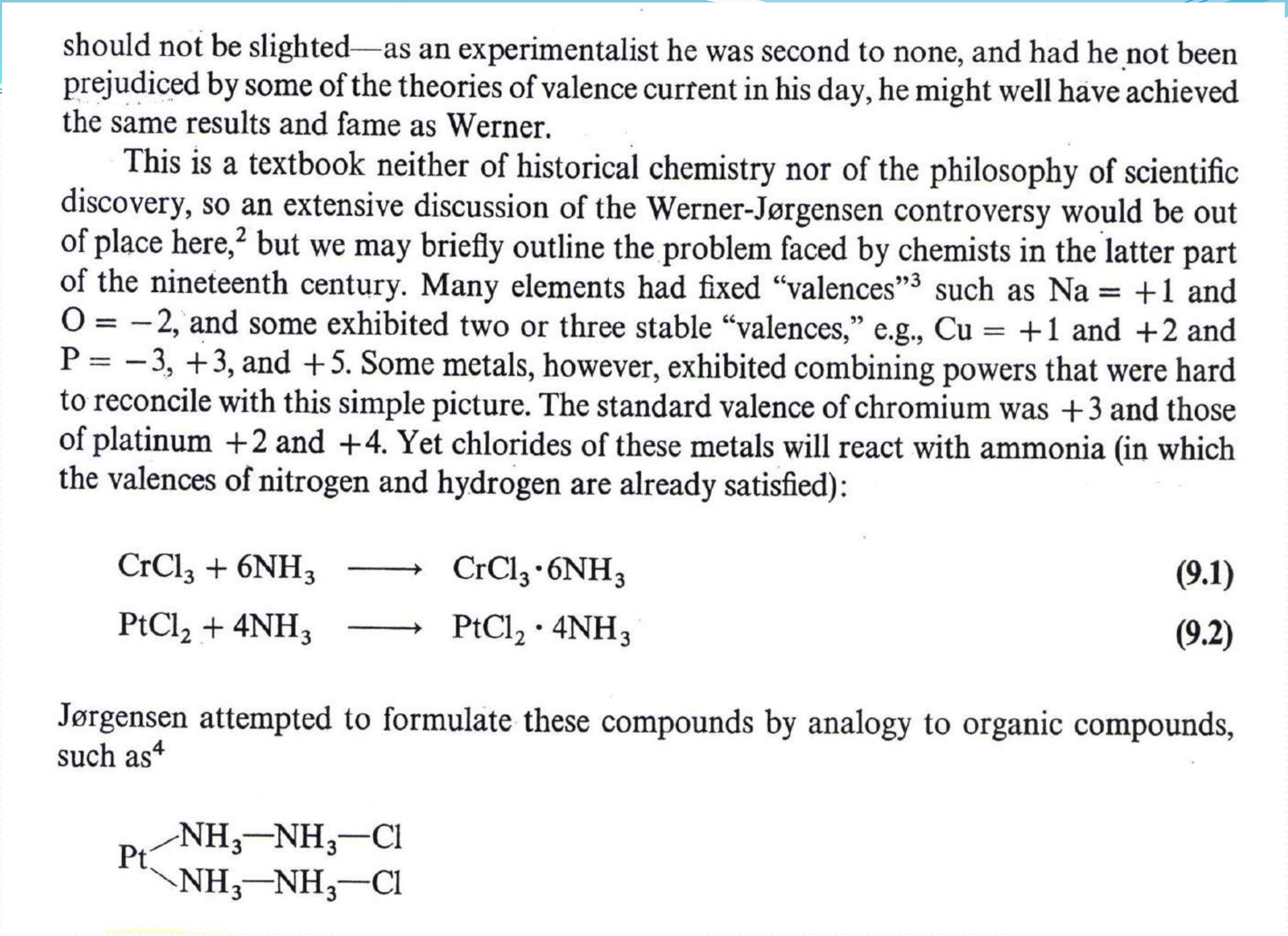
[11] J. H. Van Vleck, *J. Chem. Phys.*, **1935**, *3*, 807.

[12] T. E. Sloan, "Nomenclature of Coordination Compounds,", in G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, 1987, Vol. 1, pp. 109–134; G. J. Leigh, ed., International Union of Pure and Applied Chemistry, *Nomenclature of Inorganic Chemistry: Recommendations 1990*, Blackwell Scientific Publications, Cambridge, MA, 1990; J. A. McCleverty and N. G. Connelly, eds., International Union of Pure and Applied Chemistry, *Nomenclature of Inorganic Chemistry II: Recommendations 2000*, Royal Society of Chemistry, Cambridge, UK, 2001.



Coordination chemistry: theory

Coordination compounds have always been a challenge to the inorganic chemist. In the early days of chemistry they seemed unusual (hence the name "complex" ions) and seemed to defy the usual rules of valence. Today they comprise a large body of current inorganic research. A survey of articles in recent issues of the journal *Inorganic Chemistry* indicates that perhaps 70% could be considered to deal with coordination compounds. Although the usual bonding theories can be extended to accommodate these compounds, they still provide stimulating problems to be resolved. In synthetic work they continue to provide a challenge in the laboratory. The rapidly developing field of bioinorganic chemistry is centered on the presence of coordination compounds in living systems.



should not be slighted—as an experimentalist he was second to none, and had he not been prejudiced by some of the theories of valence current in his day, he might well have achieved the same results and fame as Werner.

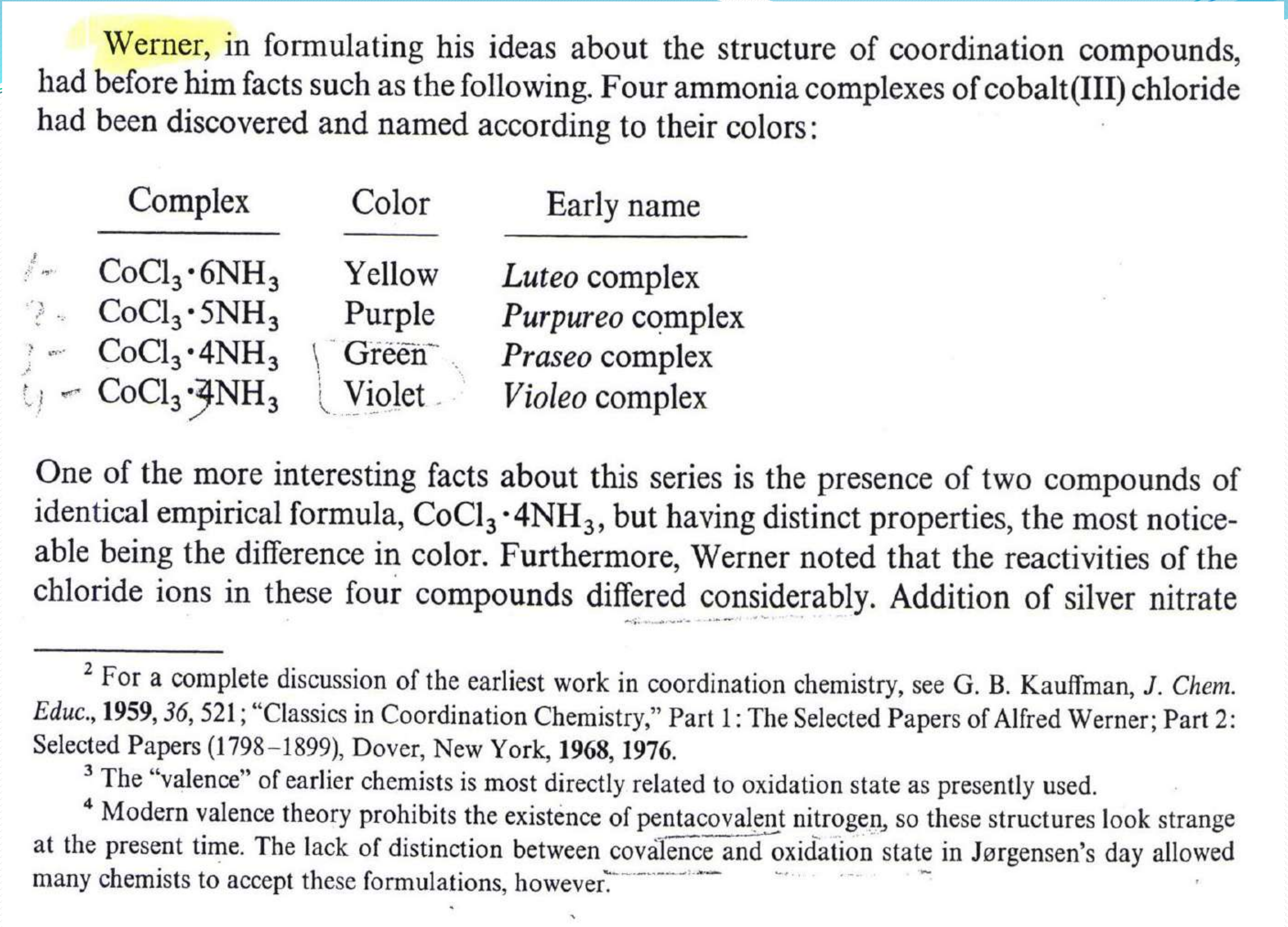
This is a textbook neither of historical chemistry nor of the philosophy of scientific discovery, so an extensive discussion of the Werner-Jørgensen controversy would be out of place here,[2] but we may briefly outline the problem faced by chemists in the latter part of the nineteenth century. Many elements had fixed "valences"[3] such as $Na = +1$ and $O = -2$, and some exhibited two or three stable "valences," e.g., $Cu = +1$ and $+2$ and $P = -3$, $+3$, and $+5$. Some metals, however, exhibited combining powers that were hard to reconcile with this simple picture. The standard valence of chromium was $+3$ and those of platinum $+2$ and $+4$. Yet chlorides of these metals will react with ammonia (in which the valences of nitrogen and hydrogen are already satisfied):

$$CrCl_3 + 6NH_3 \longrightarrow CrCl_3 \cdot 6NH_3 \tag{9.1}$$

$$PtCl_2 + 4NH_3 \longrightarrow PtCl_2 \cdot 4NH_3 \tag{9.2}$$

Jørgensen attempted to formulate these compounds by analogy to organic compounds, such as[4]

$$Pt\begin{array}{l} \diagup NH_3{-}NH_3{-}Cl \\ \diagdown NH_3{-}NH_3{-}Cl \end{array}$$



Werner, in formulating his ideas about the structure of coordination compounds, had before him facts such as the following. Four ammonia complexes of cobalt(III) chloride had been discovered and named according to their colors:

	Complex	Color	Early name
1 -	$CoCl_3 \cdot 6NH_3$	Yellow	*Luteo* complex
2 -	$CoCl_3 \cdot 5NH_3$	Purple	*Purpureo* complex
3 -	$CoCl_3 \cdot 4NH_3$	Green	*Praseo* complex
4 -	$CoCl_3 \cdot 4NH_3$	Violet	*Violeo* complex

One of the more interesting facts about this series is the presence of two compounds of identical empirical formula, $CoCl_3 \cdot 4NH_3$, but having distinct properties, the most noticeable being the difference in color. Furthermore, Werner noted that the reactivities of the chloride ions in these four compounds differed considerably. Addition of silver nitrate

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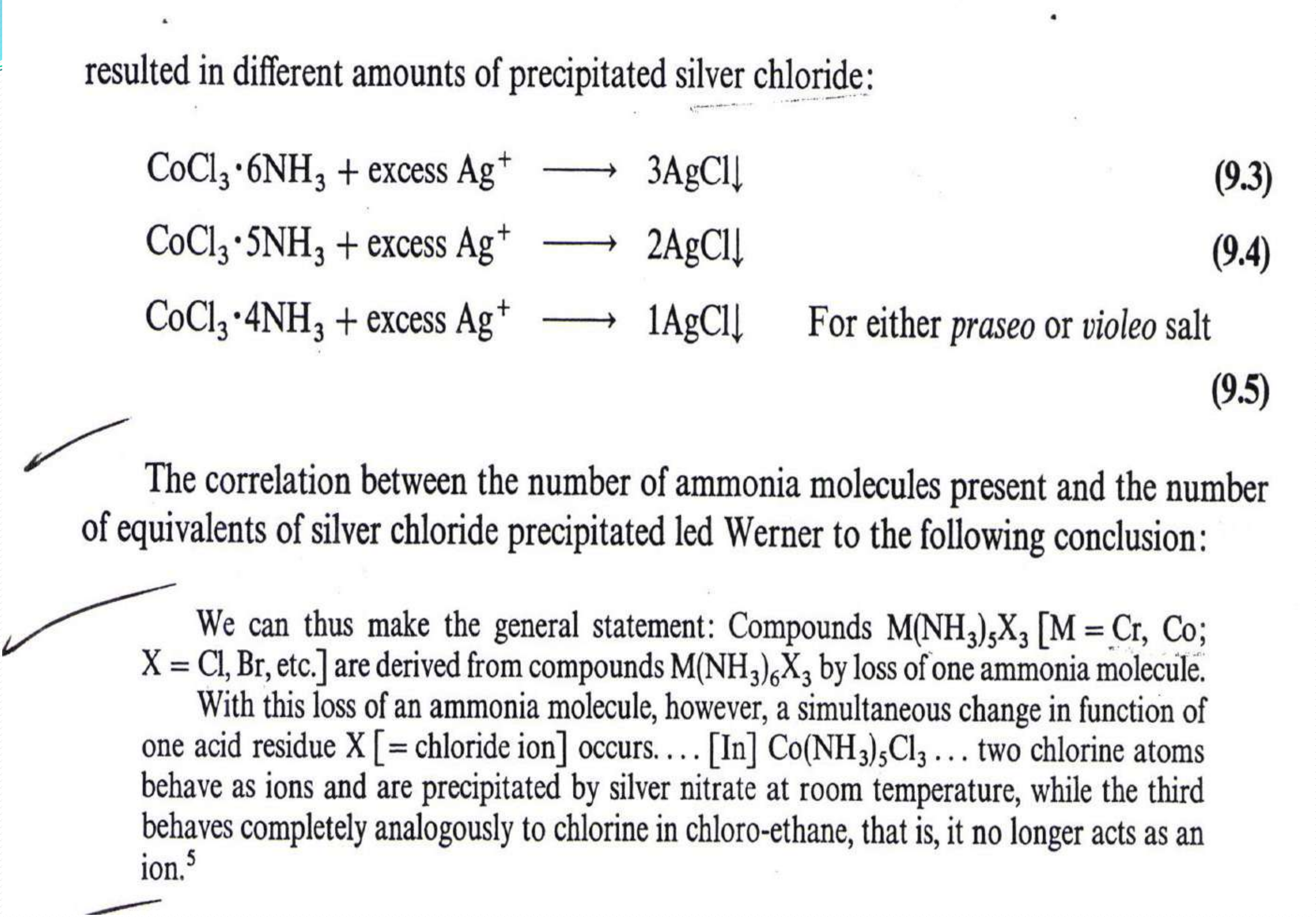
[2] For a complete discussion of the earliest work in coordination chemistry, see G. B. Kauffman, *J. Chem. Educ.*, **1959**, *36*, 521; "Classics in Coordination Chemistry," Part 1: The Selected Papers of Alfred Werner; Part 2: Selected Papers (1798–1899), Dover, New York, **1968**, **1976**.

[3] The "valence" of earlier chemists is most directly related to oxidation state as presently used.

[4] Modern valence theory prohibits the existence of pentacovalent nitrogen, so these structures look strange at the present time. The lack of distinction between covalence and oxidation state in Jørgensen's day allowed many chemists to accept these formulations, however.



resulted in different amounts of precipitated silver chloride:

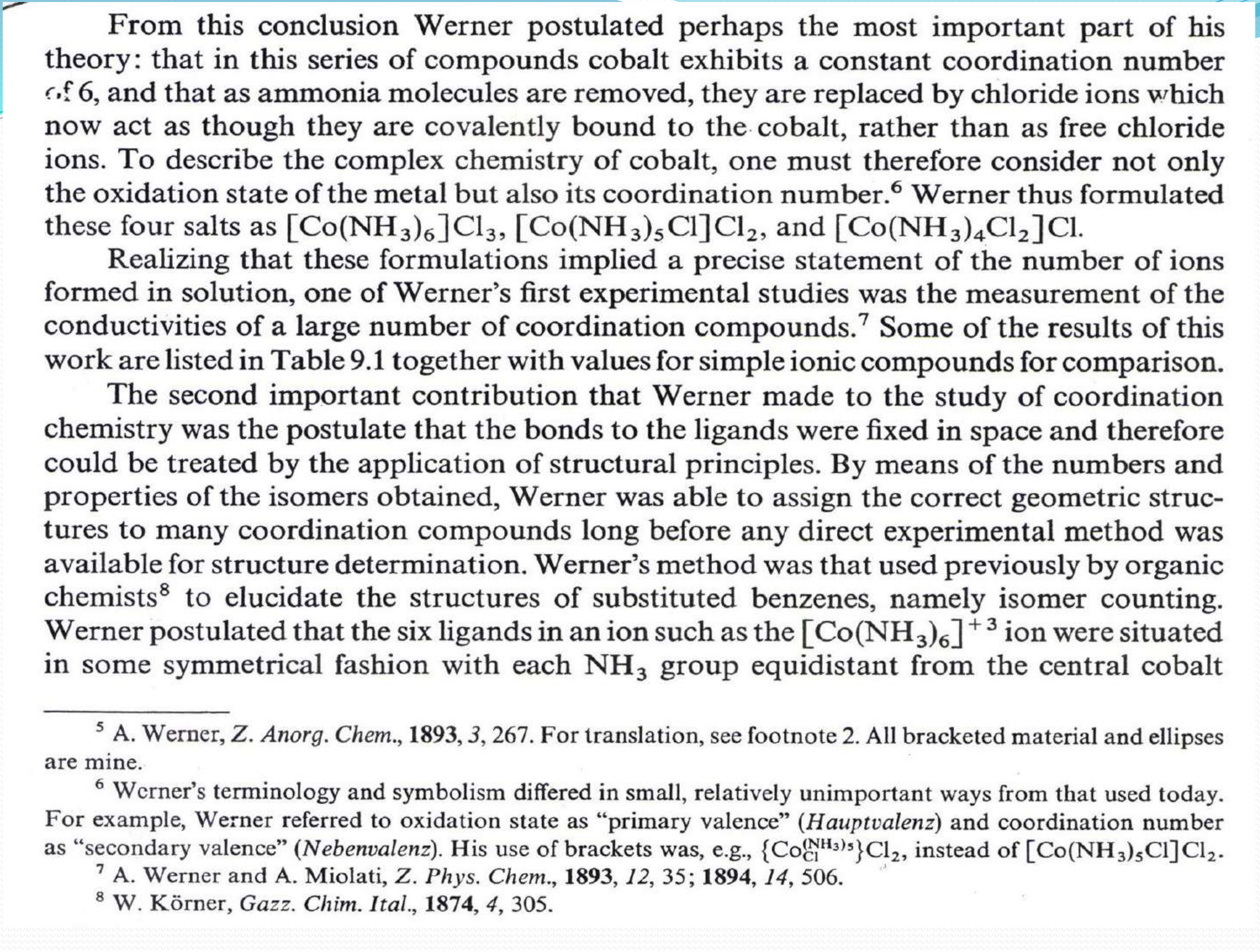
$$CoCl_3 \cdot 6NH_3 + \text{excess } Ag^+ \longrightarrow 3AgCl\downarrow \tag{9.3}$$

$$CoCl_3 \cdot 5NH_3 + \text{excess } Ag^+ \longrightarrow 2AgCl\downarrow \tag{9.4}$$

$$CoCl_3 \cdot 4NH_3 + \text{excess } Ag^+ \longrightarrow 1AgCl\downarrow \quad \text{For either } \textit{praseo} \text{ or } \textit{violeo} \text{ salt} \tag{9.5}$$

The correlation between the number of ammonia molecules present and the number of equivalents of silver chloride precipitated led Werner to the following conclusion:

> We can thus make the general statement: Compounds $M(NH_3)_5X_3$ [M = Cr, Co; X = Cl, Br, etc.] are derived from compounds $M(NH_3)_6X_3$ by loss of one ammonia molecule.
>
> With this loss of an ammonia molecule, however, a simultaneous change in function of one acid residue X [= chloride ion] occurs. . . . [In] $Co(NH_3)_5Cl_3$ . . . two chlorine atoms behave as ions and are precipitated by silver nitrate at room temperature, while the third behaves completely analogously to chlorine in chloro-ethane, that is, it no longer acts as an ion.[5]



From this conclusion Werner postulated perhaps the most important part of his theory: that in this series of compounds cobalt exhibits a constant coordination number of 6, and that as ammonia molecules are removed, they are replaced by chloride ions which now act as though they are covalently bound to the cobalt, rather than as free chloride ions. To describe the complex chemistry of cobalt, one must therefore consider not only the oxidation state of the metal but also its coordination number.[6] Werner thus formulated these four salts as $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_4Cl_2]Cl$.

Realizing that these formulations implied a precise statement of the number of ions formed in solution, one of Werner's first experimental studies was the measurement of the conductivities of a large number of coordination compounds.[7] Some of the results of this work are listed in Table 9.1 together with values for simple ionic compounds for comparison.

The second important contribution that Werner made to the study of coordination chemistry was the postulate that the bonds to the ligands were fixed in space and therefore could be treated by the application of structural principles. By means of the numbers and properties of the isomers obtained, Werner was able to assign the correct geometric structures to many coordination compounds long before any direct experimental method was available for structure determination. Werner's method was that used previously by organic chemists[8] to elucidate the structures of substituted benzenes, namely isomer counting. Werner postulated that the six ligands in an ion such as the $[Co(NH_3)_6]^{+3}$ ion were situated in some symmetrical fashion with each NH_3 group equidistant from the central cobalt

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[5] A. Werner, *Z. Anorg. Chem.*, **1893**, *3*, 267. For translation, see footnote 2. All bracketed material and ellipses are mine.

[6] Werner's terminology and symbolism differed in small, relatively unimportant ways from that used today. For example, Werner referred to oxidation state as "primary valence" (*Hauptvalenz*) and coordination number as "secondary valence" (*Nebenvalenz*). His use of brackets was, e.g., $\{Co^{(NH_3)_5}_{Cl}\}Cl_2$, instead of $[Co(NH_3)_5Cl]Cl_2$.

[7] A. Werner and A. Miolati, *Z. Phys. Chem.*, **1893**, *12*, 35; **1894**, *14*, 506.

[8] W. Körner, *Gazz. Chim. Ital.*, **1874**, *4*, 305.

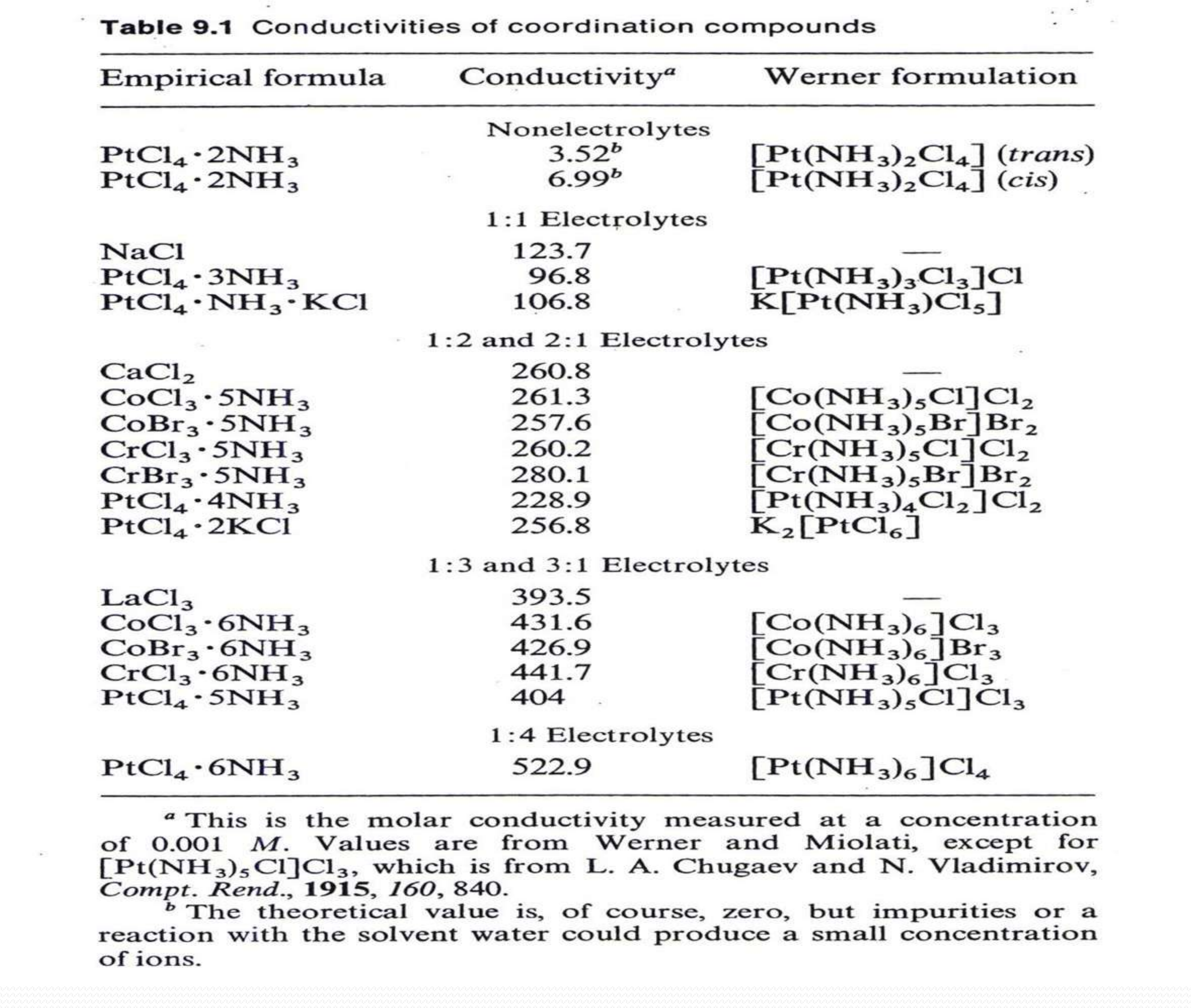
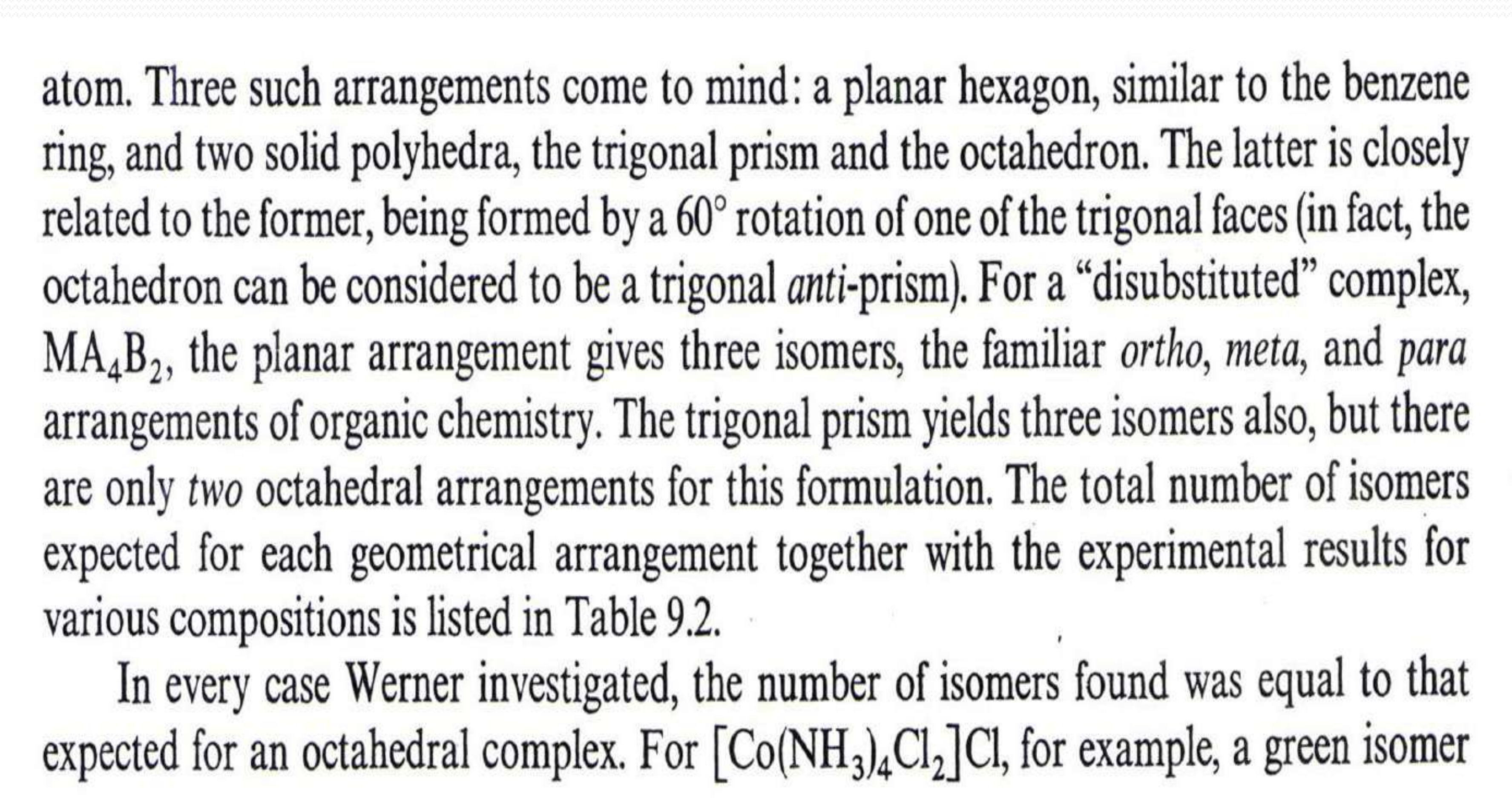


Table 9.1 Conductivities of coordination compounds

Empirical formula	Conductivity[a]	Werner formulation
	Nonelectrolytes	
$PtCl_4 \cdot 2NH_3$	3.52[b]	$[Pt(NH_3)_2Cl_4]$ (*trans*)
$PtCl_4 \cdot 2NH_3$	6.99[b]	$[Pt(NH_3)_2Cl_4]$ (*cis*)
	1:1 Electrolytes	
NaCl	123.7	—
$PtCl_4 \cdot 3NH_3$	96.8	$[Pt(NH_3)_3Cl_3]Cl$
$PtCl_4 \cdot NH_3 \cdot KCl$	106.8	$K[Pt(NH_3)Cl_5]$
	1:2 and 2:1 Electrolytes	
$CaCl_2$	260.8	—
$CoCl_3 \cdot 5NH_3$	261.3	$[Co(NH_3)_5Cl]Cl_2$
$CoBr_3 \cdot 5NH_3$	257.6	$[Co(NH_3)_5Br]Br_2$
$CrCl_3 \cdot 5NH_3$	260.2	$[Cr(NH_3)_5Cl]Cl_2$
$CrBr_3 \cdot 5NH_3$	280.1	$[Cr(NH_3)_5Br]Br_2$
$PtCl_4 \cdot 4NH_3$	228.9	$[Pt(NH_3)_4Cl_2]Cl_2$
$PtCl_4 \cdot 2KCl$	256.8	$K_2[PtCl_6]$
	1:3 and 3:1 Electrolytes	
$LaCl_3$	393.5	—
$CoCl_3 \cdot 6NH_3$	431.6	$[Co(NH_3)_6]Cl_3$
$CoBr_3 \cdot 6NH_3$	426.9	$[Co(NH_3)_6]Br_3$
$CrCl_3 \cdot 6NH_3$	441.7	$[Cr(NH_3)_6]Cl_3$
$PtCl_4 \cdot 5NH_3$	404	$[Pt(NH_3)_5Cl]Cl_3$
	1:4 Electrolytes	
$PtCl_4 \cdot 6NH_3$	522.9	$[Pt(NH_3)_6]Cl_4$

[a] This is the molar conductivity measured at a concentration of 0.001 *M*. Values are from Werner and Miolati, except for $[Pt(NH_3)_5Cl]Cl_3$, which is from L. A. Chugaev and N. Vladimirov, *Compt. Rend.*, **1915**, *160*, 840.

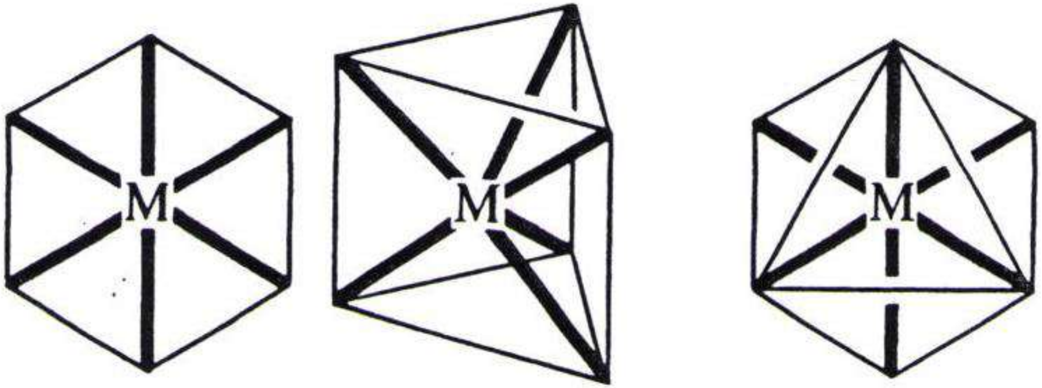
[b] The theoretical value is, of course, zero, but impurities or a reaction with the solvent water could produce a small concentration of ions.



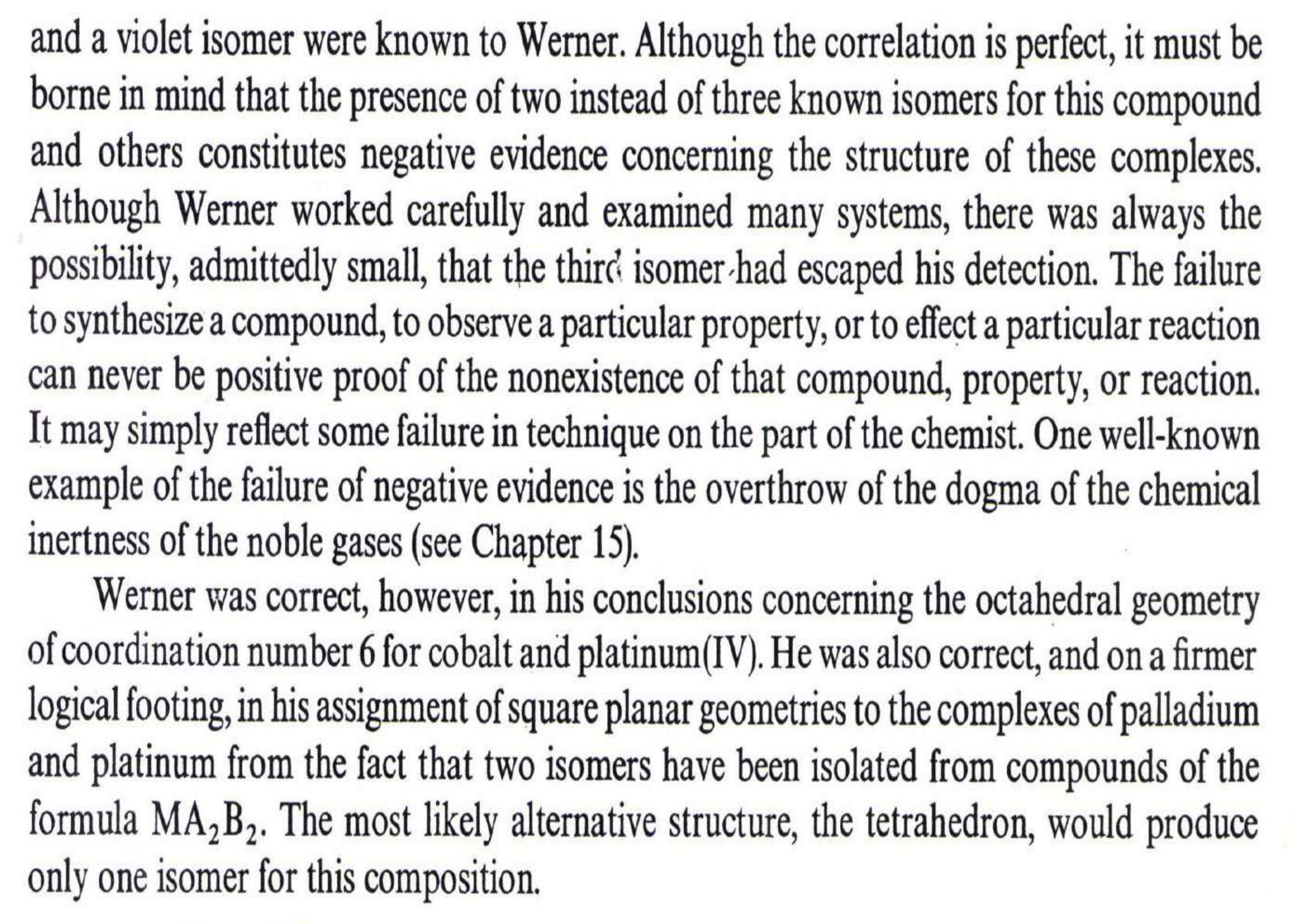
atom. Three such arrangements come to mind: a planar hexagon, similar to the benzene ring, and two solid polyhedra, the trigonal prism and the octahedron. The latter is closely related to the former, being formed by a 60° rotation of one of the trigonal faces (in fact, the octahedron can be considered to be a trigonal *anti*-prism). For a "disubstituted" complex, MA_4B_2, the planar arrangement gives three isomers, the familiar *ortho*, *meta*, and *para* arrangements of organic chemistry. The trigonal prism yields three isomers also, but there are only *two* octahedral arrangements for this formulation. The total number of isomers expected for each geometrical arrangement together with the experimental results for various compositions is listed in Table 9.2.

In every case Werner investigated, the number of isomers found was equal to that expected for an octahedral complex. For $[Co(NH_3)_4Cl_2]Cl$, for example, a green isomer

Table 9.2 Numbers of isomers expected and found for C.N. = 6

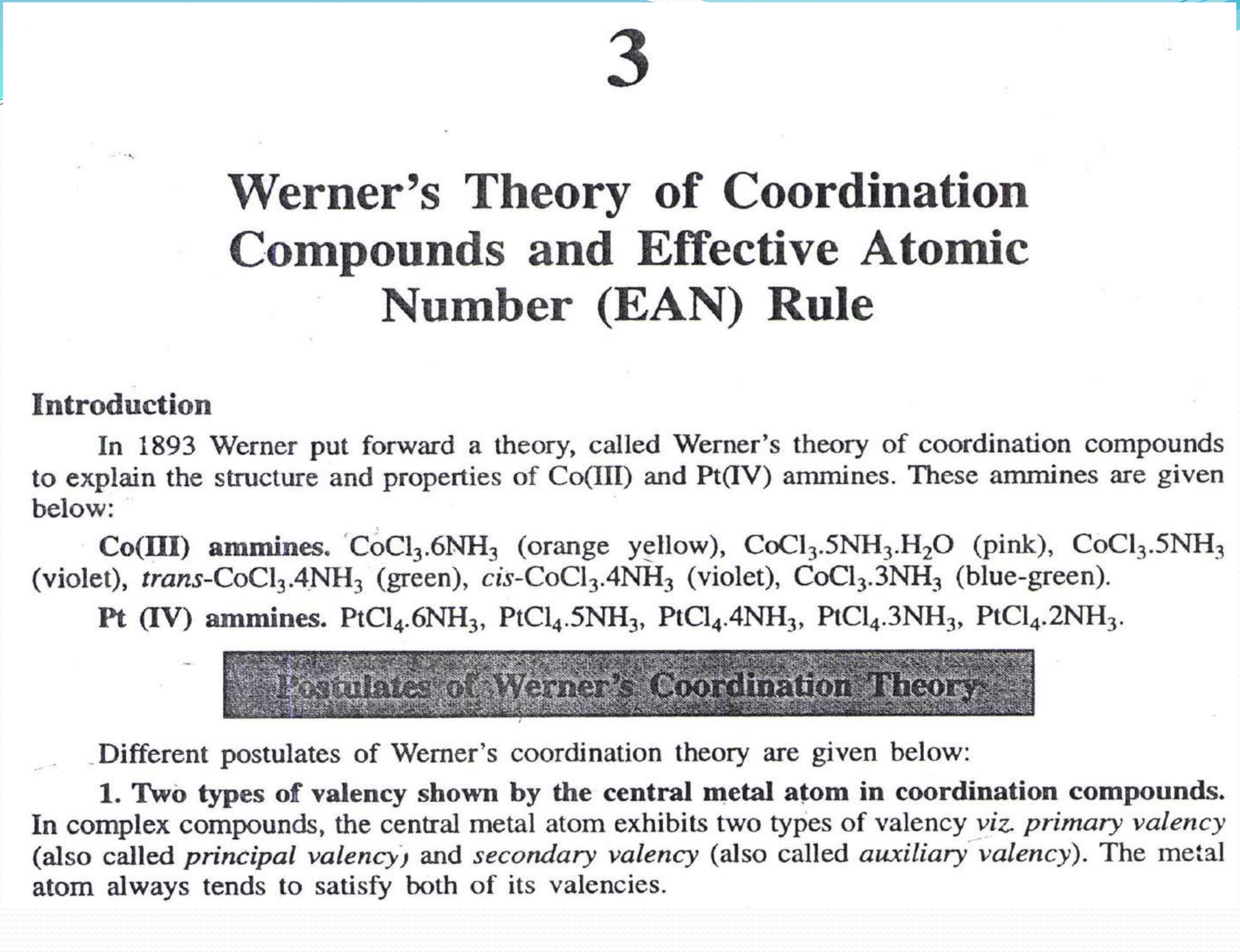


Formula	Planar	Trigonal prism	Octahedral	Experimental
MA_5B	1	1	1	1
MA_4B_2	3	3	2	2
MA_3B_3	3	3	2	2



and a violet isomer were known to Werner. Although the correlation is perfect, it must be borne in mind that the presence of two instead of three known isomers for this compound and others constitutes negative evidence concerning the structure of these complexes. Although Werner worked carefully and examined many systems, there was always the possibility, admittedly small, that the third isomer had escaped his detection. The failure to synthesize a compound, to observe a particular property, or to effect a particular reaction can never be positive proof of the nonexistence of that compound, property, or reaction. It may simply reflect some failure in technique on the part of the chemist. One well-known example of the failure of negative evidence is the overthrow of the dogma of the chemical inertness of the noble gases (see Chapter 15).

Werner was correct, however, in his conclusions concerning the octahedral geometry of coordination number 6 for cobalt and platinum(IV). He was also correct, and on a firmer logical footing, in his assignment of square planar geometries to the complexes of palladium and platinum from the fact that two isomers have been isolated from compounds of the formula MA_2B_2. The most likely alternative structure, the tetrahedron, would produce only one isomer for this composition.



3

Werner's Theory of Coordination Compounds and Effective Atomic Number (EAN) Rule

Introduction

In 1893 Werner put forward a theory, called Werner's theory of coordination compounds to explain the structure and properties of Co(III) and Pt(IV) ammines. These ammines are given below:

Co(III) ammines. $CoCl_3.6NH_3$ (orange yellow), $CoCl_3.5NH_3.H_2O$ (pink), $CoCl_3.5NH_3$ (violet), *trans*-$CoCl_3.4NH_3$ (green), *cis*-$CoCl_3.4NH_3$ (violet), $CoCl_3.3NH_3$ (blue-green).

Pt (IV) ammines. $PtCl_4.6NH_3$, $PtCl_4.5NH_3$, $PtCl_4.4NH_3$, $PtCl_4.3NH_3$, $PtCl_4.2NH_3$.

Postulates of Werner's Coordination Theory

Different postulates of Werner's coordination theory are given below:

1. Two types of valency shown by the central metal atom in coordination compounds. In complex compounds, the central metal atom exhibits two types of valency *viz. primary valency* (also called *principal valency*) and *secondary valency* (also called *auxiliary valency*). The metal atom always tends to satisfy both of its valencies.

2. Characteristics of secondary valency. (*i*) In modern terminology, the secondary valency of the metallic atom in a complex compound is equal to the **coordination number** of that metal.

(*ii*) Secondary valency of a metal is satisfied either by anions or by neutral molecules alone or by anions and neutral molecules both. For example.

(*a*) In $4KCN.Fe(CN)_2$ or $K_4[Fe(CN)_6]$, the secondary valency of Fe-atom is six and is satisfied by six CN^- ions (anions).

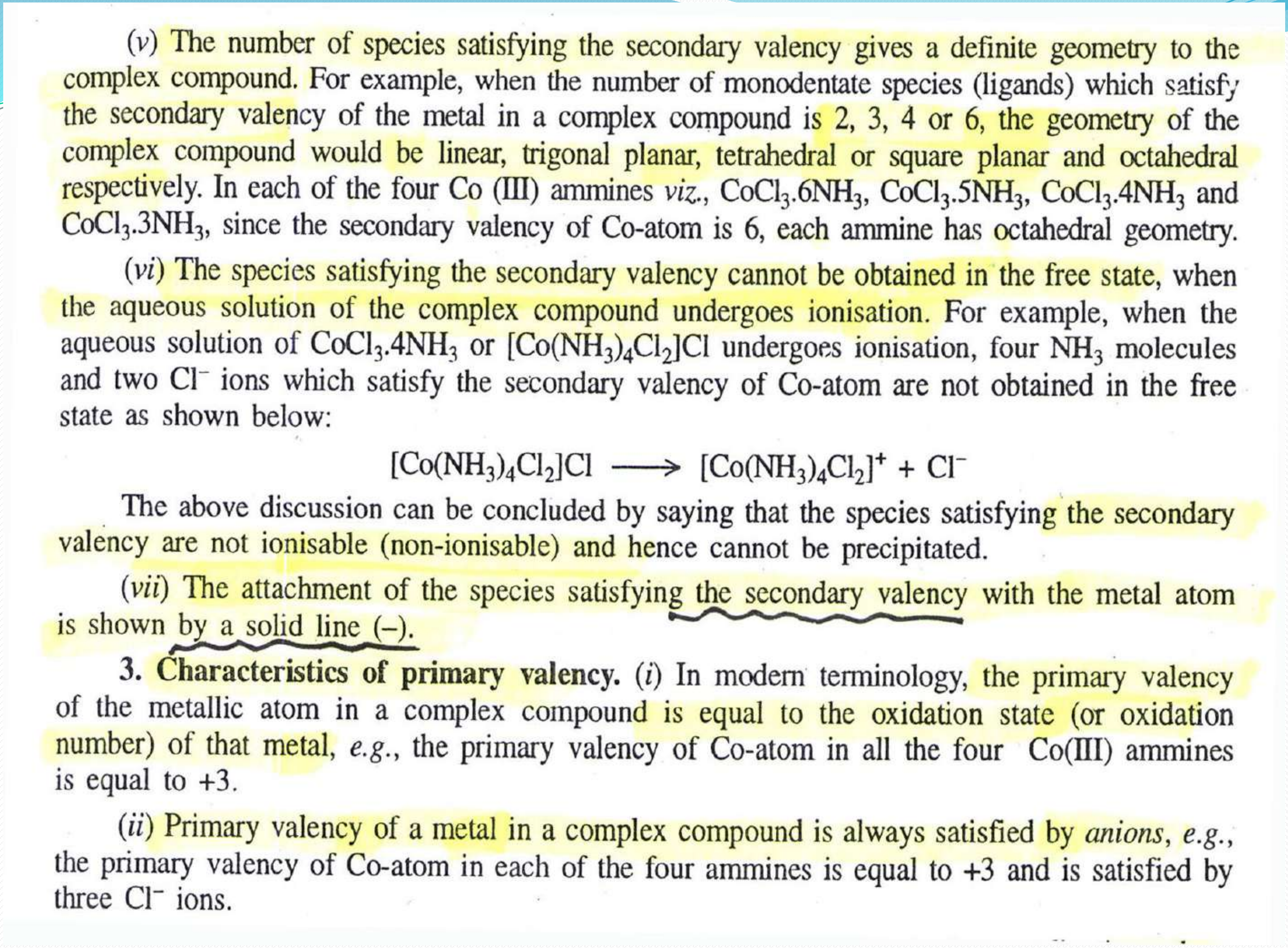
(*b*) In $CoCl_3.6NH_3$ or $[Co(NH_3)_6]Cl_3$, secondary valency of Co-atom is six and is satisfied by six NH_3 molecules (neutral molecules).

(*c*) In $CoCl_3.5NH_3$ or $[Co(NH_3)_5Cl]Cl_2$, the secondary valency of Co-atom is six and is satisfied by five NH_3 molecules (neutral molecules) and one Cl^- ion (anion).

According to modern concept of complex compounds, the species satisfying the secondary valency are called **ligands.**

(*iii*) While writing the structure of a complex compound, the species satisfying the secondary valency and the metal are written inside the coordination sphere. For example in $CoCl_3.4NH_3$, since four NH_3 molecules and two Cl^- ions satisfy the secondary valency of Co-atom, its structure is written as $[CoCl_2.4NH_3]Cl$ or $[Co(NH_3)_4Cl_2]Cl$.

(*iv*) The secondary valencies have directional nature, since the species satisfying the secondary valency (*i.e.*, ligands) are directed towards the fixed positions in space.



(*v*) The number of species satisfying the secondary valency gives a definite geometry to the complex compound. For example, when the number of monodentate species (ligands) which satisfy the secondary valency of the metal in a complex compound is 2, 3, 4 or 6, the geometry of the complex compound would be linear, trigonal planar, tetrahedral or square planar and octahedral respectively. In each of the four Co (III) ammines *viz.*, $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$, since the secondary valency of Co-atom is 6, each ammine has octahedral geometry.

(*vi*) The species satisfying the secondary valency cannot be obtained in the free state, when the aqueous solution of the complex compound undergoes ionisation. For example, when the aqueous solution of $CoCl_3.4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$ undergoes ionisation, four NH_3 molecules and two Cl^- ions which satisfy the secondary valency of Co-atom are not obtained in the free state as shown below:

$$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$$

The above discussion can be concluded by saying that the species satisfying the secondary valency are not ionisable (non-ionisable) and hence cannot be precipitated.

(*vii*) The attachment of the species satisfying the secondary valency with the metal atom is shown by a solid line (–).

3. Characteristics of primary valency. (*i*) In modern terminology, the primary valency of the metallic atom in a complex compound is equal to the oxidation state (or oxidation number) of that metal, *e.g.*, the primary valency of Co-atom in all the four Co(III) ammines is equal to +3.

(*ii*) Primary valency of a metal in a complex compound is always satisfied by *anions*, *e.g.*, the primary valency of Co-atom in each of the four ammines is equal to +3 and is satisfied by three Cl^- ions.

(*iii*) The anions satisfying the primary valency are written outside the coordination sphere while the anions which satisfy both the valencies (dual character) are written inside the coordination sphere. Thus the species satisfyinig primary valency may be present inside and/or outside the coordination sphere.

(*iv*) The species satisfying both the valencies (*i.e.*, the species placed inside the coordination sphere) are directed towards specific directions in space and hence they have directional characteristics. The species which satisfy primary valency and are placed outside the coordination sphere have no directional characteristics.

(*v*) The species satisfying the primary valency do not give any geometry to the complex compound.

(*vi*) The species satisfying the primary valency can be obtained either completely or partially in their free state, when the complex compound undergoes ionisation in aqueous solution.

Examples (*a*) When the aqueous solution of $CoCl_3.6NH_3$ or $[Co(NH_3)_6]Cl_3$ undergoes ionisation, all the three Cl^- ions which satisfy primary valency of Co-atom are obtained in the free state.

$$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$$

(*b*) Although the primary valency of Co-atom in $CoCl_3.5NH_3$ or $[Co(NH_3)_5Cl]Cl_2$ is satisfied by three Cl^- ions, only two Cl^- ions are obtained in the free state, when the aqueous solution of this ammine undergoes ionisation.

$$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

The above discussion shows that all or some of the species satisfying the primary valencies are ionisable and hence can be precipitated by means of a suitable precipitating agent. For example, in the above ammine two Cl^- ions can be precipitated as AgCl (white ppt.) by adding aqueous solution of $AgNO_3$.

$$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

$$2Ag^+ + 2Cl^- \longrightarrow 2AgCl \ (\textit{white ppt.})$$

From the above discussion we can conclude that all the anions placed outside the coordination sphere can be obtained in the free state and hence can be precipitated. Thus all the anions placed outside the coordination sphere are ionisable.

(*vii*) The attachment of the species satisfying the primary valency to the metal is shown by broken line (– – – –).

4. How to show the attachment between the central metal and the species satisfying both the valencies. The attachment between the metal and the species which satisfy both the valencies is shown by a combined solid-broken line ($\overset{\text{————}}{- - - -}$). For example in $CoCl_3.5NH_3$ or $[Co(NH_3)_5Cl]Cl_2$, since one Cl^- ion satisfies primary as well as secondary valency of Co-atom, the attachment of this Cl^- ion to Co-atom is shown as Co^{3+} $\overset{\text{————}}{- - - -}$ Cl^-.

To explain the structure of Co(III) ammines on the basis of Werner's coordination theory

With the help of the postulates of Werner's coordination theory, the structure of Co (III) ammines *viz.* $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ can well be explained.

In all these ammines, the primary valency of cobalt is equal to 3 while the secondary valency is equal to 6. Primary valency of 3 is satisfied by three Cl^- ions and hence these ions are attached with Co^{3+} ion by dotted line (----). Secondary valency of six is satisfied either by six NH_3 molecules alone or by both NH_3 molecules and Cl^- ions. The species satisfying the secondary valency are attached with Co^{3+} ion by solid line (——).

1. $CoCl_3.6NH_3$. The primary valency of Co-atom which is equal to 3 is satisfied by three Cl^- ions and hence the attachment of these ions with Co^{3+} ion is shown by broken lines [Fig. 3.1 (*a*)].

When this ammine is acted upon by an aqueous solution of $AgNO_3$, all the three Cl^- ions present in this ammine are precipitated as AgCl (white ppt).

$$CoCl_3.6NH_3 \longrightarrow [Co.6NH_3]^{3+} + 3Cl^-$$

$$3Ag^+ + 3Cl^- \longrightarrow 3AgCl \ (\textit{white ppt})$$

The precipitation of all the three Cl^- ions indicates that these ions are outside the coordination sphere and it is only six NH_3 molecules which, along with Co atom, are present inside coordination sphere. Thus the structure of $CoCl_3.6NH_3$ can be written as $[Co.6NH_3]Cl_3$ or $[Co(NH_3)_6]Cl_3$. This structure shows that the secondary valency of Co atom which is equal to six is satisfied by six NH_3 molecules placed inside the coordination sphere and hence the attachment of NH_3 molecules to Co-atom is shown by solid lines [See Fig. 3.1 (*a*)].

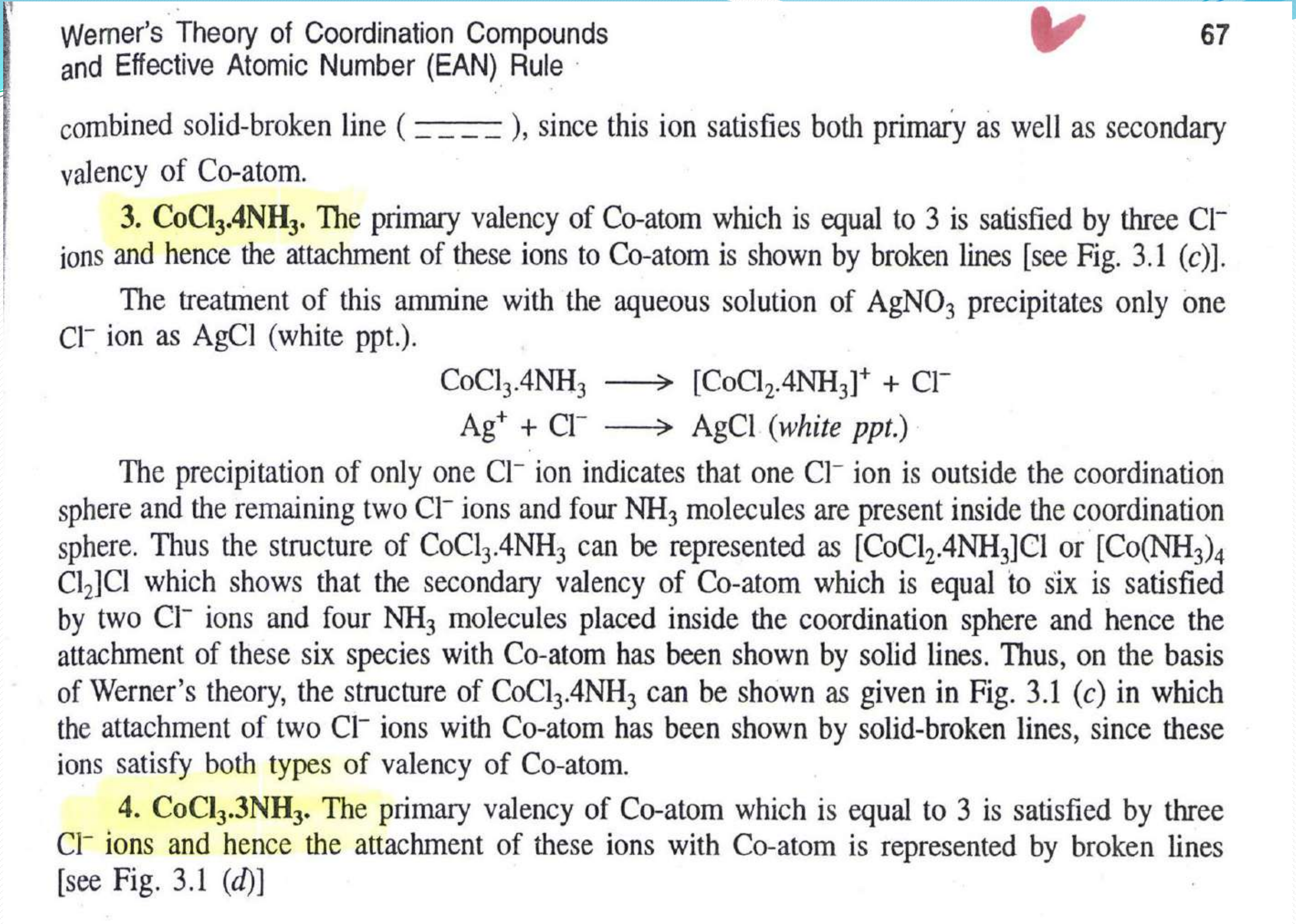
2. $CoCl_3.5NH_3$. The primary valency of Co-atom in this ammine is equal to 3 and is satisfied by three Cl^- ions. The attachment of these ions with Co^{3+} ion is, therefore, shown by broken lines [Fig. 3.1 (*b*)].

The treatment of this ammine with the aqueous solution of $AgNO_3$ precipitates only two Cl^- ions as AgCl (white ppt.)

$$CoCl_3.5NH_3 \longrightarrow [CoCl.5NH_3]^{2+} + 2Cl^-$$

$$2Ag^+ + 2Cl^- \longrightarrow 2AgCl \text{ (\textit{white ppt.})}$$

The precipitation of only two Cl^- ions indicates that two Cl^- ions are outside the coordination sphere and the remaining one Cl^- ion and five NH_3 molecules are present inside the coordination sphere. Thus on the basis of these observations, the structure of $CoCl_3.5NH_3$ can be written as $[CoCl.5NH_3]Cl_2$ or $[Co(NH_3)_5Cl]Cl_2$. This structure shows that the secondary valency of Co-atom which is equal to six is satisfied by one Cl^- ion and five NH_3 molecules placed inside the coordination sphere. The attachment of one Cl^- ion and five NH_3 molecules to Co-atom is, therefore, shown by solid lines. The above discussion shows that, on the basis of Werner's theory, the structure of $CoCl_3.5NH_3$ can be shown as depicted in Fig. 3.1 (*b*). This figure shows that out of the three Cl^- ions, one Cl^- ion is attached with Co-atom by a



combined solid-broken line ($\overline{- - - -}$), since this ion satisfies both primary as well as secondary valency of Co-atom.

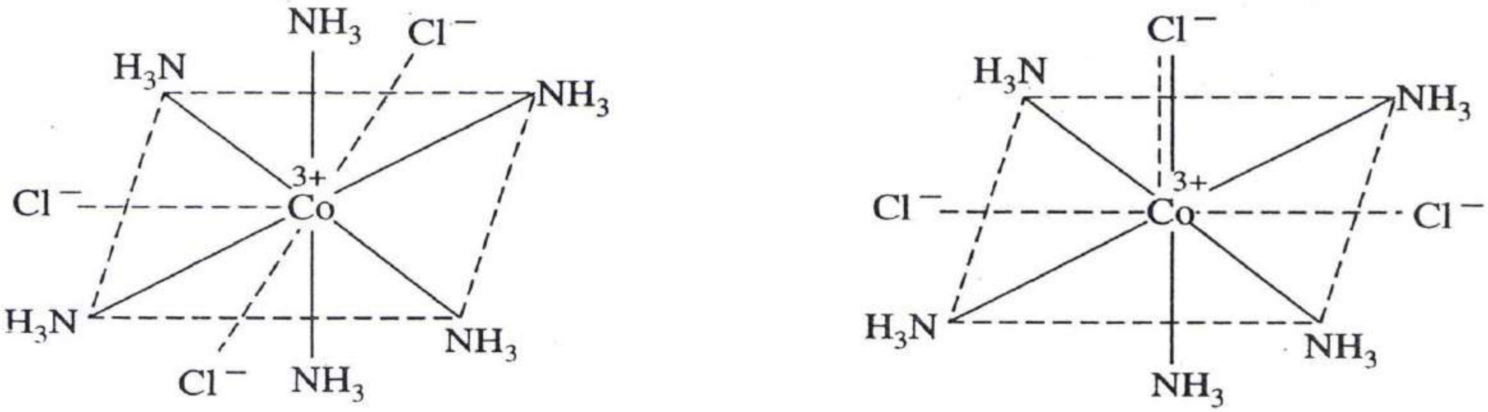
3. $CoCl_3.4NH_3$. The primary valency of Co-atom which is equal to 3 is satisfied by three Cl^- ions and hence the attachment of these ions to Co-atom is shown by broken lines [see Fig. 3.1 (*c*)].

The treatment of this ammine with the aqueous solution of $AgNO_3$ precipitates only one Cl^- ion as AgCl (white ppt.).

$$CoCl_3.4NH_3 \longrightarrow [CoCl_2.4NH_3]^+ + Cl^-$$
$$Ag^+ + Cl^- \longrightarrow AgCl \ (\textit{white ppt.})$$

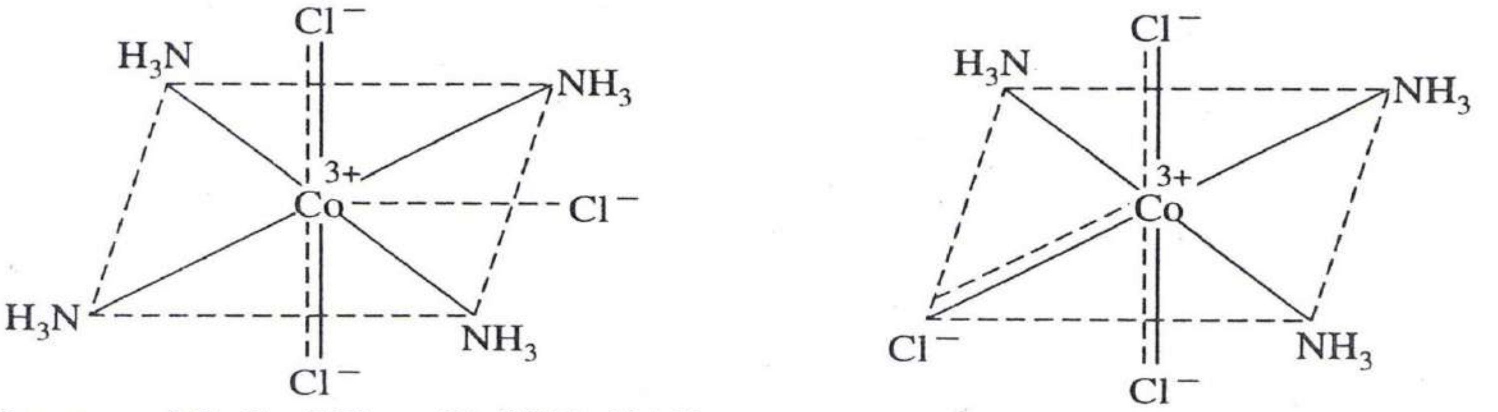
The precipitation of only one Cl^- ion indicates that one Cl^- ion is outside the coordination sphere and the remaining two Cl^- ions and four NH_3 molecules are present inside the coordination sphere. Thus the structure of $CoCl_3.4NH_3$ can be represented as $[CoCl_2.4NH_3]Cl$ or $[Co(NH_3)_4Cl_2]Cl$ which shows that the secondary valency of Co-atom which is equal to six is satisfied by two Cl^- ions and four NH_3 molecules placed inside the coordination sphere and hence the attachment of these six species with Co-atom has been shown by solid lines. Thus, on the basis of Werner's theory, the structure of $CoCl_3.4NH_3$ can be shown as given in Fig. 3.1 (*c*) in which the attachment of two Cl^- ions with Co-atom has been shown by solid-broken lines, since these ions satisfy both types of valency of Co-atom.

4. $CoCl_3.3NH_3$. The primary valency of Co-atom which is equal to 3 is satisfied by three Cl^- ions and hence the attachment of these ions with Co-atom is represented by broken lines [see Fig. 3.1 (*d*)]



(*a*) Structure of $CoCl_3.6NH_3$ or $[Co(NH_3)_6]Cl_3$ Secondary valency of six is satisfied by six NH_3 molecules.

(*b*) Structure of $CoCl_3.5NH_3$. (or $[Co(NH_3)_5Cl]\ Cl_2$. Secondary valency of six is satisfied by five NH_3 molecules and one Cl^- ion.



(*c*) Structure of $CoCl_3.4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$. Secondary valency of six is satisfied by four NH_3 molecules and two Cl^- ions.

(*d*) Structure of $CoCl_3.3NH_3$ or $[Co(NH_3)_3Cl_3]^0$. Secondary valency of six is satisfied by three NH_3 molecules and three Cl^- ions.

Fig. 3.1. Structure of Co (III) ammines *viz.* $CoCl_3.6NH_3$, $CoCl_3.5NH_3$., $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ on the basis of Werner's coordination theory. In all these ammines the primary valency of Co-atom is equal to 3 and secondary valency is equal to six. Primary valency of three is satisfied by three Cl^- ions.

When this ammine is treated with the aqueous solution of $AgNO_3$, no precipitate is obtained. The non-formation of any precipitate shows that no Cl^- ion is outside the coordination sphere, *i.e.*, all the three Cl^- ions and three NH_3, along with Co-atom, are present inside the coordination sphere. Thus the structure of this ammine can be written as $[CoCl_3.3NH_3]^0$ or $[Co(NH_3)_3Cl_3]^0$. This structure shows that the secondary valency of Co-atom which is equal to six is satisfied by three Cl^- ions and three NH_3 molecules placed inside the co-ordination sphere. Thus the linking of these six species with Co-atom is represented by solid lines. This discussion indicates that, on the basis of Werner's theory, the structure of $CoCl_3.3NH_3$ can be shown as given in Fig. 3.1 (*d*) in which the attachment of three Cl^- ions with Co-atom has been represented by solid-broken lines, since these ions satisfy both types of valency of Co-atom.

Experimental evidences in favour of Werner's theory

We have said that the Co(III) ammines given above can be represented as $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH)_3Cl_3]$ respectively. These structures have been confirmed by the following studies :

1. Cryoscopic measurements. Cryoscopic measurements (*i.e.*, the measurement of the depression in freezing points of aqueous solutions) gives the number of ions furnished by the dissociation of one molecule of the compound. This measurement for Co (III) ammines has also indicated that these compounds dissociate to give 4 (for $CoCl_3.6NH_3$), 3 (for $CoCl_3.5NH_3$), 2(for $CoCl_3.4NH_3$) and 1 (for $CoCl_3.3NH_3$) particles (ionic or molecular) (See Table 3.1).

2. Molar electrolytic conductance (or conductivity) measurements. Measurement of molar conductance of a compound at its large dilution gives the sum of the electrical charges on the positive and negative ions furnished by each molecule of the compound. Molar conductance value for each Co (III) ammine has been determined. These values have shown that the number of electrical charges given by these ammines is 6 (for $CoCl_3.6NH_3$), 4 (for $CoCl_3.5NH_3$); 2(for $CoCl_3.4NH_3$) and zero or nil (for $CoCl_3.3NH_3$). Total number of ions obtained by the ionisation of the ammines decreases with the decrease of magnitude of molar conductance value of the ammines (See Table 3.1).

3. Precipitation method. When a given ammine is treated with an aqueous solution of $AgNO_3$, some Cl^- ions get precipitated as AgCl. The number of Cl^- ions precipitated is the number of Cl^- ions that are ionisable and hence are present outside the coordination sphere. $CoCl_3.3NH_3$ gives no precipitite, showing that all the three Cl^- ions are present in the coordination sphere. Thus since the number of Cl^- ions precipitated by adding $AgNO_3$ solution to $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$ ammines is 3, 2 and 1 respectively, the number of Cl^- ions present outside the coordination sphere is also equal to 3, 2 and 1 respectively. $CoCl_3.3NH_3$ gives no precipitate (*i.e.*, gives no Cl^- ions) with $AgNO_3$ solution and hence all the three Cl^- ions are present in the coordination sphere (See Table 3.1).

To explain the structure of Pt(IV) ammines on the basis of Werner's coordination theory

We have already said the Pt(IV) gives five ammines which are $PtCl_4.6NH_3$, $PtCl_4.5NH_3$, $PtCl_4.4NH_3$, $PtCl_4.3NH_3$ and $PtCl_4.2NH_3$. In each of these ammines, primary valency of Pt is equal to its oxidation state (= +4) while the secondary valency is equal to 6. Thus each ammine has octahedral geometry. Cryoscopic measurements have shown that the number of particles obtained by the ionisation of these ammines is equal to 5, 4, 3, 2, and 1 respectively. Molar conductance measurements have revealed that the number of electrical charges obtained as a result of their ionisation is 8 (+ 4, – 4), 6(+3, –3), 4(+2, –2), 2(+1, –1) and zero. These studies show that the structure of these ammines can be written as shown in Table 3.1.

Sidgwick's Electronic Concept of Coordinate Bond

In 1916 Lewis introduced a concept of two-electron covalent bond between two atoms in a molecule. According to this concept a covalent bond is formed between two atoms of a

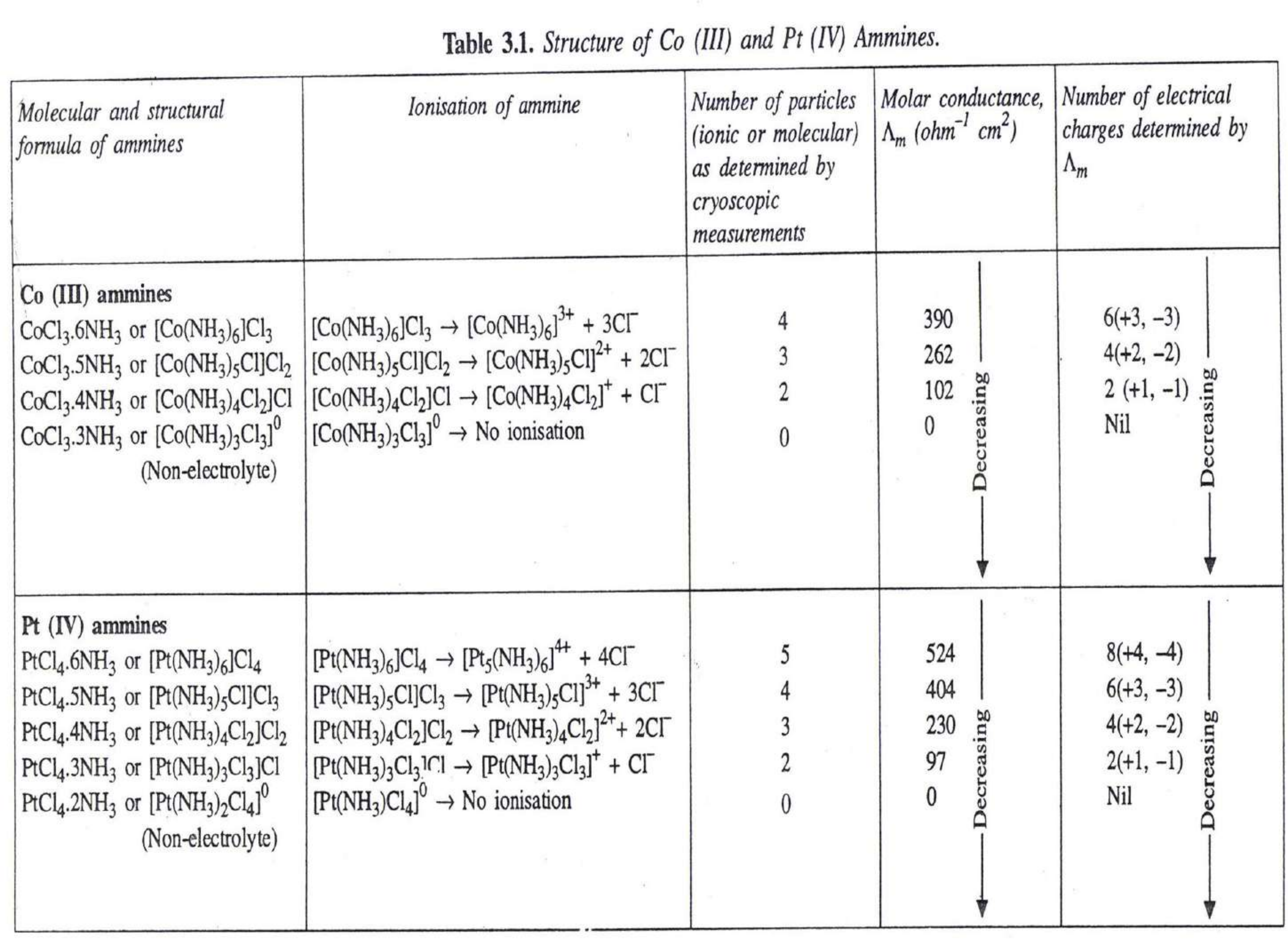
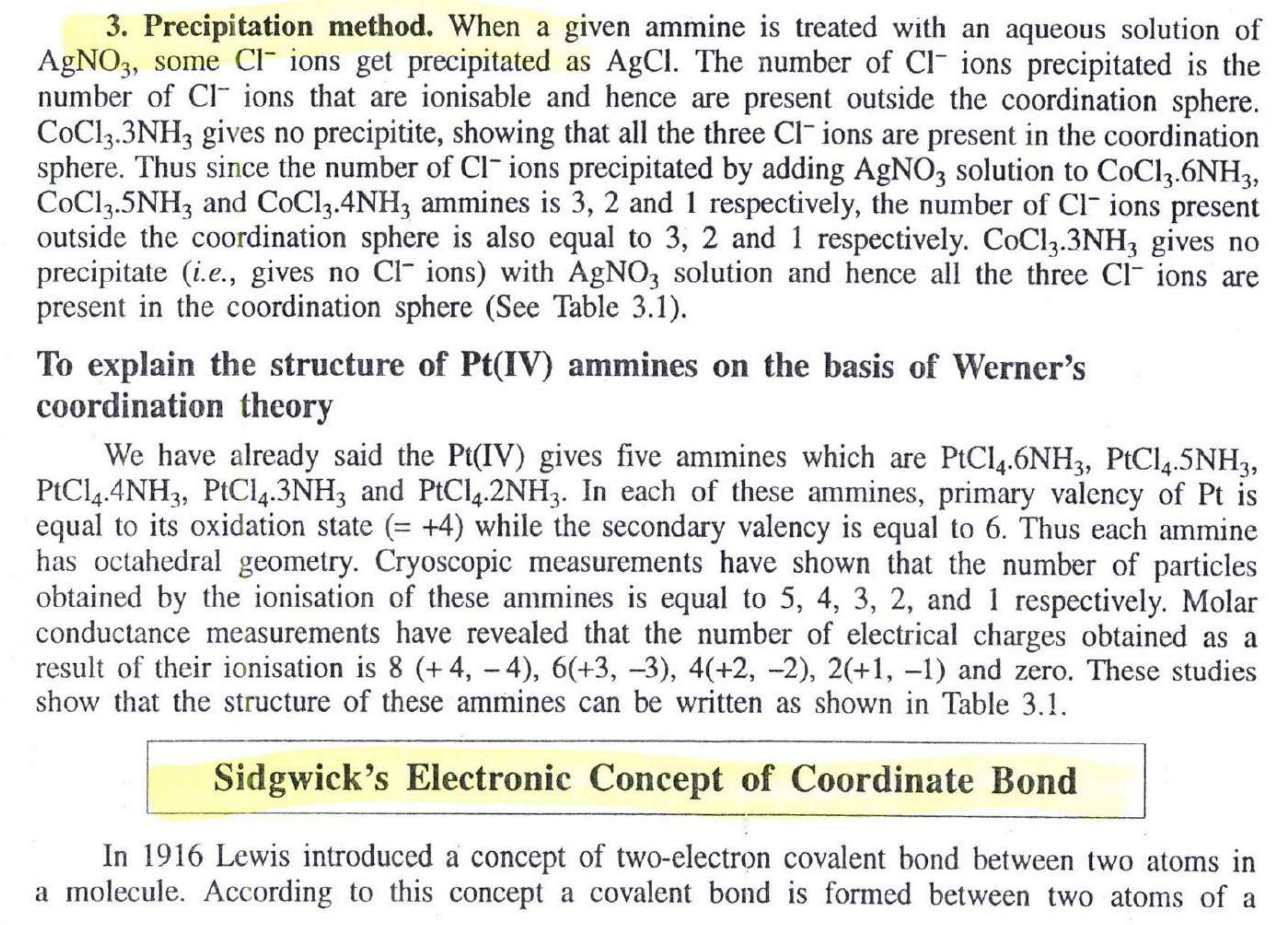


Table 3.1. *Structure of Co (III) and Pt (IV) Ammines.*

Molecular and structural formula of ammines	*Ionisation of ammine*	*Number of particles (ionic or molecular) as determined by cryoscopic measurements*	*Molar conductance, Λ_m (ohm^{-1} cm^2)*	*Number of electrical charges determined by Λ_m*
Co (III) ammines			Decreasing ↓	Decreasing ↓
$CoCl_3.6NH_3$ or $[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$	4	390	6(+3, −3)
$CoCl_3.5NH_3$ or $[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]Cl_2 \rightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$	3	262	4(+2, −2)
$CoCl_3.4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]Cl \rightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$	2	102	2 (+1, −1)
$CoCl_3.3NH_3$ or $[Co(NH_3)_3Cl_3]^0$ (Non-electrolyte)	$[Co(NH_3)_3Cl_3]^0 \rightarrow$ No ionisation	0	0	Nil
Pt (IV) ammines			Decreasing ↓	Decreasing ↓
$PtCl_4.6NH_3$ or $[Pt(NH_3)_6]Cl_4$	$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt_5(NH_3)_6]^{4+} + 4Cl^-$	5	524	8(+4, −4)
$PtCl_4.5NH_3$ or $[Pt(NH_3)_5Cl]Cl_3$	$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$	4	404	6(+3, −3)
$PtCl_4.4NH_3$ or $[Pt(NH_3)_4Cl_2]Cl_2$	$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$	3	230	4(+2, −2)
$PtCl_4.3NH_3$ or $[Pt(NH_3)_3Cl_3]Cl$	$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^+ + Cl^-$	2	97	2(+1, −1)
$PtCl_4.2NH_3$ or $[Pt(NH_3)_2Cl_4]^0$ (Non-electrolyte)	$[Pt(NH_3)Cl_4]^0 \rightarrow$ No ionisation	0	0	Nil



3. Precipitation method. When a given ammine is treated with an aqueous solution of $AgNO_3$, some Cl^- ions get precipitated as AgCl. The number of Cl^- ions precipitated is the number of Cl^- ions that are ionisable and hence are present outside the coordination sphere. $CoCl_3.3NH_3$ gives no precipitite, showing that all the three Cl^- ions are present in the coordination sphere. Thus since the number of Cl^- ions precipitated by adding $AgNO_3$ solution to $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$ ammines is 3, 2 and 1 respectively, the number of Cl^- ions present outside the coordination sphere is also equal to 3, 2 and 1 respectively. $CoCl_3.3NH_3$ gives no precipitate (*i.e.*, gives no Cl^- ions) with $AgNO_3$ solution and hence all the three Cl^- ions are present in the coordination sphere (See Table 3.1).

To explain the structure of Pt(IV) ammines on the basis of Werner's coordination theory

We have already said the Pt(IV) gives five ammines which are $PtCl_4.6NH_3$, $PtCl_4.5NH_3$, $PtCl_4.4NH_3$, $PtCl_4.3NH_3$ and $PtCl_4.2NH_3$. In each of these ammines, primary valency of Pt is equal to its oxidation state (= +4) while the secondary valency is equal to 6. Thus each ammine has octahedral geometry. Cryoscopic measurements have shown that the number of particles obtained by the ionisation of these ammines is equal to 5, 4, 3, 2, and 1 respectively. Molar conductance measurements have revealed that the number of electrical charges obtained as a result of their ionisation is 8 (+ 4, – 4), 6(+3, –3), 4(+2, –2), 2(+1, –1) and zero. These studies show that the structure of these ammines can be written as shown in Table 3.1.

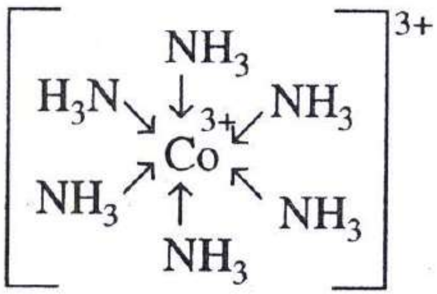
Sidgwick's Electronic Concept of Coordinate Bond

In 1916 Lewis introduced a concept of two-electron covalent bond between two atoms in a molecule. According to this concept a covalent bond is formed between two atoms of a molecule by the sharing of an electron pair. Sidgwick (1927) extended this Lewis concept of covalent bond and introduced a new concept of *coordinate bond* which is also some times called *polar* or *dative bond*. According to this Sidgwick's concept the *ligands donate the electron pair to the central metal ion and thus form a coordinate bond*, $M \leftarrow L$ which indicates that the ligand, L (*i.e.*, donor) has donated an electron pair to the metal ion, M (*i.e.*, accept). This concept is based on the fact that *all the ligands contain at least one lone pair of electrons*. Thus on the basis of Sidgwick's concept, the structure of the complex ion, $[Co(NH_3)_6]^{3+}$, can be shown as given in the margin. Evidently, in the formation of the bonds between the six ligands (which are NH_3 molecules) and the central metal Co^{3+} ion, the N-atom of each NH_3 molecule donates an electron pair to Co^{3+} ion. Thus in all twelve electrons (*i.e.*, six electron pairs) are donated by six NH_3 ligands to Co^{3+} ion. The donation of an electron pair by NH_3 molecule has been represented by an arrow. Coordinate bond formed is not very different from a covalent bond. The only difference lies in the mode of its formation.

Limitations of Sidgwick's concept of coordinate bond

The donation of one electron pair by each of the ligands to the central metal ion to form $L \rightarrow M$ coordinate bond in complexes accumulates negative charge on the central metal ion which is most unlikely. For example in $[Co^{3+}(NH_3)_6]^{3+}$, six NH_3 molecules donate half share of 12 electrons (*i.e.*, 6 electrons) to Co^{3+} ion and thus +3 charge on cobalt atom is reduced to –3 $(+3 - 6 = -3)$. Such an accumulation of negative charge on the central atom is unlikely.

Pauling suggested that the accumulation of undue negative charge on the central metal ion can be prevented, if it is assumed that *the metal–ligand bond has some ionic character (Electro-neutrality principle)* and in *addition to σ-bond, the central atom also forms a π-bond with the ligand (π-bonding in complexes).*



Formation of six $H_3N \rightarrow Co^{3+}$ bonds in $[Co(NH_3)_6]^{3+}$ ion.

Sidgwick's Effective Atomic Number (EAN) Rule

On the basis of his concept of coordinate bond, Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through L → M bonding, the total number of electrons on the central atom, including those gained from ligands in the bonding, is called the effective atomic number (EAN) of the cental metal ion and in many cases this total number of electrons (*i.e.*, EAN) surrounding the coordinated metal ion is equal to the atomic number of the inert gas which follows the central metal atom in the periodic table. This is called *Effective Atomic Number Rule or Noble Gas Rule*. When the EAN is 36 (Kr), 54 (Xe) or 86 (Rn), the rule is said to be followed.

To calculate EAN of the central metal atom in complex ions

EAN of the central metal atom/ion in a given complex ion is given by:

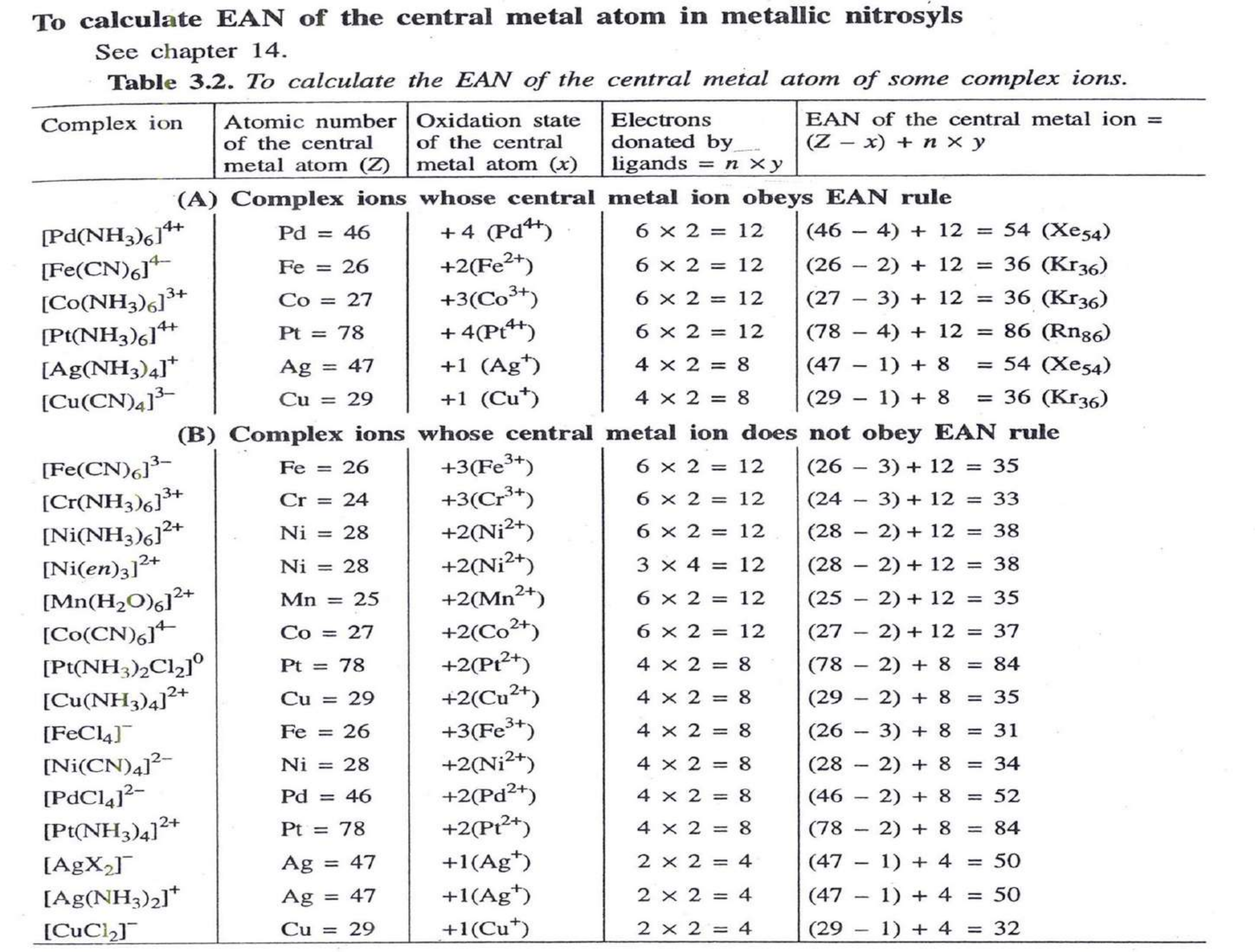
$$\text{EAN} = (Z - x) + n \times y$$

Here Z = atomic number of the central metal atom, x = oxidation state of the central metal ion, n = number of ligands and y = number of electrons donated by one ligand. With the help of this formula, EAN of the central metal atom or ion of some 2-, 4- and 6-coordinated complex ions has been calculated as shown in Table 3.2.

This table shows that many complex ions donot obey EAN rule, *i.e.*, in case of many complex ions, the EAN of the central metal is some units more or less than the atomic number of the next inert gas.

To calculate EAN of the central metal atom in carbonyls

See chapter 13.

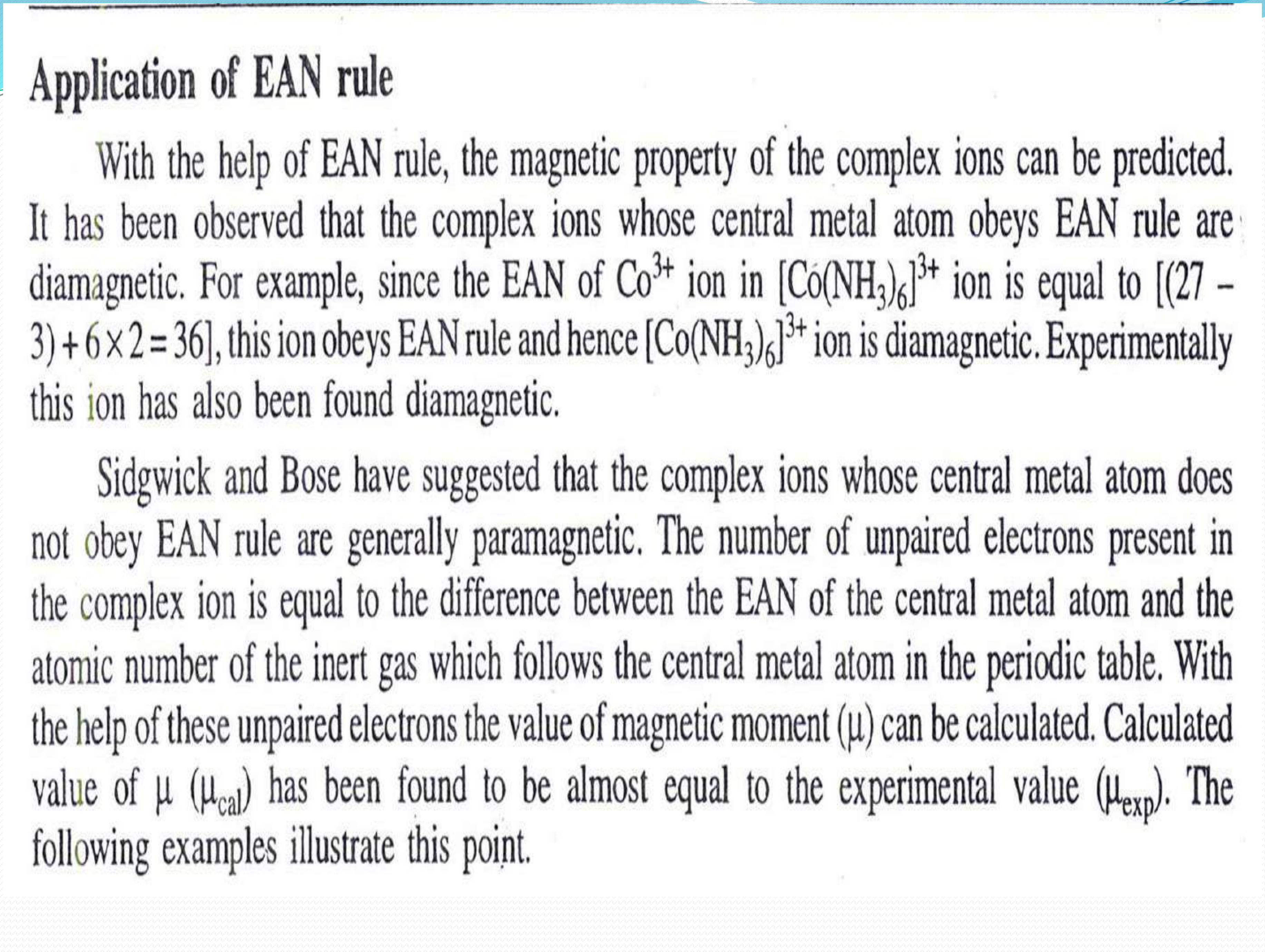


To calculate EAN of the central metal atom in metallic nitrosyls

See chapter 14.

Table 3.2. *To calculate the EAN of the central metal atom of some complex ions.*

Complex ion	Atomic number of the central metal atom (Z)	Oxidation state of the central metal atom (*x*)	Electrons donated by ligands = *n* × *y*	EAN of the central metal ion = (*Z* – *x*) + *n* × *y*
(A) Complex ions whose central metal ion obeys EAN rule				
$[Pd(NH_3)_6]^{4+}$	Pd = 46	+ 4 (Pd^{4+})	6 × 2 = 12	(46 – 4) + 12 = 54 (Xe_{54})
$[Fe(CN)_6]^{4-}$	Fe = 26	+2(Fe^{2+})	6 × 2 = 12	(26 – 2) + 12 = 36 (Kr_{36})
$[Co(NH_3)_6]^{3+}$	Co = 27	+3(Co^{3+})	6 × 2 = 12	(27 – 3) + 12 = 36 (Kr_{36})
$[Pt(NH_3)_6]^{4+}$	Pt = 78	+ 4(Pt^{4+})	6 × 2 = 12	(78 – 4) + 12 = 86 (Rn_{86})
$[Ag(NH_3)_4]^{+}$	Ag = 47	+1 (Ag^{+})	4 × 2 = 8	(47 – 1) + 8 = 54 (Xe_{54})
$[Cu(CN)_4]^{3-}$	Cu = 29	+1 (Cu^{+})	4 × 2 = 8	(29 – 1) + 8 = 36 (Kr_{36})
(B) Complex ions whose central metal ion does not obey EAN rule				
$[Fe(CN)_6]^{3-}$	Fe = 26	+3(Fe^{3+})	6 × 2 = 12	(26 – 3) + 12 = 35
$[Cr(NH_3)_6]^{3+}$	Cr = 24	+3(Cr^{3+})	6 × 2 = 12	(24 – 3) + 12 = 33
$[Ni(NH_3)_6]^{2+}$	Ni = 28	+2(Ni^{2+})	6 × 2 = 12	(28 – 2) + 12 = 38
$[Ni(en)_3]^{2+}$	Ni = 28	+2(Ni^{2+})	3 × 4 = 12	(28 – 2) + 12 = 38
$[Mn(H_2O)_6]^{2+}$	Mn = 25	+2(Mn^{2+})	6 × 2 = 12	(25 – 2) + 12 = 35
$[Co(CN)_6]^{4-}$	Co = 27	+2(Co^{2+})	6 × 2 = 12	(27 – 2) + 12 = 37
$[Pt(NH_3)_2Cl_2]^0$	Pt = 78	+2(Pt^{2+})	4 × 2 = 8	(78 – 2) + 8 = 84
$[Cu(NH_3)_4]^{2+}$	Cu = 29	+2(Cu^{2+})	4 × 2 = 8	(29 – 2) + 8 = 35
$[FeCl_4]^{-}$	Fe = 26	+3(Fe^{3+})	4 × 2 = 8	(26 – 3) + 8 = 31
$[Ni(CN)_4]^{2-}$	Ni = 28	+2(Ni^{2+})	4 × 2 = 8	(28 – 2) + 8 = 34
$[PdCl_4]^{2-}$	Pd = 46	+2(Pd^{2+})	4 × 2 = 8	(46 – 2) + 8 = 52
$[Pt(NH_3)_4]^{2+}$	Pt = 78	+2(Pt^{2+})	4 × 2 = 8	(78 – 2) + 8 = 84
$[AgX_2]^{-}$	Ag = 47	+1(Ag^{+})	2 × 2 = 4	(47 – 1) + 4 = 50
$[Ag(NH_3)_2]^{+}$	Ag = 47	+1(Ag^{+})	2 × 2 = 4	(47 – 1) + 4 = 50
$[CuCl_2]^{-}$	Cu = 29	+1(Cu^{+})	2 × 2 = 4	(29 – 1) + 4 = 32



Application of EAN rule

With the help of EAN rule, the magnetic property of the complex ions can be predicted. It has been observed that the complex ions whose central metal atom obeys EAN rule are diamagnetic. For example, since the EAN of Co^{3+} ion in $[Co(NH_3)_6]^{3+}$ ion is equal to $[(27 - 3) + 6 \times 2 = 36]$, this ion obeys EAN rule and hence $[Co(NH_3)_6]^{3+}$ ion is diamagnetic. Experimentally this ion has also been found diamagnetic.

Sidgwick and Bose have suggested that the complex ions whose central metal atom does not obey EAN rule are generally paramagnetic. The number of unpaired electrons present in the complex ion is equal to the difference between the EAN of the central metal atom and the atomic number of the inert gas which follows the central metal atom in the periodic table. With the help of these unpaired electrons the value of magnetic moment (μ) can be calculated. Calculated value of μ (μ_{cal}) has been found to be almost equal to the experimental value (μ_{exp}). The following examples illustrate this point.

1. $[Cu(NH_3)_4]^{2+}$ ion. EAN of $Cu^{2+} = (29 - 2) + 4 \times 2 = 35$

$\therefore$ No. of unpaired electrons = Atomic number of Kr − 35 = 36 − 35 = 1

$$\therefore \qquad \mu_{cal} = 1.73 \text{ B.M.}, \ \mu_{exp} = 1.82 \text{ B.M.}$$

2. **$[Cr(NH_3)_6]^{3+}$ ion.** EAN of $Cr^{3+} = (24 - 3) + 2 \times 6 = 21 + 12 = 33$

No. of unpaired electrons = Atomic number of Kr − 33 = 36 − 33 = 3

$$\therefore \qquad \mu_{cal} = 3.88 \text{ B.M.}, \ \mu_{exp} = 3.8 \text{ B.M.}$$

Although the central metal ion in $[Ni(dmg)_2]^{2+}$, $[Pt(NH_3)_2Cl_2]^0$, $[AuBr_4Cl]^-$ etc. does not obey EAN rule, these species are diamagnetic. Thus these complex ions donot obey the suggestion given by Sidgwick and Bose.

SOME TYPICAL PROBLEMS WITH SOLUTIONS

Problem 1. *The compound $CoCl_3.4NH_3$ contains only one Cl^- ion that is precipitated immediately on the addition of Ag^+ ions. Draw the structure of the compound on the basis of Werner's coordination theory.* (*Delhi1999*)

Solution. Since the C.N. of Co-atom is 6 and only one Cl^- ion is precipitated on the addition of Ag^+ ions, it contains only one Cl^- ion outside the coordination sphere and the structure of the given compound can be written as $[Co(NH_3)_4Cl_2]^+Cl^-$.

$$[Co(NH_3)_4Cl_2]^+Cl^- \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$$

$$Ag^+ + Cl^- \longrightarrow AgCl \text{ (ppt)}$$

On the basis of Werner's coordination theory the structure of $CoCl_3.4NH_3$ can be drawn as shown in Fig. 3.2

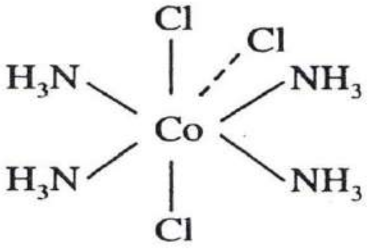


Fig. 3.2. Structure of $CoCl_3.4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$ on the basis of Werner's coordination theory.

Problem 2. *Molar conductance of the complex, M* $(NH_3)_5X_4$ *(X = monodentate ligand and M has C.N. = 6) is ~ 400* ohm^{-1}*. Write the structure of the complex.* *[Delhi 2000]*

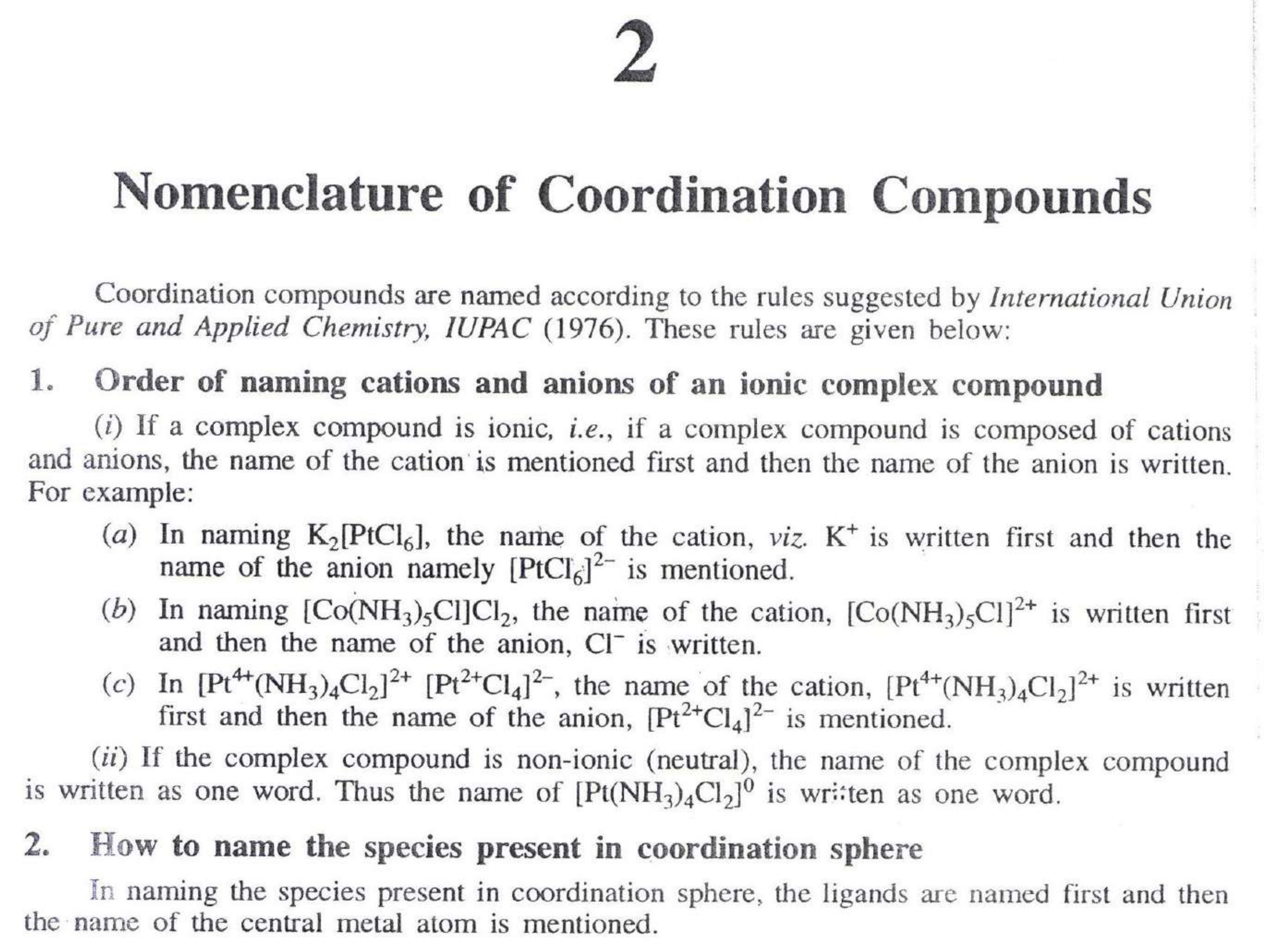
Solution. The given value of molar conductance indicates that the given complex, on ionisation in solution, gives four ions *viz* $[M(NH_3)_5X]^{3+}$ and $3X^-$.

$$M(NH_3)_5X_4 \longrightarrow \underbrace{[M(NH_3)_5X]^{3+} + 3X^-}_{\text{Four ions}}$$

Thus the structure of the complex can be written as $[M(NH_3)_5X]^{3+}X_3^-$.

Problem 3. *A coordination compound has the formula* $CoCl_3.4NH_3$*. It does not liberate* NH_3 *but precipitates* Cl^- *ions as AgCl. Give the IUPAC name of the compound and write its structural formula.*

Solution. Since the given compound does not give NH_3 but precipitates Cl^- ions as AgCl and the C.N. of Co-atom is 6, all the four NH_3 molecules and two Cl^- ions act as ligands and hence are present inside the coordination sphere. The remaining Cl^- ion is present outside the coordination sphere and is ionisable. Thus the structural formula of the compound is $[Co(NH_3)_4Cl_2]Cl$. Obviously, the IUPAC name of this compound is tetraminedichlorocobalt (III) chloride.



2

Nomenclature of Coordination Compounds

Coordination compounds are named according to the rules suggested by *International Union of Pure and Applied Chemistry, IUPAC* (1976). These rules are given below:

1. Order of naming cations and anions of an ionic complex compound

(*i*) If a complex compound is ionic, *i.e.*, if a complex compound is composed of cations and anions, the name of the cation is mentioned first and then the name of the anion is written. For example:

(*a*) In naming $K_2[PtCl_6]$, the name of the cation, *viz.* K^+ is written first and then the name of the anion namely $[PtCl_6]^{2-}$ is mentioned.

(*b*) In naming $[Co(NH_3)_5Cl]Cl_2$, the name of the cation, $[Co(NH_3)_5Cl]^{2+}$ is written first and then the name of the anion, Cl^- is written.

(*c*) In $[Pt^{4+}(NH_3)_4Cl_2]^{2+}$ $[Pt^{2+}Cl_4]^{2-}$, the name of the cation, $[Pt^{4+}(NH_3)_4Cl_2]^{2+}$ is written first and then the name of the anion, $[Pt^{2+}Cl_4]^{2-}$ is mentioned.

(*ii*) If the complex compound is non-ionic (neutral), the name of the complex compound is written as one word. Thus the name of $[Pt(NH_3)_4Cl_2]^0$ is written as one word.

2. How to name the species present in coordination sphere

In naming the species present in coordination sphere, the ligands are named first and then the name of the central metal atom is mentioned.

3. How to name the ligands?

(*i*) **How to name neutral ligands?** See Table 1.1, page 5 (chapter 1).

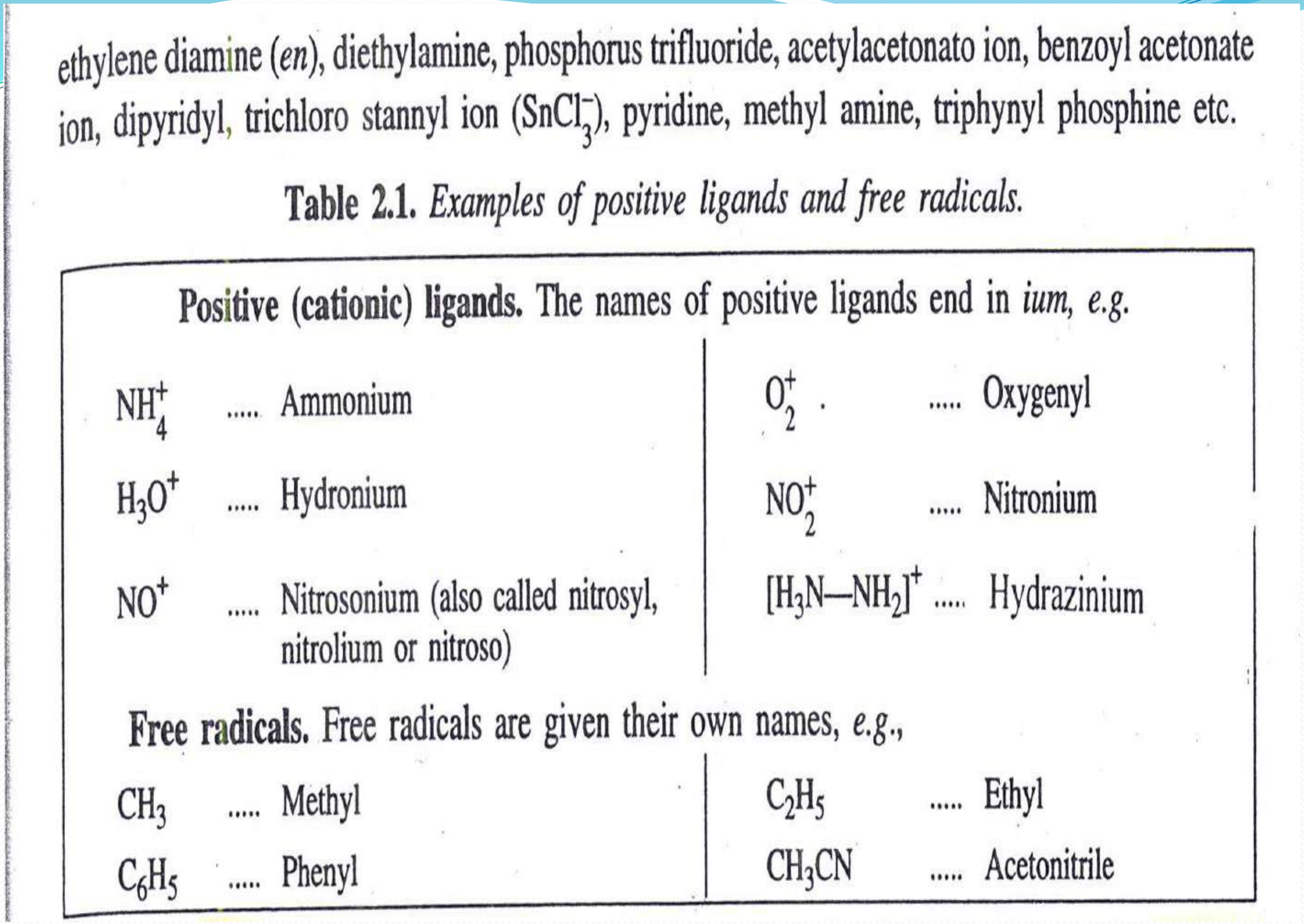
(*ii*) **How to name negative (anionic) ligands?** The names of negative ligands end in *o*. Examples of such ligands have already been given in Table 1.1. on page 5 (chapter 1).

(*iii*) **How to name positive ligands?** The names of positive ligands which are rare, end in *ium*. Examples of some positive ligands are given in Table 2.1.

(*iv*) **How to name free radicals?** Free radicals are given their own names. These are supposed to be neutral species, *i.e.*, they donot contain any charge on them. Examples of some free radicals are given in Table 2.1.

(*v*) **How to indicate the number of ligands.** (*a*) If a complex contains two or more simple ligands of the same type (*e.g.* Cl^-, Br^-, NO_2^-, $C_2O_4^{2-}$, NH_3, H_2O etc.), their number is indicated by putting prefixes *di* (for 2), *tri* (for 3), *tetra* (for 4), *penta* (for 5), *hexa* (for 6), *septa* (for 7), *octa* (for 8), *nona* (for 9), *deca* (for 10), *undeca* (for 11), *dodeca* (for 12) etc. before their names.

(*b*) If a complex contains two or more complex ligands or organic molecules which already have *di*, *tri* etc. in their names, their number is indicated by putting the prefixes *bis* (for 2), *tris* (for 3), *tetrakis* (for 4), *pentakis* (for 5), *hexakis* (for 6), *hepta* (for 7), *octa* (for 8), *nona* (for 9), *deca* (for 10), *undeca* (for 11), *dodeca* (for 12) etc. before their names. The name of the complex ligand or organic molecule is written in bracket. Examples of complex ligands are



ethylene diamine (*en*), diethylamine, phosphorus trifluoride, acetylacetonato ion, benzoyl acetonate ion, dipyridyl, trichloro stannyl ion ($SnCl_3^-$), pyridine, methyl amine, triphynyl phosphine etc.

Table 2.1. *Examples of positive ligands and free radicals.*

Positive (cationic) ligands. The names of positive ligands end in *ium*, *e.g.*

NH_4^+	Ammonium	O_2^+	Oxygenyl
H_3O^+	Hydronium	NO_2^+	Nitronium
NO^+	Nitrosonium (also called nitrosyl, nitrolium or nitroso)	$[H_3N—NH_2]^+$	Hydrazinium

Free radicals. Free radicals are given their own names, *e.g.*,

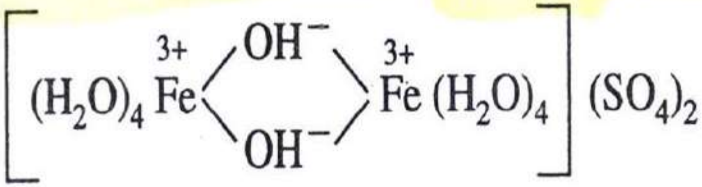
CH_3	Methyl	C_2H_5	Ethyl
C_6H_5	Phenyl	CH_3CN	Acetonitrile

(*vi*) **How to name bridging ligands.** (*a*) If a complex has bridging ligands, the prefix μ (mu) is used before the name of each of the ligands. For example

$$[(NH_3)_5Co—NH_2—Co(NH_3)_4(H_2O)]Cl_5$$

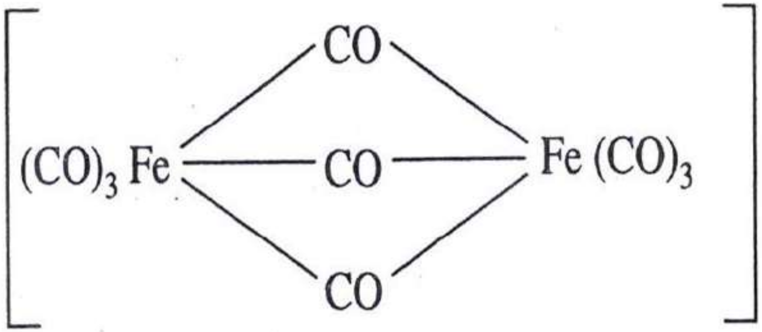
is called pentammine cobalt (III) μ-amido tetrammine aquo cobalt (III) chloride or nonammine aquo (μ-amido) dicobalt (III) chloride.

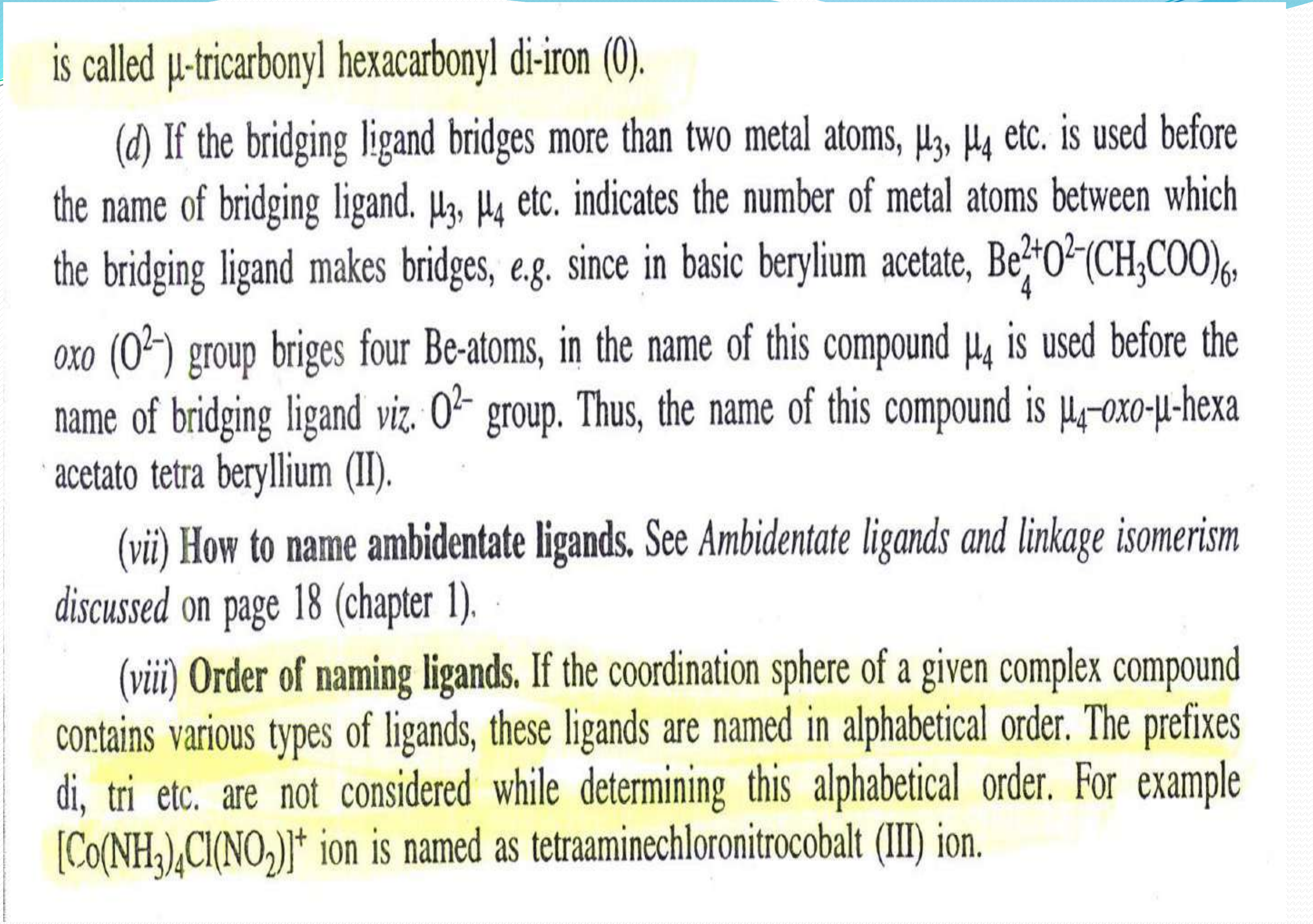
(*b*) If a complex has two similar bridging ligands, μ-*di* is used for its name. For example:



is called tetraquo iron (III) μ-dihydroxo tetraquo iron (III) sulphate *or* octaquo μ-di-hydroxo di-iron (III) sulphate.

(*c*) When the same ligand is present as a bridging ligand and as a non-bridging (terminal) ligand, the bridging ligand is named first. In case of the presence of three similar bridging ligands, μ-tri is used before their name. For example





is called μ-tricarbonyl hexacarbonyl di-iron (0).

(*d*) If the bridging ligand bridges more than two metal atoms, μ_3, μ_4 etc. is used before the name of bridging ligand. μ_3, μ_4 etc. indicates the number of metal atoms between which the bridging ligand makes bridges, *e.g.* since in basic berylium acetate, $Be_4^{2+}O^{2-}(CH_3COO)_6$, *oxo* ($O^{2-}$) group briges four Be-atoms, in the name of this compound μ_4 is used before the name of bridging ligand *viz.* O^{2-} group. Thus, the name of this compound is μ_4–*oxo*-μ-hexa acetato tetra beryllium (II).

(*vii*) **How to name ambidentate ligands.** See *Ambidentate ligands and linkage isomerism discussed* on page 18 (chapter 1).

(*viii*) **Order of naming ligands.** If the coordination sphere of a given complex compound contains various types of ligands, these ligands are named in alphabetical order. The prefixes di, tri etc. are not considered while determining this alphabetical order. For example $[Co(NH_3)_4Cl(NO_2)]^+$ ion is named as tetraaminechloronitrocobalt (III) ion.

6. How to name optical isomers

We know that *dextro* and *levo* forms are optically active isomers while *meso* form in optically inactive. Dextro form is represented by putting *d* or (+) before its name or formula. Similarly levo form is designated by putting *l* or (–) before its name or formula. Meso form is called *meso* isomer. Thus dextro potassium trioxalatoiridate (III) is formulated as *d* or (+) $K_3[Ir^{3+}(C_2O_4)_2]$.

7. How to name complex compounds containing optically active ligands

See "*Optical isomerism in octahedral complexes containing active ligands*" discussed in chapter 4.

Solved Examples

Example 1. *Write the names of the complex compounds/ions having the following formula*

(i) $[Fe(H_2O)_5(NO)]^{2+}$

(ii) $Na_2[Fe(CN)_5(NO)]$

(iii) $[Co(N_3)(NH_3)_5]SO_4$

(iv) $K_2[OsNCl_5]$

(v) $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$

(vi) $K[CrF_4O]$

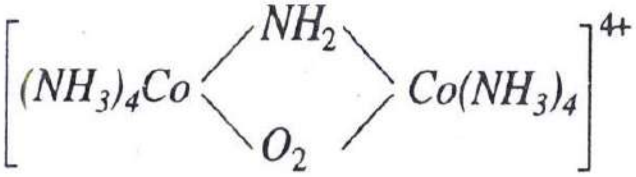
(vii) $Na[BH(OCH_3)_3]$

(viii) $[Pt(NH_3)_4Cl_2][PtCl_4]$

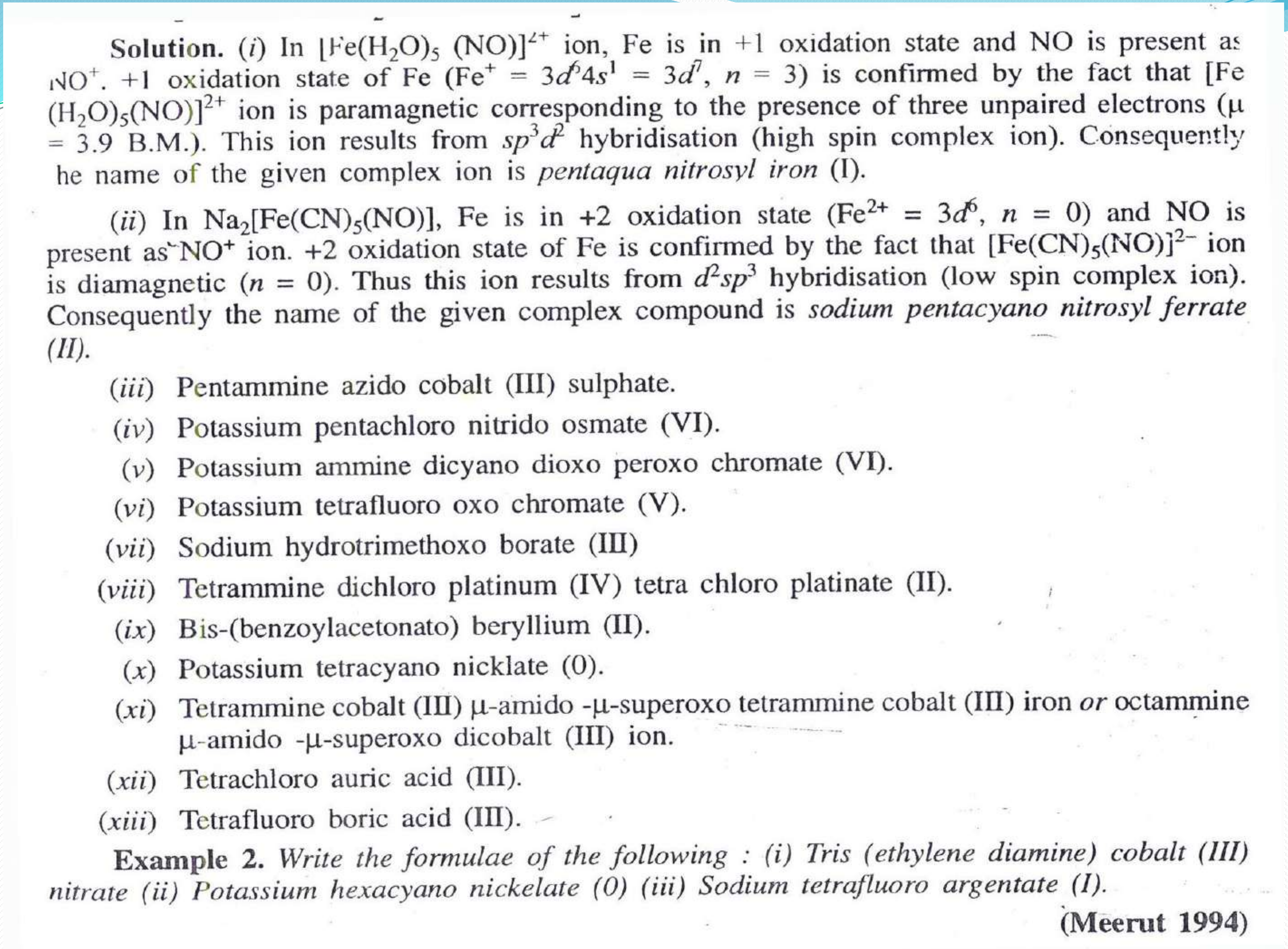
(ix) $[Be(CH_3-CO-CH-CO-C_6H_5)_2]^0$

(x) $K_4[Ni(CN)_4]$

(xi)



(xii) $H[AuCl_4]$ (xiii) $H[BF_4]$



Solution. (*i*) In $[Fe(H_2O)_5(NO)]^{2+}$ ion, Fe is in +1 oxidation state and NO is present as NO^+. +1 oxidation state of Fe ($Fe^+ = 3d^6 4s^1 = 3d^7$, $n = 3$) is confirmed by the fact that $[Fe(H_2O)_5(NO)]^{2+}$ ion is paramagnetic corresponding to the presence of three unpaired electrons ($\mu = 3.9$ B.M.). This ion results from sp^3d^2 hybridisation (high spin complex ion). Consequently he name of the given complex ion is *pentaqua nitrosyl iron* (I).

(*ii*) In $Na_2[Fe(CN)_5(NO)]$, Fe is in +2 oxidation state ($Fe^{2+} = 3d^6$, $n = 0$) and NO is present as NO^+ ion. +2 oxidation state of Fe is confirmed by the fact that $[Fe(CN)_5(NO)]^{2-}$ ion is diamagnetic ($n = 0$). Thus this ion results from d^2sp^3 hybridisation (low spin complex ion). Consequently the name of the given complex compound is *sodium pentacyano nitrosyl ferrate (II)*.

(*iii*) Pentammine azido cobalt (III) sulphate.

(*iv*) Potassium pentachloro nitrido osmate (VI).

(*v*) Potassium ammine dicyano dioxo peroxo chromate (VI).

(*vi*) Potassium tetrafluoro oxo chromate (V).

(*vii*) Sodium hydrotrimethoxo borate (III)

(*viii*) Tetrammine dichloro platinum (IV) tetra chloro platinate (II).

(*ix*) Bis-(benzoylacetonato) beryllium (II).

(*x*) Potassium tetracyano nicklate (0).

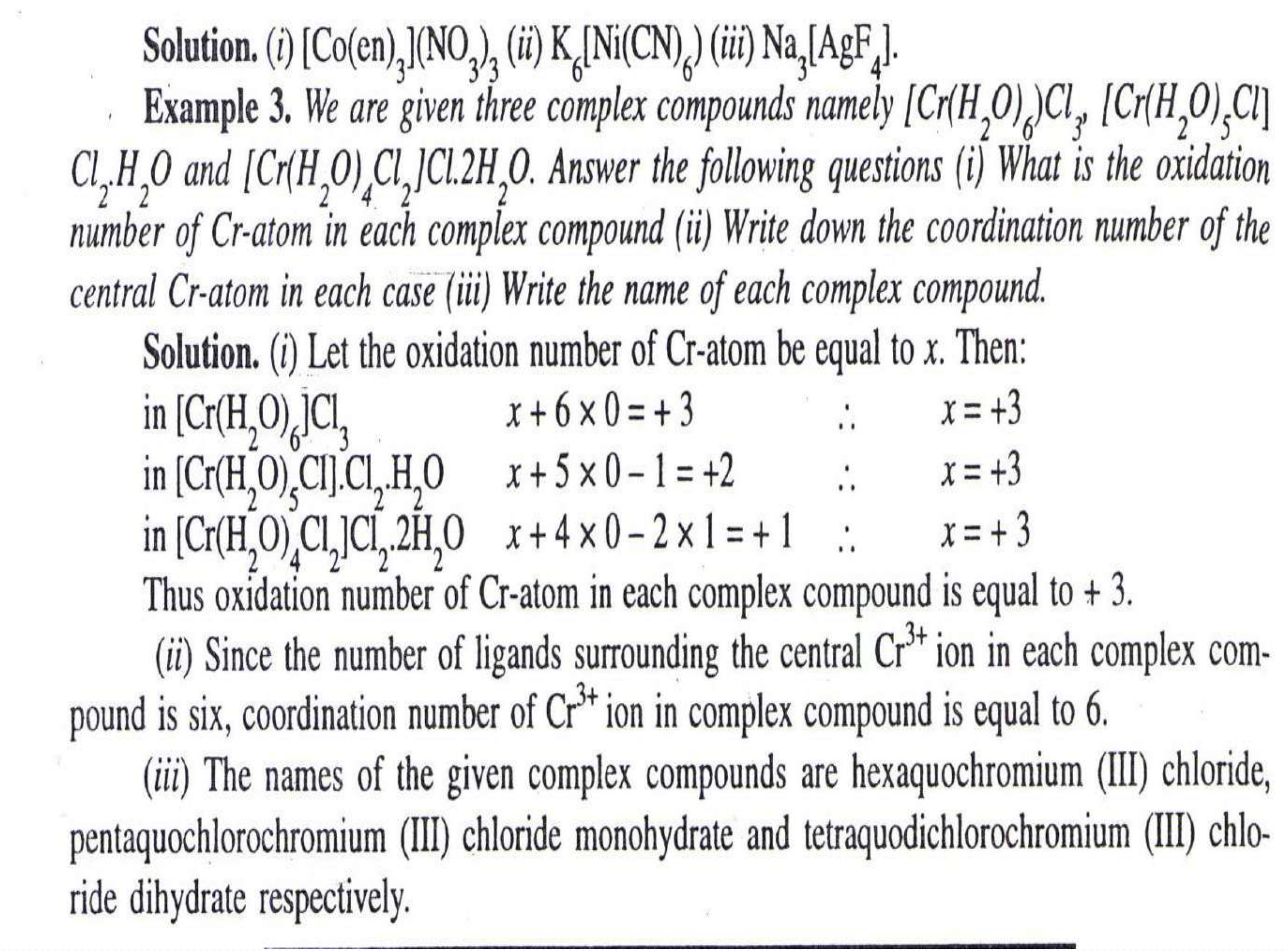
(*xi*) Tetrammine cobalt (III) μ-amido -μ-superoxo tetrammine cobalt (III) iron *or* octammine μ-amido -μ-superoxo dicobalt (III) ion.

(*xii*) Tetrachloro auric acid (III).

(*xiii*) Tetrafluoro boric acid (III).

Example 2. *Write the formulae of the following : (i) Tris (ethylene diamine) cobalt (III) nitrate (ii) Potassium hexacyano nickelate (0) (iii) Sodium tetrafluoro argentate (I).*

(Meerut 1994)



Solution. (*i*) $[Co(en)_3](NO_3)_3$ (*ii*) $K_6[Ni(CN)_6)$ (*iii*) $Na_3[AgF_4]$.

Example 3. *We are given three complex compounds namely* $[Cr(H_2O)_6)Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$ *and* $[Cr(H_2O)_4Cl_2]Cl.2H_2O$. *Answer the following questions (i) What is the oxidation number of Cr-atom in each complex compound (ii) Write down the coordination number of the central Cr-atom in each case (iii) Write the name of each complex compound.*

Solution. (*i*) Let the oxidation number of Cr-atom be equal to x. Then:

in $[Cr(H_2O)_6]Cl_3$ $\quad x + 6 \times 0 = +3 \quad \therefore \quad x = +3$

in $[Cr(H_2O)_5Cl].Cl_2.H_2O$ $\quad x + 5 \times 0 - 1 = +2 \quad \therefore \quad x = +3$

in $[Cr(H_2O)_4Cl_2]Cl_2.2H_2O$ $\quad x + 4 \times 0 - 2 \times 1 = +1 \quad \therefore \quad x = +3$

Thus oxidation number of Cr-atom in each complex compound is equal to + 3.

(*ii*) Since the number of ligands surrounding the central Cr^{3+} ion in each complex compound is six, coordination number of Cr^{3+} ion in complex compound is equal to 6.

(*iii*) The names of the given complex compounds are hexaquochromium (III) chloride, pentaquochlorochromium (III) chloride monohydrate and tetraquodichlorochromium (III) chloride dihydrate respectively.

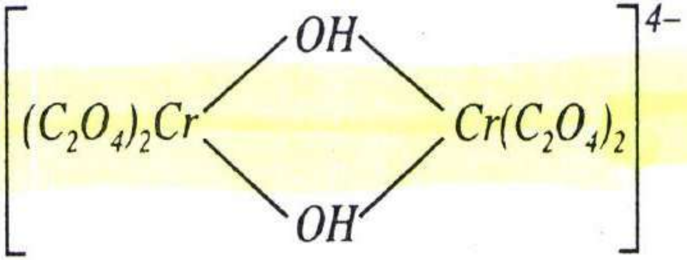
SOME TYPICAL PROBLEMS WITH SOLUTIONS

Problem 1. *Write the names of the following complex compoundis according to IUPAC system of nomenclature.*

(A) (i) $Ca[Fe(CN)_6]$ (ii) $[Fe(H_2O)_6]SO_4$ (iii) $[Co(NH_3)_5Cl]Cl_2$ (iv) $[PtCl_2(NH_3)_2]$

(Delhi 1996)

(B) (i)



(ii) $[Pt(py)_4)][PtCl_4]$ (iii) $[Ir(en)_2Cl_2]^+$

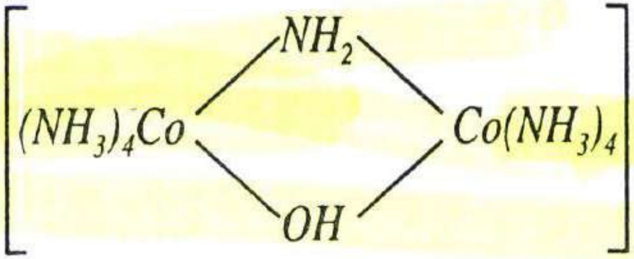
(iv) $[Ni(NH_3)_2(en)](CH_3COO)_2$. (Delhi 1997)

(C) (i) $[PdI_2(ONO)_2(H_2O)_2]^{2-}$ (ii) $[Co(en)_3]_2(SO_4)_3$ (iii) $(CH_3)_4N[Cr(SCN)_4(NO)_2]$

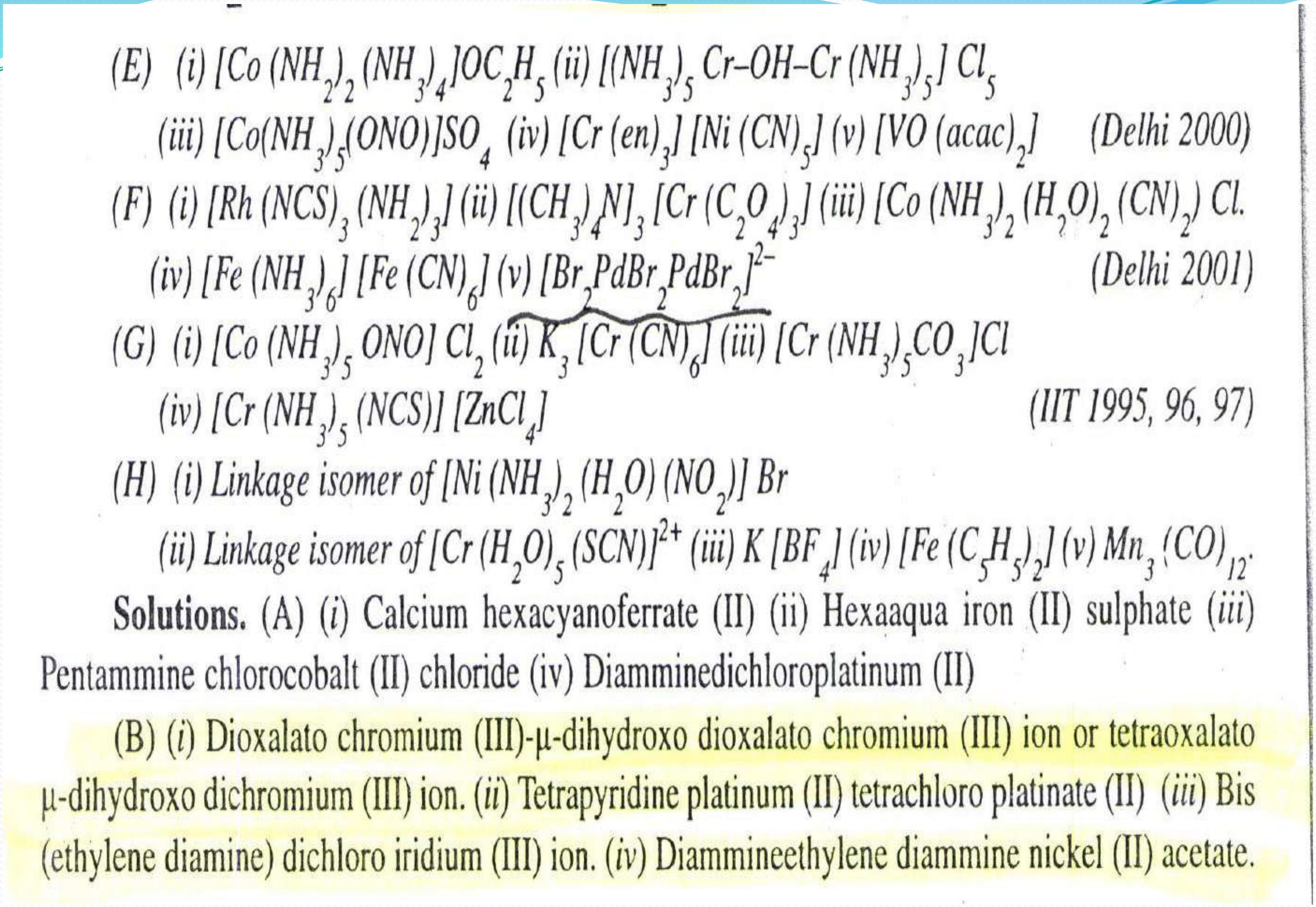
(iv) $Na[Au(CN)_2)$ (Delhi 1998)

(D) (i) $(CH_3)_4N[Cr(NH_3)_2(NCS)_4]$ (ii) $[Co(en)_2(ONO]Cl]Cl$

(iii)



$(NO_3)_4$ (iv) $[Cr(NH_3)_6][CoF_6]$ (Delhi 1999)



(E) (i) $[Co(NH_2)_2(NH_3)_4]OC_2H_5$ (ii) $[(NH_3)_5Cr–OH–Cr(NH_3)_5]Cl_5$

(iii) $[Co(NH_3)_5(ONO)]SO_4$ (iv) $[Cr(en)_3][Ni(CN)_5]$ (v) $[VO(acac)_2]$ *(Delhi 2000)*

(F) (i) $[Rh(NCS)_3(NH_2)_3]$ (ii) $[(CH_3)_4N]_3[Cr(C_2O_4)_3]$ (iii) $[Co(NH_3)_2(H_2O)_2(CN)_2)Cl$.

(iv) $[Fe(NH_3)_6][Fe(CN)_6]$ (v) $[Br_2PdBr_2PdBr_2]^{2-}$ *(Delhi 2001)*

(G) (i) $[Co(NH_3)_5ONO]Cl_2$ (ii) $K_3[Cr(CN)_6]$ (iii) $[Cr(NH_3)_5CO_3]Cl$

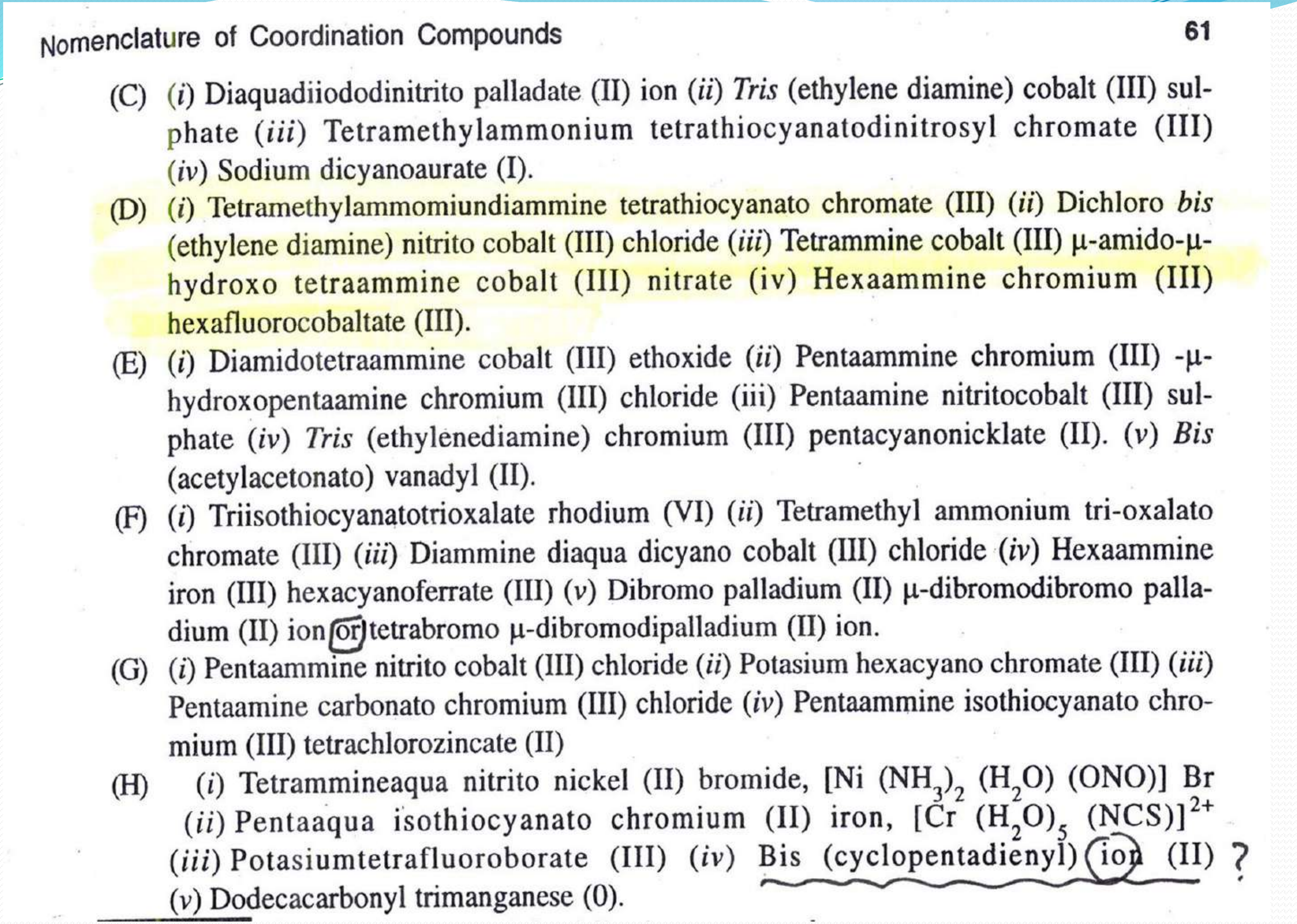
(iv) $[Cr(NH_3)_5(NCS)][ZnCl_4]$ *(IIT 1995, 96, 97)*

(H) (i) *Linkage isomer of* $[Ni(NH_3)_2(H_2O)(NO_2)]Br$

(ii) *Linkage isomer of* $[Cr(H_2O)_5(SCN)]^{2+}$ (iii) $K[BF_4]$ (iv) $[Fe(C_5H_5)_2]$ (v) $Mn_3(CO)_{12}$.

Solutions. (A) (*i*) Calcium hexacyanoferrate (II) (ii) Hexaaqua iron (II) sulphate (*iii*) Pentammine chlorocobalt (II) chloride (iv) Diamminedichloroplatinum (II)

(B) (*i*) Dioxalato chromium (III)-μ-dihydroxo dioxalato chromium (III) ion or tetraoxalato μ-dihydroxo dichromium (III) ion. (*ii*) Tetrapyridine platinum (II) tetrachloro platinate (II) (*iii*) Bis (ethylene diamine) dichloro iridium (III) ion. (*iv*) Diammineethylene diammine nickel (II) acetate.



(C) (*i*) Diaquadiiododinitrito palladate (II) ion (*ii*) *Tris* (ethylene diamine) cobalt (III) sulphate (*iii*) Tetramethylammonium tetrathiocyanatodinitrosyl chromate (III) (*iv*) Sodium dicyanoaurate (I).

(D) (*i*) Tetramethylammomiundiammine tetrathiocyanato chromate (III) (*ii*) Dichloro *bis* (ethylene diamine) nitrito cobalt (III) chloride (*iii*) Tetrammine cobalt (III) μ-amido-μ-hydroxo tetraammine cobalt (III) nitrate (iv) Hexaammine chromium (III) hexafluorocobaltate (III).

(E) (*i*) Diamidotetraammine cobalt (III) ethoxide (*ii*) Pentaammine chromium (III) -μ-hydroxopentaamine chromium (III) chloride (iii) Pentaamine nitritocobalt (III) sulphate (*iv*) *Tris* (ethylenediamine) chromium (III) pentacyanonicklate (II). (*v*) *Bis* (acetylacetonato) vanadyl (II).

(F) (*i*) Triisothiocyanatotrioxalate rhodium (VI) (*ii*) Tetramethyl ammonium tri-oxalato chromate (III) (*iii*) Diammine diaqua dicyano cobalt (III) chloride (*iv*) Hexaammine iron (III) hexacyanoferrate (III) (*v*) Dibromo palladium (II) μ-dibromodibromo palladium (II) ion or tetrabromo μ-dibromodipalladium (II) ion.

(G) (*i*) Pentaammine nitrito cobalt (III) chloride (*ii*) Potasium hexacyano chromate (III) (*iii*) Pentaamine carbonato chromium (III) chloride (*iv*) Pentaammine isothiocyanato chromium (III) tetrachlorozincate (II)

(H) (*i*) Tetrammineaqua nitrito nickel (II) bromide, $[Ni\ (NH_3)_2\ (H_2O)\ (ONO)]\ Br$ (*ii*) Pentaaqua isothiocyanato chromium (II) iron, $[Cr\ (H_2O)_5\ (NCS)]^{2+}$ (*iii*) Potasiumtetrafluoroborate (III) (*iv*) Bis (cyclopentadienyl) ion (II) ? (*v*) Dodecacarbonyl trimanganese (0).

Problem 2. *Write the formula of the following compounds.*

(A) *(i) Dichlorotetraaquachromium (III) nitrate (ii) Potassium tetracyanonickelate (II) (iii) Hexaamine cobalt (III) hexacyanochromate (III) (iv) Tetrachloro mono(ethylenediamine) platinum (IV).* *(Delhi 1996)*

(B) *(i) Octacarbonyl-μ-dicarbonyl diiron (0) (ii) Ammonium pentafluoroaquanickelate (IV) (iii) Tetrammineaqua bromo cobalt (III) chloride (iv) Sodium dithiosulphatoagentate (I) (v) Bromodichloro iodopalladate (III) ion.* *(Delhi 1997)*

(C) *(i) Tetraammine carbonato cobalt (III) chloride (ii) Calciumhexacyanoferrate (II) (iii) Potassium trioxalatoaluminate (III) (iv) Sodium oxotetrafluorochromate (IV).* *(Delhi 1998)*

(D) *(i) Potassium tetrafluoroargentate (I) (ii) Dichloro bis (ethylenediamine) cobalt (II) (iii) Trans-chloronitrodiammine cobalt (II) (iv) Octacarbonyl-μ-dicarbonyl diiron (0)* *(Delhi 1999)*

(E) *(i) Cis-dichloro tetraammine cobalt (III) chloride (ii) Diammine silver (I) tetracyanoferrate (III) (iii) Potassium tetraazidocobaltate (III)* *(Delhi 2000)*

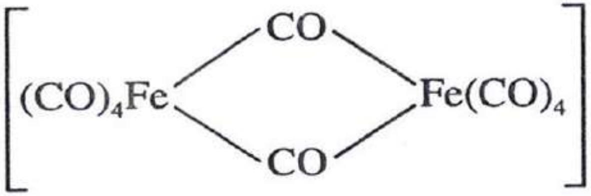
(F) *(i) Octacarbonyl-μ-dicarbonyl diiron (0) (ii) Sodium dithiosulphatoargentate (I) (iii) Diammine silver (II) tetra chloroplatinate (II).* *(Delhi 2001)*

(G) *(i) Pentaammine chlorocobalt (III) ion (ii) Lithiumtetrahydroaluminate (III)* *(IIT 1997)*

(H) *(i) Bis(acetylacetonato) oxovanadium (IV) (ii) Dichloroplatinum (IV) tetrachloroplatinate (II)*

Solution.

(A) (*i*) $[Cr(H_2O)_4Cl_2]NO_3$ (*ii*) $K_2[Ni(CN)_4]$ (*iii*) $[Co(NH_3)_6][Cr(CN)_6]$ (*iv*) $[Pt(en)Cl_4]$

(B) (*i*) 

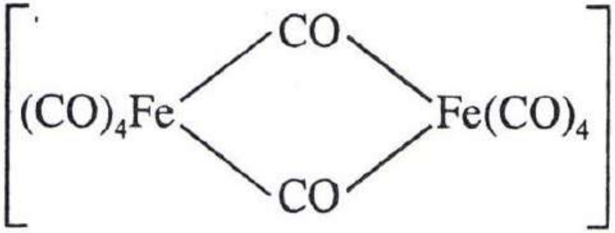
(*ii*) $NH_4[NiF_5(H_2O)]$ (*iii*) $[Co(NH_3)_4Br(H_2O)]Cl_2$

(*iv*) $Na_3 [Ag (S_2O_3)_2]$ (*v*) $[Pd BrCl_2I]^-$

(C) (*i*) $[Co (NH_3)_4 CO_3] Cl$ (*ii*) $Ca_2 [Fe (CN)_6]$ (*iii*) $K_3[Al (C_2O_4)_3]$ (*iv*) $Na_2 [Cr OF_4]$

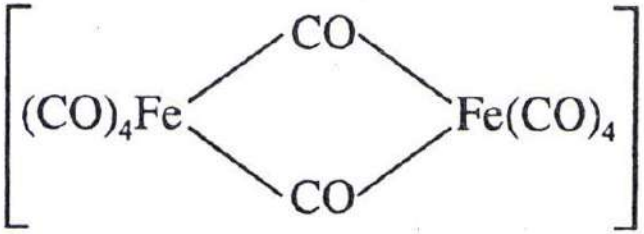
(D) (*i*) $K_3 [Ag F_4]$ (*ii*) $[Co (en)_2 Cl_2]$ (*iii*) *Trans*-$[Pt (NH_3)_2Cl (NO_2)]$

(*iv*)



(E) (*i*) *Cis* $[Co (NH_3)_4 Cl_2)]Cl$ (*ii*) $[Ag (NH_3)_2] [Fe (CN)_4]$ (*iii*) $K [Co (N_3)_4]$

(F) (*i*)



(*ii*) $Na_3 [Ag (S_2O_3)_2]$ (*iii*) $[Ag (NH_3)_2] [Pt Cl_4)$

(G) (*i*) $[Co (NH_3)_5 Cl]^{2+}$ (ii) $Li [AlH_4]$

(H) (*i*) $[V (acac)_2O]$ (*ii*) $[PtCl_2] [PtCl_4]$

Problem 3. *The valency of Cr in* $[Cr(H_2O)_4Cl_2]^+$ *ion is:*

(*a*) 3 (*b*) 1 (*c*) 6 (*d*) 5 (*MLNR 1993*)

Solution and explanation. Answer is (*a*)

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

$$\therefore \quad x = +3$$

Problem 4. *The oxidation number of Pt in* $[Pt(C_2H_4)Cl_3]^-$ *ion is:*

(a) + 1 (b) + 2 (c) + 3 (d) + 4

Solution and explanation. Answer is (*b*)

$$x + 4 \times 0 + 3 \times (-1) = -1$$

$$\therefore \quad x = -1 + 3 = +2$$

Problems 5. *The formula of dichlorobis(urea) copper (II) is:*

(a) $[Cu\{O = C(NH_2)\}_2]Cl_2$ (b) $[CuCl_2\{O = C(NH_2)_2\}]$

(c) $[Cu\{O = C(NH_2)_2\}Cl]Cl$ (d) $[CuCl_2\{O = C(NH_2)_2\}_2]$

Solution. Answer is (*d*)

Problem 6. *The IUPAC name of* $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ *is:*

(a) Triammine chloro bromonitro platinum (IV) chloride

(b) Triammine chlorobromonitro chloro platinum (IV) chloride

(c) Triammine bromochloronitroplatinum (IV) chloride

(d) Triammine nitro chlorobromoplatinum (IV) chloride

Solution and explanation Answer is (*c*). The names of ligands are written in the alphabetical order.

University Questions

1. Write the IUPAC name of the following compounds/ions.

(A) (*i*) $[Cr(NH_3)_5CO_3]Cl$ (*IIT 96*)

(*ii*) $[Cu(NH_3)_4]SO_4$ (*Meerut 95*)

(*iii*) $[Cr(H_2O)_5Cl]Cl_2$ (*Meerut 95*)

2. Write the formula of the following compounds :

(*a*) Octa aquo m-dihydroxo *di* iron (III) ion.

(*b*) Ammonium hexaisothiocyanato chromate (III).

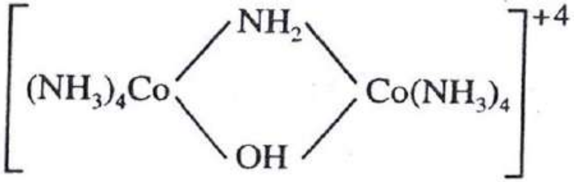
(c) Ammonium hexathio-cyanato platinate (IV) (*Meerut 97*)

3. Write IUPAC names of the following coordination compounds :

(*i*) $NH_4\left[Cr(NCS)_4(NH_3)_2\right]$ (*ii*) $\left[Co(en)_2(ONO)Cl\right]Cl$

(*iii*) $\left[Cr(H_2O)_5Cl\right]Cl_2$

(*iv*)



4. Write IUPAC name of $\left[Cr(H_2O)_4Cl_2\right]NO_3$ (Nagpur 2002)

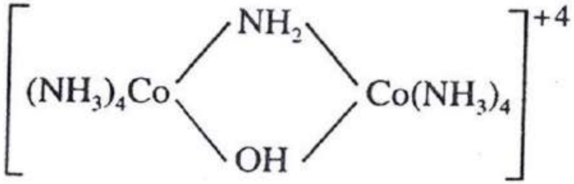
5. (*a*) Write the names of the following complexes as per the IUPAC system :

(*i*) $\left[CoCl(NO_2)(NH_3)_4\right]Cl$

(*ii*) $\left[CuCl_2\{O=C(NH_2)_2\}\right]$

(*iii*) $Na\left[PtBrCl(NO_2)(NH_3)\right]$

(*iv*)



(*b*) Write the formula of the following compounds :

(*i*) Pentaaquonitrosyl iron (I)

(*ii*) Sodium pentacyanonitrosyl ferrate (II)

(*iii*) Tetraammine dichloroplatinum (IV) tetrachloroplatinate (II)

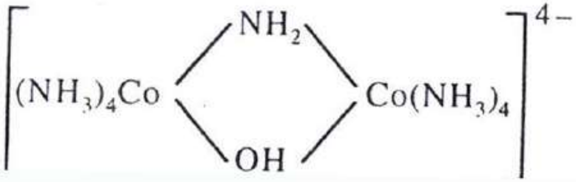
(*iv*) Potassium hexacyanoferrate (II) (*Delhi 2002*)

6. Write down the IUPAC names of the following :

(*i*) $\left[Co(NH_3)_3NO_2Cl\,CN\right]$

(*ii*) $\left[Cr(NH_3)_6\right]\left[Co(CN)_6\right]$

(*iii*)



(*Rohilkhand 2003*)

5. (*a*) Write IUPAC names of the following complexes :

(*i*) $Na[Au(CN)_4]$ (*ii*) $[Pt(en)_2(SCN)_2(NO_3)_2]$

(*iii*) $(NH_4)_3[Co(NO_2)_2(C_2O_4)_2]$ (*iv*) $[Cr(H_2O)_4ONOCl]Cl_2$

(*v*) $K_4[Zn(OH)_2(NCS)_4]$

(*b*) Write the formulae of the following :

(*i*) Aquopentammine cobalt (III) nitrate

(*ii*) Tetrammine platinum (II) tetrachloro platinate (II)

(*iii*) Potassium hexanitro cobaltate (III)

(*iv*) Chloroslulfato diammine platinum (I) bromide. *(Delhi 2003).*

7. Write the IUPAC name of the following complex compounds :–

(*i*) $[Co^{III}(NH_3)_4Cl_2]Cl$ (*ii*) $K_2[Pt^{IV}Cl_6]$. *(Nagpur 2003).*

8. Write down the IUPAC name of the following complexes :

(*i*) $[Pt(py)_4][PtCl_4]$ (*ii*) $K_4[Ni(CN)_4]$ *(Bhopal 2004)*

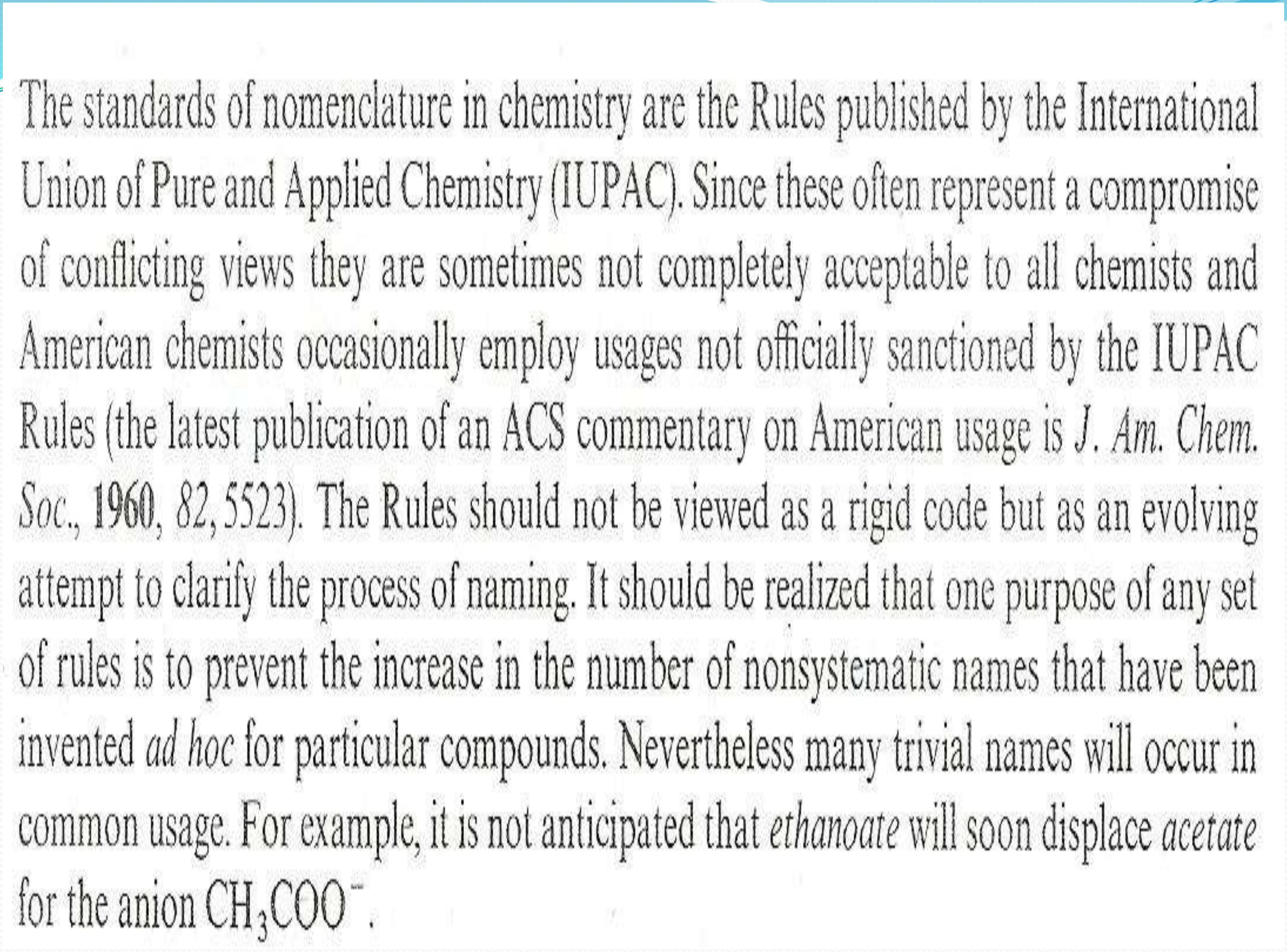
9. (*a*) Write the IUPAC names of the following :

(*i*) $Fe[Fe(CN)_6]$ (*ii*) $K_3[Al(C_2O_4)_3]$ (*iii*) $[Co(en)_3]Cl_3$

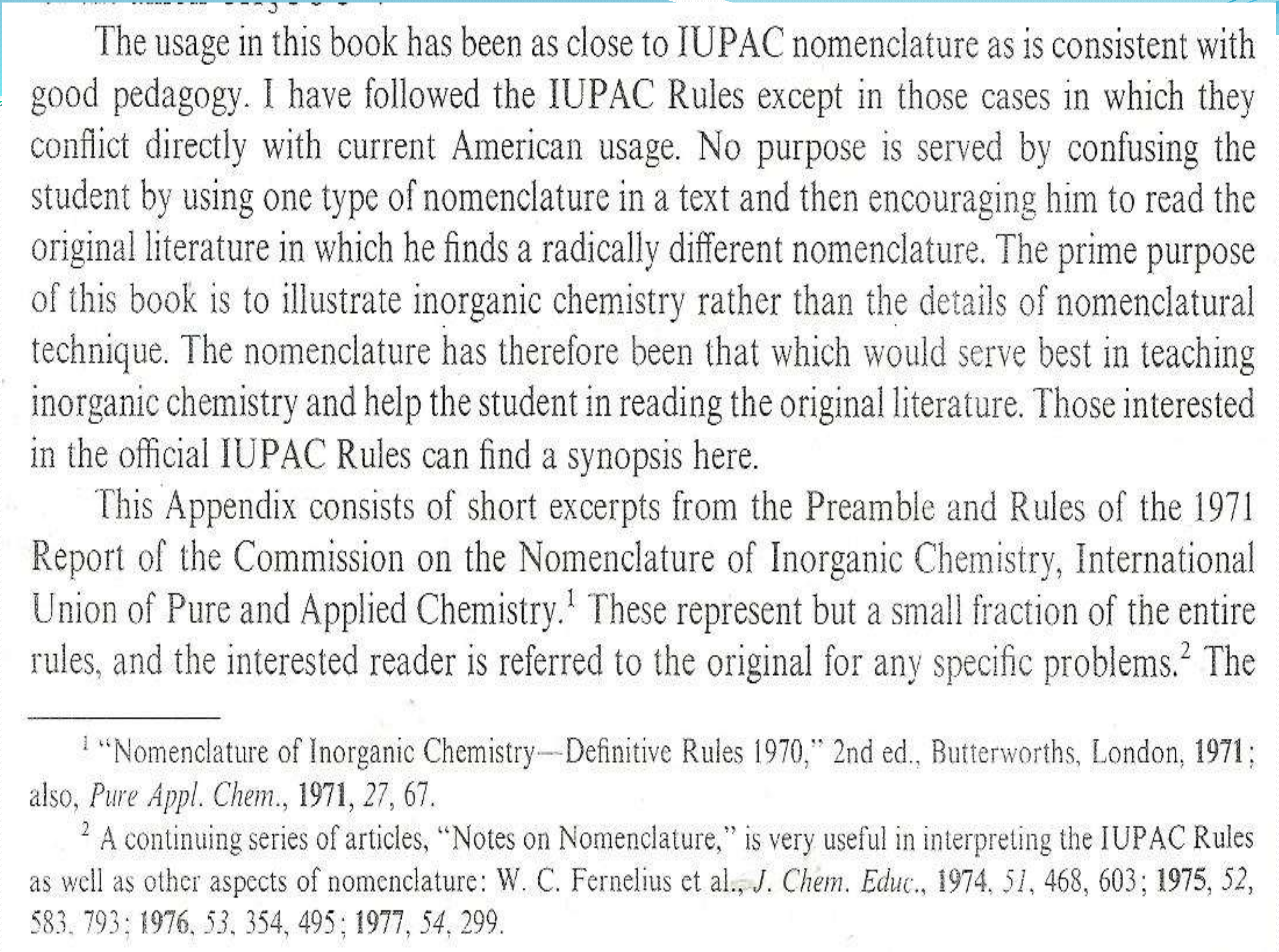
(*b*) Give IUPAC name of $[PtCl_2(C_2H_4)(NH_3)]$. *(GND Amritsar, 2004)*

J

The rules of inorganic nomenclature



The standards of nomenclature in chemistry are the Rules published by the International Union of Pure and Applied Chemistry (IUPAC). Since these often represent a compromise of conflicting views they are sometimes not completely acceptable to all chemists and American chemists occasionally employ usages not officially sanctioned by the IUPAC Rules (the latest publication of an ACS commentary on American usage is *J. Am. Chem. Soc.*, **1960**, *82*, 5523). The Rules should not be viewed as a rigid code but as an evolving attempt to clarify the process of naming. It should be realized that one purpose of any set of rules is to prevent the increase in the number of nonsystematic names that have been invented *ad hoc* for particular compounds. Nevertheless many trivial names will occur in common usage. For example, it is not anticipated that *ethanoate* will soon displace *acetate* for the anion CH_3COO^-.



The usage in this book has been as close to IUPAC nomenclature as is consistent with good pedagogy. I have followed the IUPAC Rules except in those cases in which they conflict directly with current American usage. No purpose is served by confusing the student by using one type of nomenclature in a text and then encouraging him to read the original literature in which he finds a radically different nomenclature. The prime purpose of this book is to illustrate inorganic chemistry rather than the details of nomenclatural technique. The nomenclature has therefore been that which would serve best in teaching inorganic chemistry and help the student in reading the original literature. Those interested in the official IUPAC Rules can find a synopsis here.

This Appendix consists of short excerpts from the Preamble and Rules of the 1971 Report of the Commission on the Nomenclature of Inorganic Chemistry, International Union of Pure and Applied Chemistry.[1] These represent but a small fraction of the entire rules, and the interested reader is referred to the original for any specific problems.[2] The

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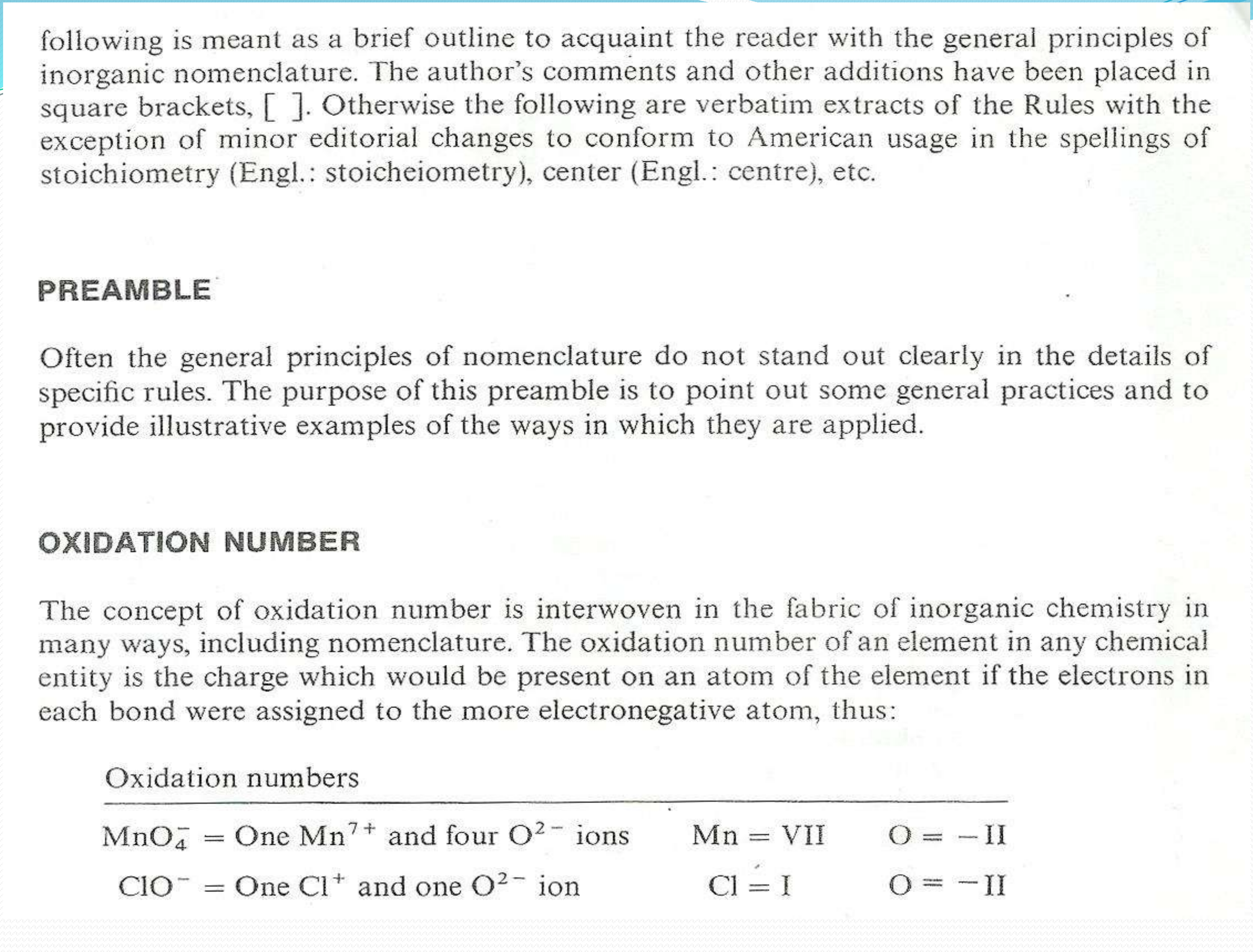
[1] "Nomenclature of Inorganic Chemistry—Definitive Rules 1970," 2nd ed., Butterworths, London, **1971**; also, *Pure Appl. Chem.*, **1971**, *27*, 67.

[2] A continuing series of articles, "Notes on Nomenclature," is very useful in interpreting the IUPAC Rules as well as other aspects of nomenclature: W. C. Fernelius et al., *J. Chem. Educ.*, **1974**, *51*, 468, 603; **1975**, *52*, 583, 793; **1976**, *53*, 354, 495; **1977**, *54*, 299.



following is meant as a brief outline to acquaint the reader with the general principles of inorganic nomenclature. The author's comments and other additions have been placed in square brackets, [ ]. Otherwise the following are verbatim extracts of the Rules with the exception of minor editorial changes to conform to American usage in the spellings of stoichiometry (Engl.: stoicheiometry), center (Engl.: centre), etc.

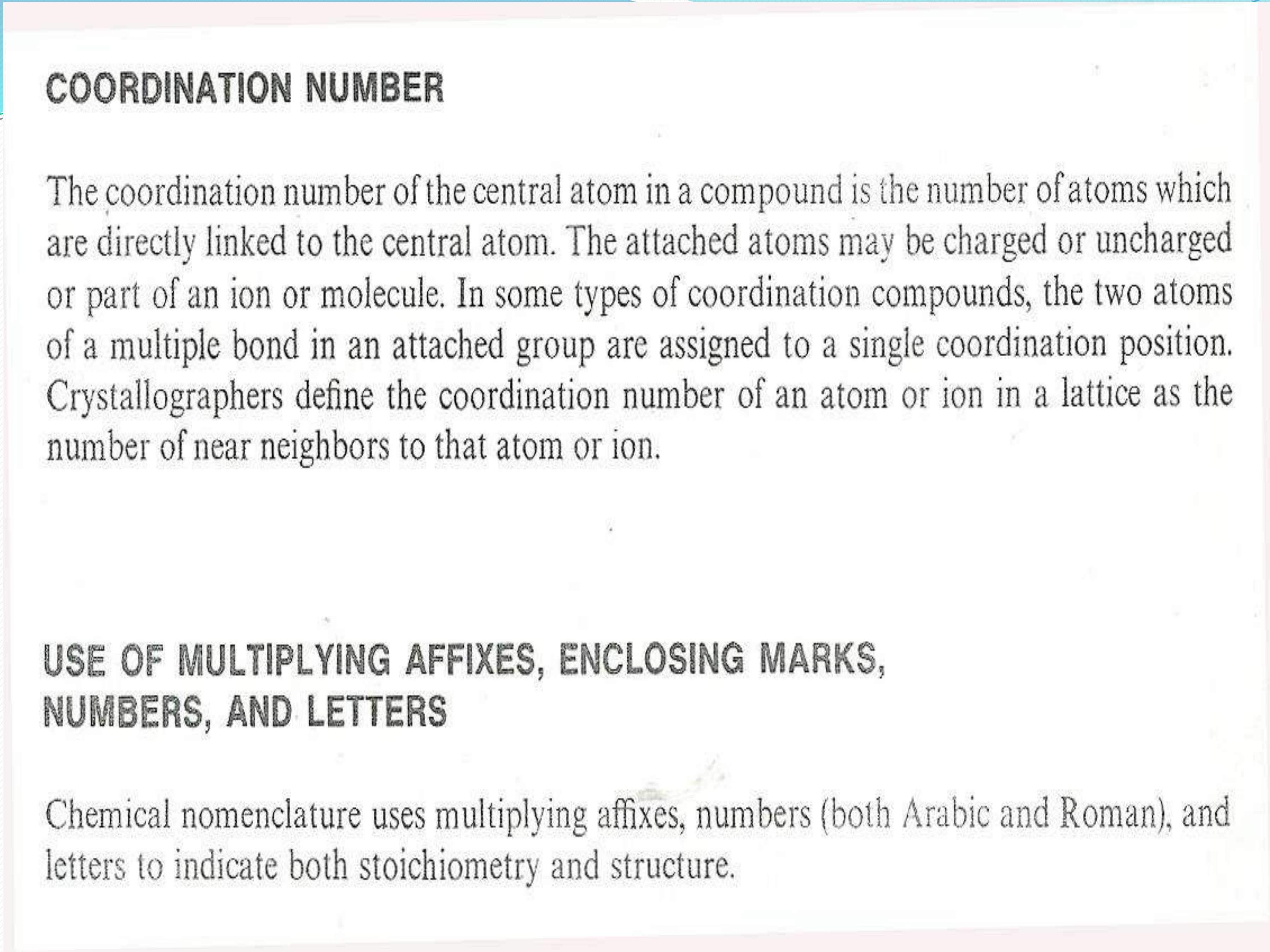
PREAMBLE

Often the general principles of nomenclature do not stand out clearly in the details of specific rules. The purpose of this preamble is to point out some general practices and to provide illustrative examples of the ways in which they are applied.

OXIDATION NUMBER

The concept of oxidation number is interwoven in the fabric of inorganic chemistry in many ways, including nomenclature. The oxidation number of an element in any chemical entity is the charge which would be present on an atom of the element if the electrons in each bond were assigned to the more electronegative atom, thus:

Oxidation numbers		
MnO_4^- = One Mn^{7+} and four O^{2-} ions	Mn = VII	O = −II
ClO^- = One Cl^+ and one O^{2-} ion	Cl = I	O = −II

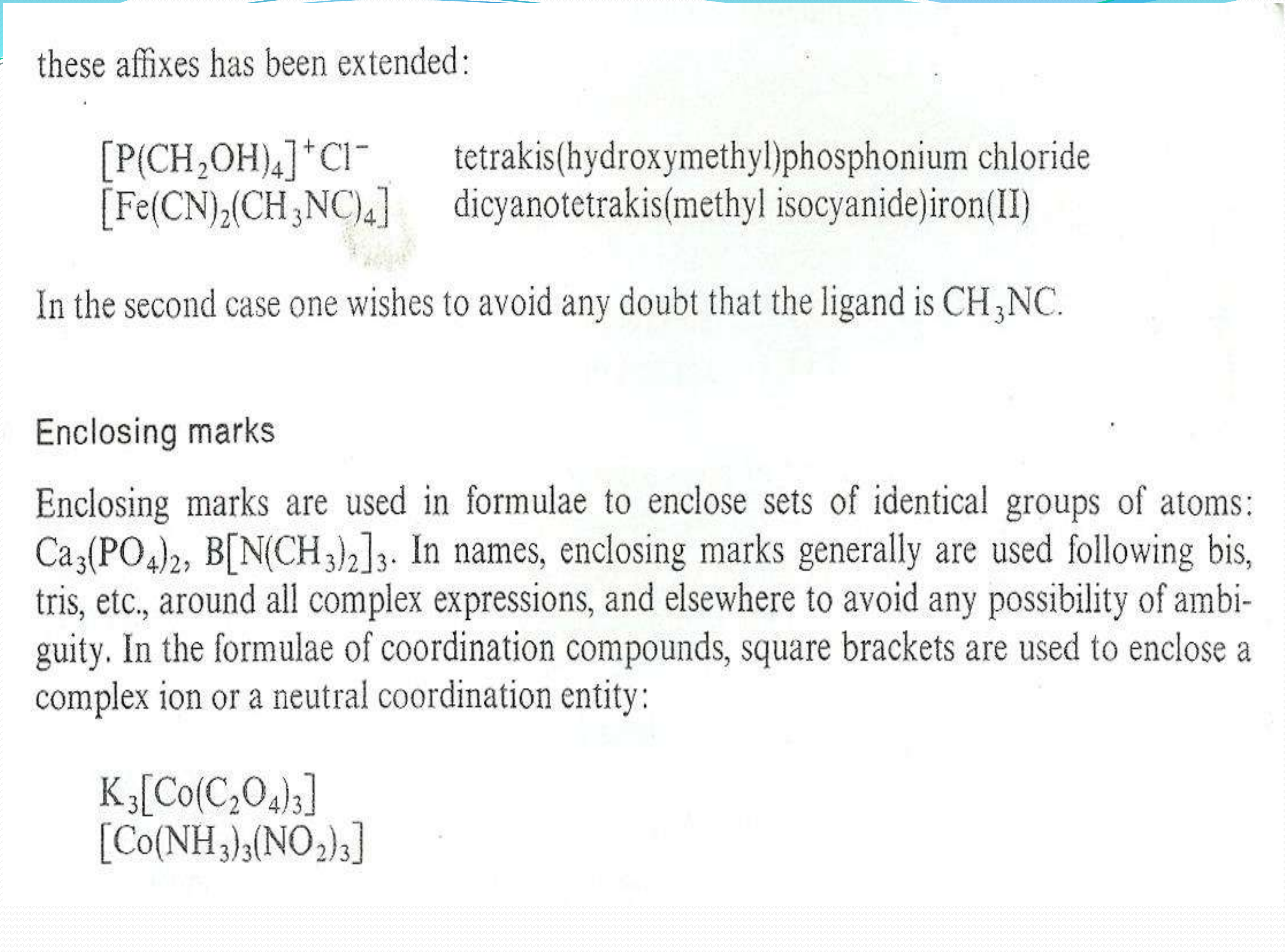


COORDINATION NUMBER

The coordination number of the central atom in a compound is the number of atoms which are directly linked to the central atom. The attached atoms may be charged or uncharged or part of an ion or molecule. In some types of coordination compounds, the two atoms of a multiple bond in an attached group are assigned to a single coordination position. Crystallographers define the coordination number of an atom or ion in a lattice as the number of near neighbors to that atom or ion.

USE OF MULTIPLYING AFFIXES, ENCLOSING MARKS, NUMBERS, AND LETTERS

Chemical nomenclature uses multiplying affixes, numbers (both Arabic and Roman), and letters to indicate both stoichiometry and structure.



these affixes has been extended:

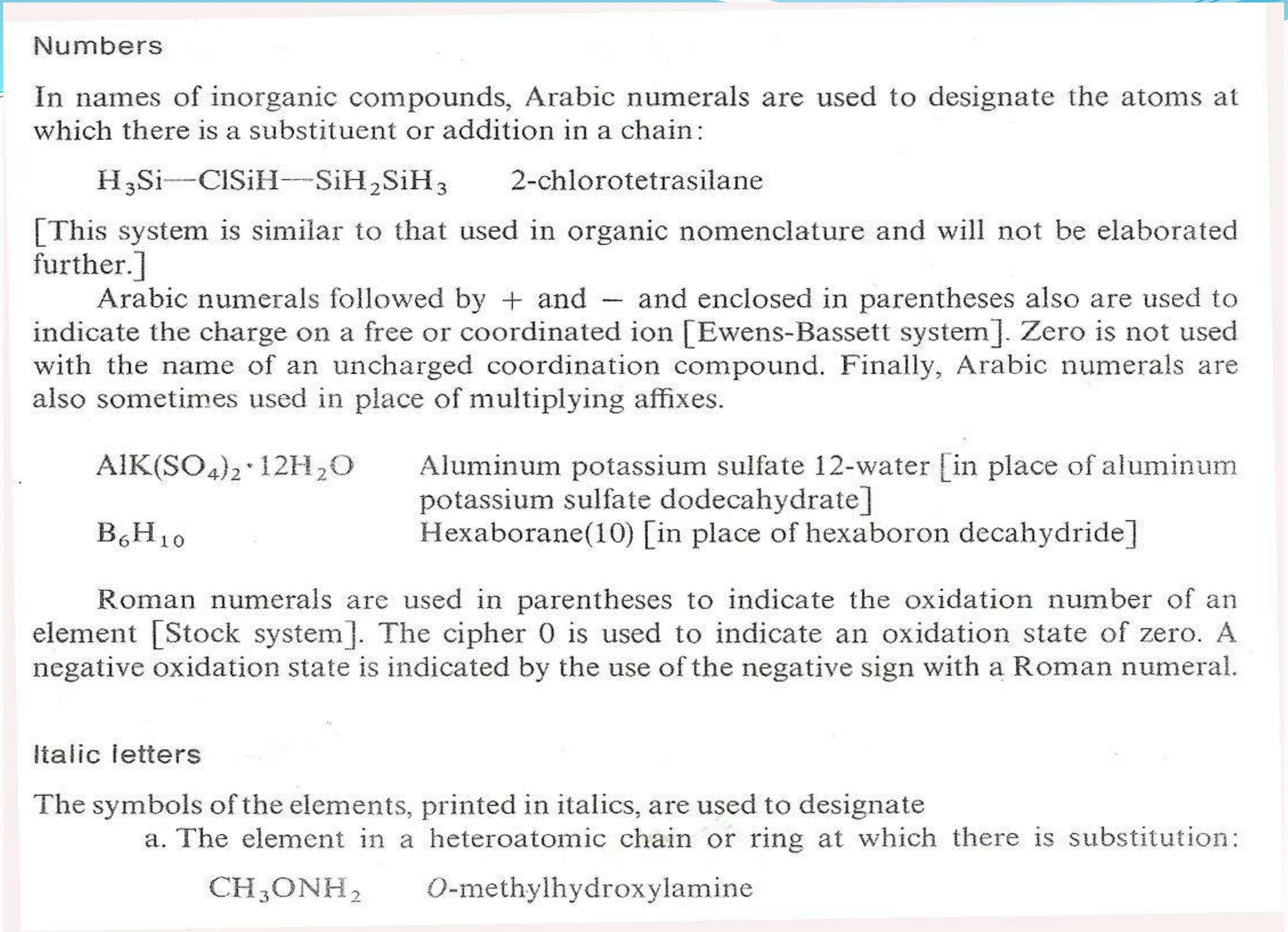
$[P(CH_2OH)_4]^+Cl^-$	tetrakis(hydroxymethyl)phosphonium chloride
$[Fe(CN)_2(CH_3NC)_4]$	dicyanotetrakis(methyl isocyanide)iron(II)

In the second case one wishes to avoid any doubt that the ligand is CH_3NC.

Enclosing marks

Enclosing marks are used in formulae to enclose sets of identical groups of atoms: $Ca_3(PO_4)_2$, $B[N(CH_3)_2]_3$. In names, enclosing marks generally are used following bis, tris, etc., around all complex expressions, and elsewhere to avoid any possibility of ambiguity. In the formulae of coordination compounds, square brackets are used to enclose a complex ion or a neutral coordination entity:

$K_3[Co(C_2O_4)_3]$
$[Co(NH_3)_3(NO_2)_3]$



Numbers

In names of inorganic compounds, Arabic numerals are used to designate the atoms at which there is a substituent or addition in a chain:

$H_3Si—ClSiH—SiH_2SiH_3$	2-chlorotetrasilane

[This system is similar to that used in organic nomenclature and will not be elaborated further.]

Arabic numerals followed by + and − and enclosed in parentheses also are used to indicate the charge on a free or coordinated ion [Ewens-Bassett system]. Zero is not used with the name of an uncharged coordination compound. Finally, Arabic numerals are also sometimes used in place of multiplying affixes.

$AlK(SO_4)_2 \cdot 12H_2O$	Aluminum potassium sulfate 12-water [in place of aluminum potassium sulfate dodecahydrate]
B_6H_{10}	Hexaborane(10) [in place of hexaboron decahydride]

Roman numerals are used in parentheses to indicate the oxidation number of an element [Stock system]. The cipher 0 is used to indicate an oxidation state of zero. A negative oxidation state is indicated by the use of the negative sign with a Roman numeral.

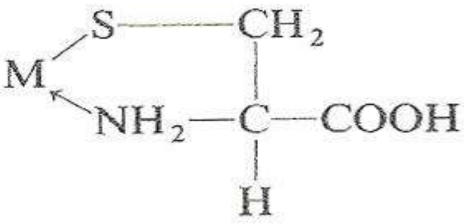
Italic letters

The symbols of the elements, printed in italics, are used to designate

a. The element in a heteroatomic chain or ring at which there is substitution:

CH_3ONH_2	*O*-methylhydroxylamine

b. The element in a ligand which is coordinated to a central atom:



cysteinato—*S*,*N* . . .

c. The presence of bonds between two metal atoms:

$(OC)_3Fe(C_2H_5S)_2Fe(CO)_3$ bis(μ-ethylthio)bis(tricarbonyliron)(Fe—Fe)

d. The point of attachment in some addition compounds:

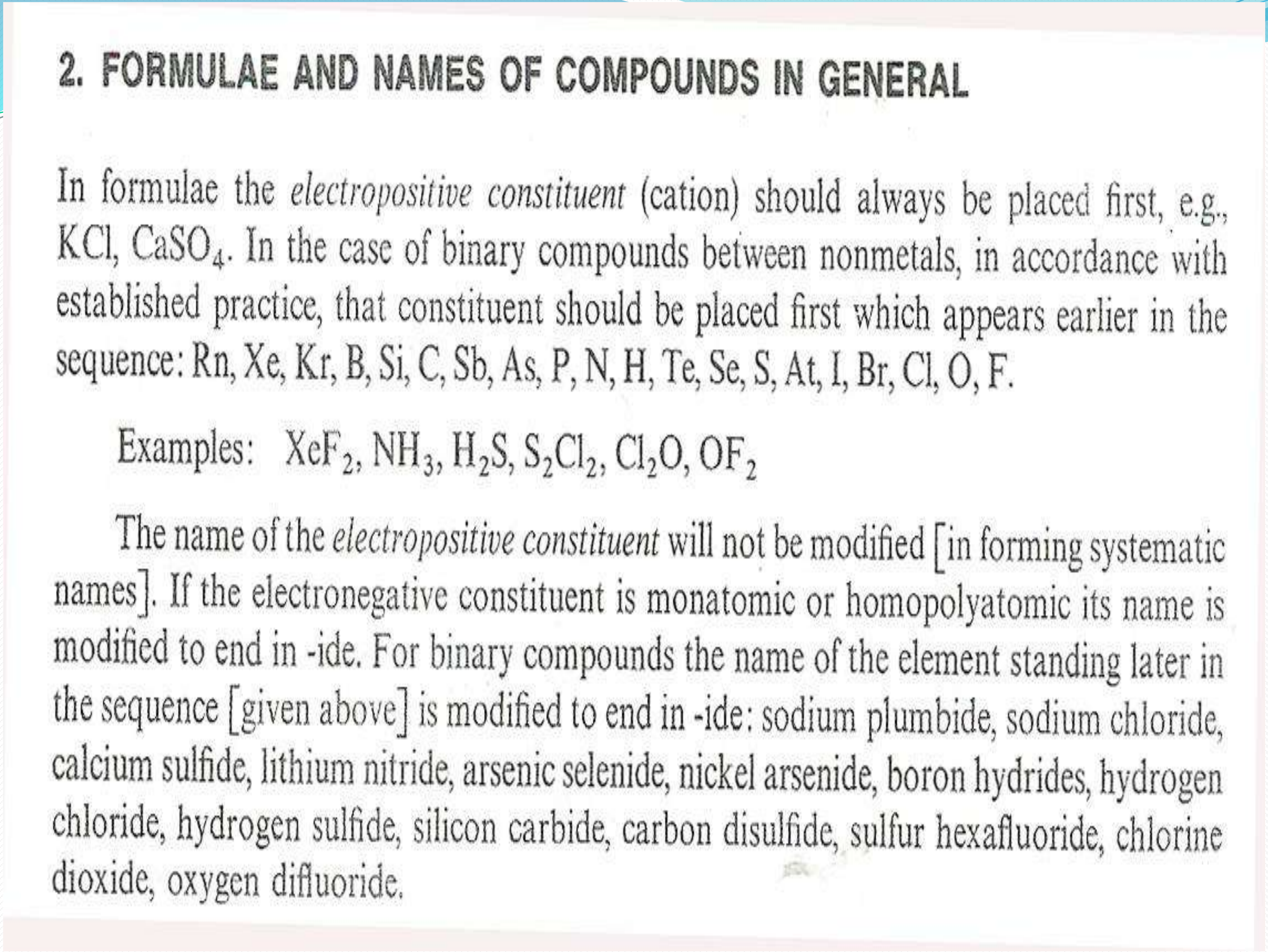
$CH_3ONH_2 \cdot BH_3$ *O*-methylhdroxylamine(*N*—*B*)borane

1. ELEMENTS

[A complete list of accepted names of elements, their atomic numbers, and their atomic weights may be found in Appendix K.]

The mass number, atomic number, number of atoms, and ionic charge of an element may be indicated by means of four indices placed around the symbol. The positions are to be occupied thus:

Left upper index	mass number
Left lower index	atomic number
Right lower index	number of atoms
Right upper index	ionic charge



2. FORMULAE AND NAMES OF COMPOUNDS IN GENERAL

In formulae the *electropositive constituent* (cation) should always be placed first, e.g., KCl, $CaSO_4$. In the case of binary compounds between nonmetals, in accordance with established practice, that constituent should be placed first which appears earlier in the sequence: Rn, Xe, Kr, B, Si, C, Sb, As, P, N, H, Te, Se, S, At, I, Br, Cl, O, F.

Examples: XeF_2, NH_3, H_2S, S_2Cl_2, Cl_2O, OF_2

The name of the *electropositive constituent* will not be modified [in forming systematic names]. If the electronegative constituent is monatomic or homopolyatomic its name is modified to end in -ide. For binary compounds the name of the element standing later in the sequence [given above] is modified to end in -ide: sodium plumbide, sodium chloride, calcium sulfide, lithium nitride, arsenic selenide, nickel arsenide, boron hydrides, hydrogen chloride, hydrogen sulfide, silicon carbide, carbon disulfide, sulfur hexafluoride, chlorine dioxide, oxygen difluoride.

If the electronegative constituent is heteropolyatomic it should be designated by the termination -ate. In certain exceptional cases the termination -ide and -ite are used [see below].

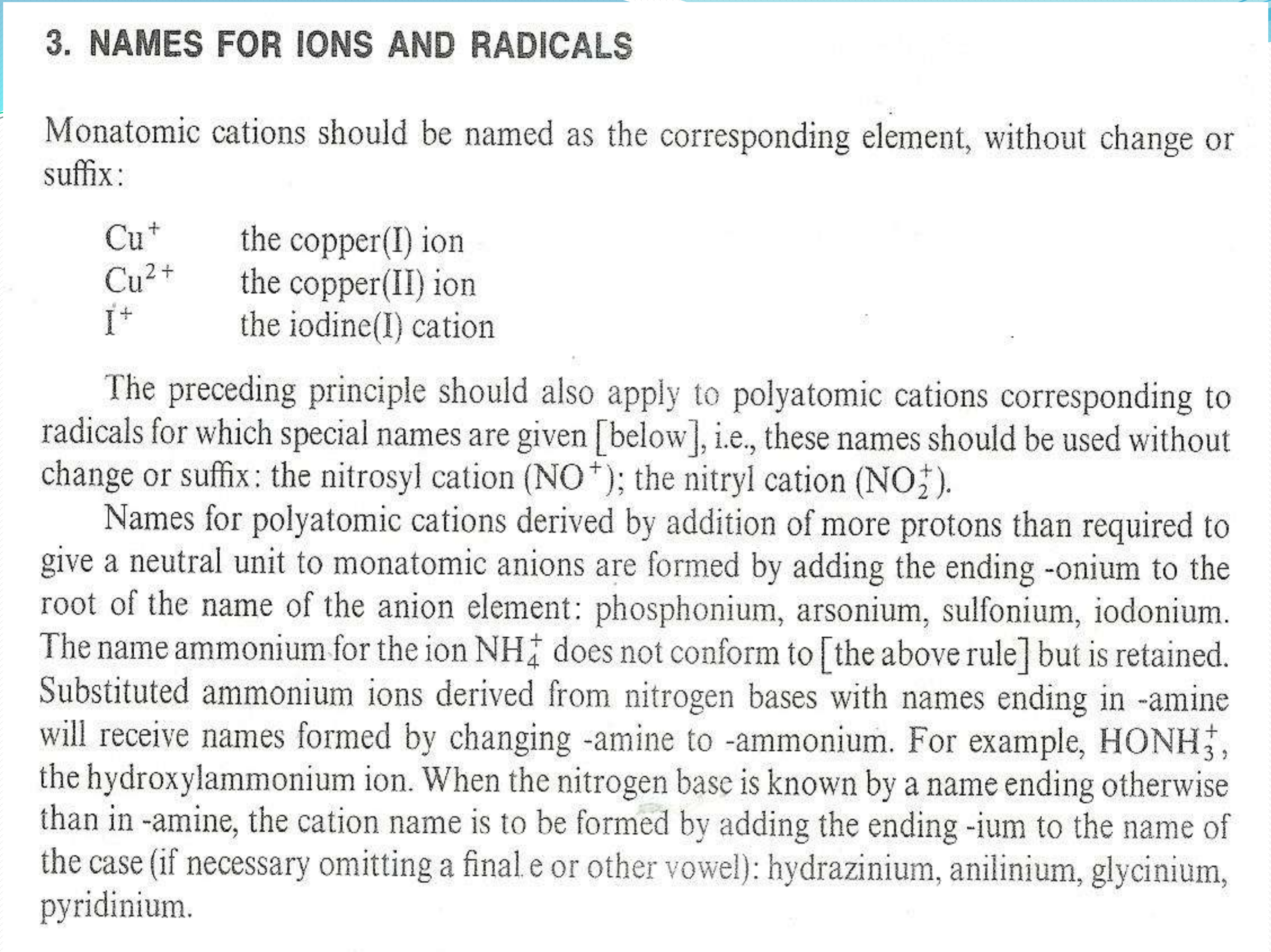
In inorganic compounds it is generally possible in a polyatomic group to indicate a *characteristic atom* (as in ClO^-) or a *central atom* (as in ICl_4^-). Such a polyatomic group is designated as a *complex*, and the atoms, radicals, or molecules bound to the characteristic or central atom are termed *ligands*.

In this case the name of a negatively charged complex should be formed from the name of the characteristic or central element modified to end in -ate. [For examples, see Section 7.]

Binary hydrogen compounds may be named by the principles [given above]. Volatile hydrides, except those of Group VII and of oxygen and nitrogen, may also be named by citing the root name of the element followed by the suffix -ane. If the molecule contains more than one atom of that element, the number is indicated by the appropriate Greek prefix.

Recognized exceptions are water, ammonia, [and] hydrazine, owing to long usage. Phosphine, arsine, stibine, and bismuthine are also allowed. However, for all molecular hydrides containing more than one atom of the element, "-ane" names should be used.

B_2H_6	diborane	PbH_4	plumbane
Si_3H_8	trisilane	H_2S_n	polysulfane



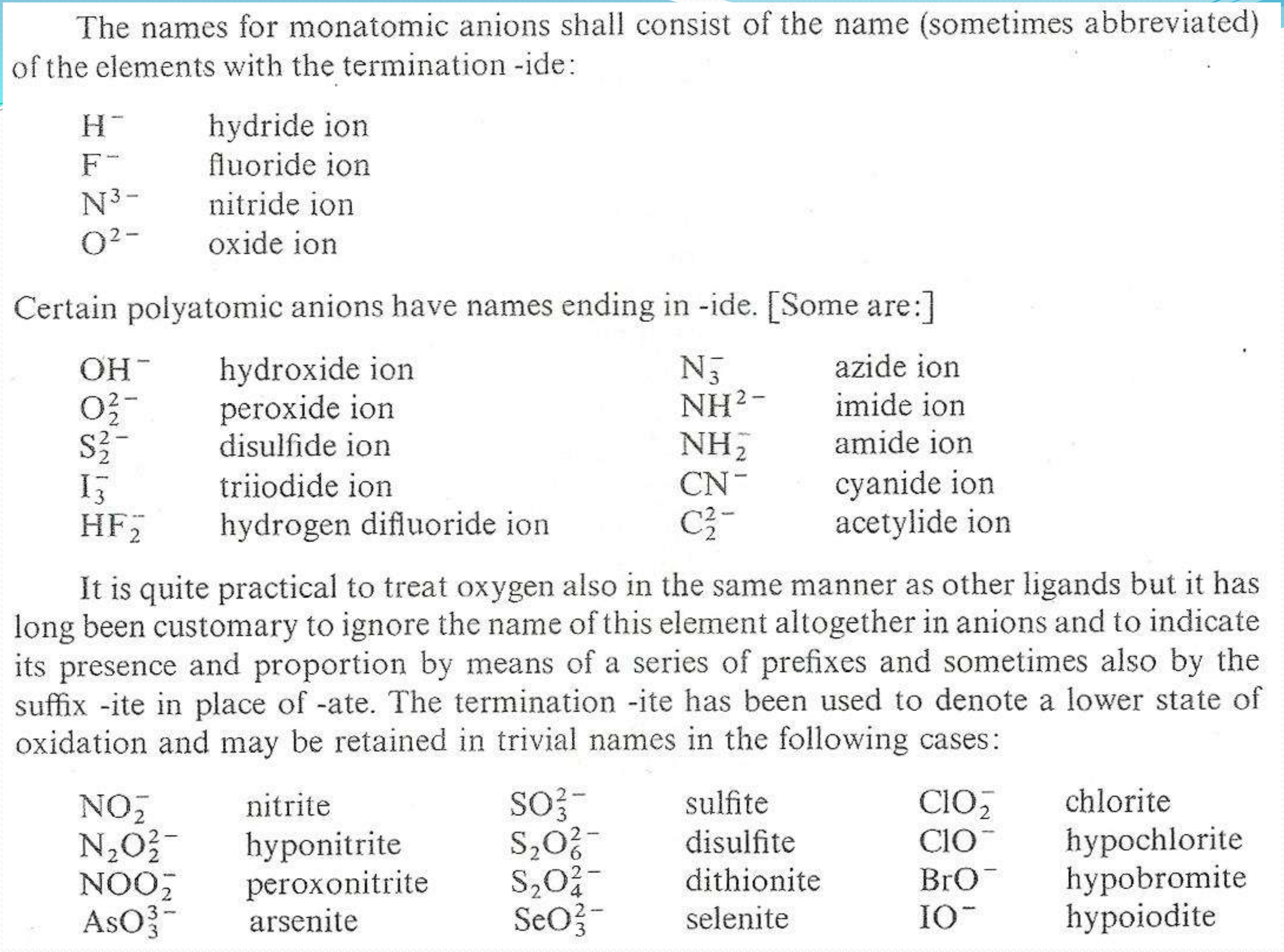
3. NAMES FOR IONS AND RADICALS

Monatomic cations should be named as the corresponding element, without change or suffix:

Cu^+	the copper(I) ion
Cu^{2+}	the copper(II) ion
I^+	the iodine(I) cation

The preceding principle should also apply to polyatomic cations corresponding to radicals for which special names are given [below], i.e., these names should be used without change or suffix: the nitrosyl cation (NO^+); the nitryl cation (NO_2^+).

Names for polyatomic cations derived by addition of more protons than required to give a neutral unit to monatomic anions are formed by adding the ending -onium to the root of the name of the anion element: phosphonium, arsonium, sulfonium, iodonium. The name ammonium for the ion NH_4^+ does not conform to [the above rule] but is retained. Substituted ammonium ions derived from nitrogen bases with names ending in -amine will receive names formed by changing -amine to -ammonium. For example, $HONH_3^+$, the hydroxylammonium ion. When the nitrogen base is known by a name ending otherwise than in -amine, the cation name is to be formed by adding the ending -ium to the name of the case (if necessary omitting a final e or other vowel): hydrazinium, anilinium, glycinium, pyridinium.



The names for monatomic anions shall consist of the name (sometimes abbreviated) of the elements with the termination -ide:

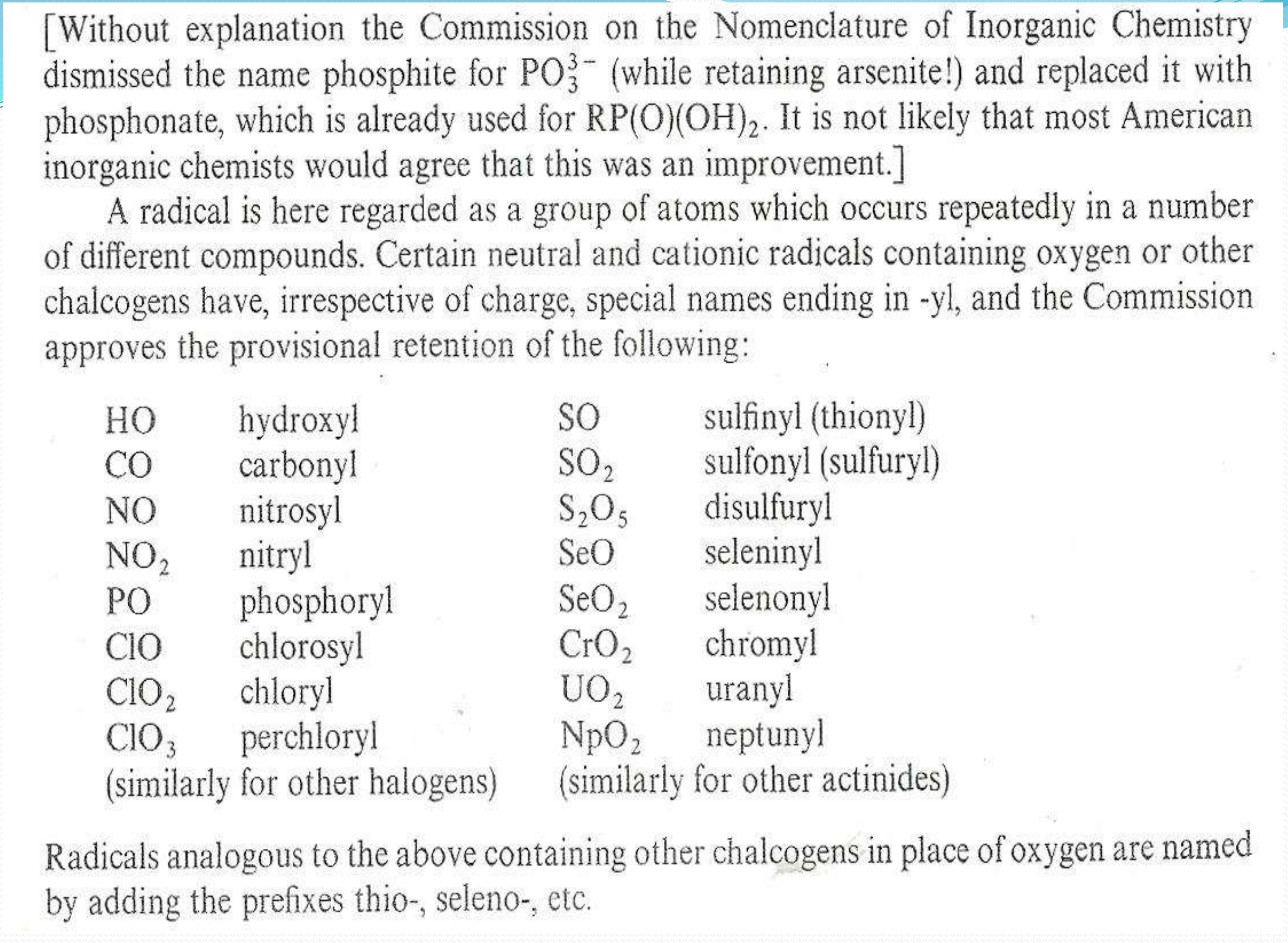
H^-	hydride ion
F^-	fluoride ion
N^{3-}	nitride ion
O^{2-}	oxide ion

Certain polyatomic anions have names ending in -ide. [Some are:]

OH^-	hydroxide ion	N_3^-	azide ion
O_2^{2-}	peroxide ion	NH^{2-}	imide ion
S_2^{2-}	disulfide ion	NH_2^-	amide ion
I_3^-	triiodide ion	CN^-	cyanide ion
HF_2^-	hydrogen difluoride ion	C_2^{2-}	acetylide ion

It is quite practical to treat oxygen also in the same manner as other ligands but it has long been customary to ignore the name of this element altogether in anions and to indicate its presence and proportion by means of a series of prefixes and sometimes also by the suffix -ite in place of -ate. The termination -ite has been used to denote a lower state of oxidation and may be retained in trivial names in the following cases:

NO_2^-	nitrite	SO_3^{2-}	sulfite	ClO_2^-	chlorite
$N_2O_2^{2-}$	hyponitrite	$S_2O_6^{2-}$	disulfite	ClO^-	hypochlorite
NOO_2^-	peroxonitrite	$S_2O_4^{2-}$	dithionite	BrO^-	hypobromite
AsO_3^{3-}	arsenite	SeO_3^{2-}	selenite	IO^-	hypoiodite

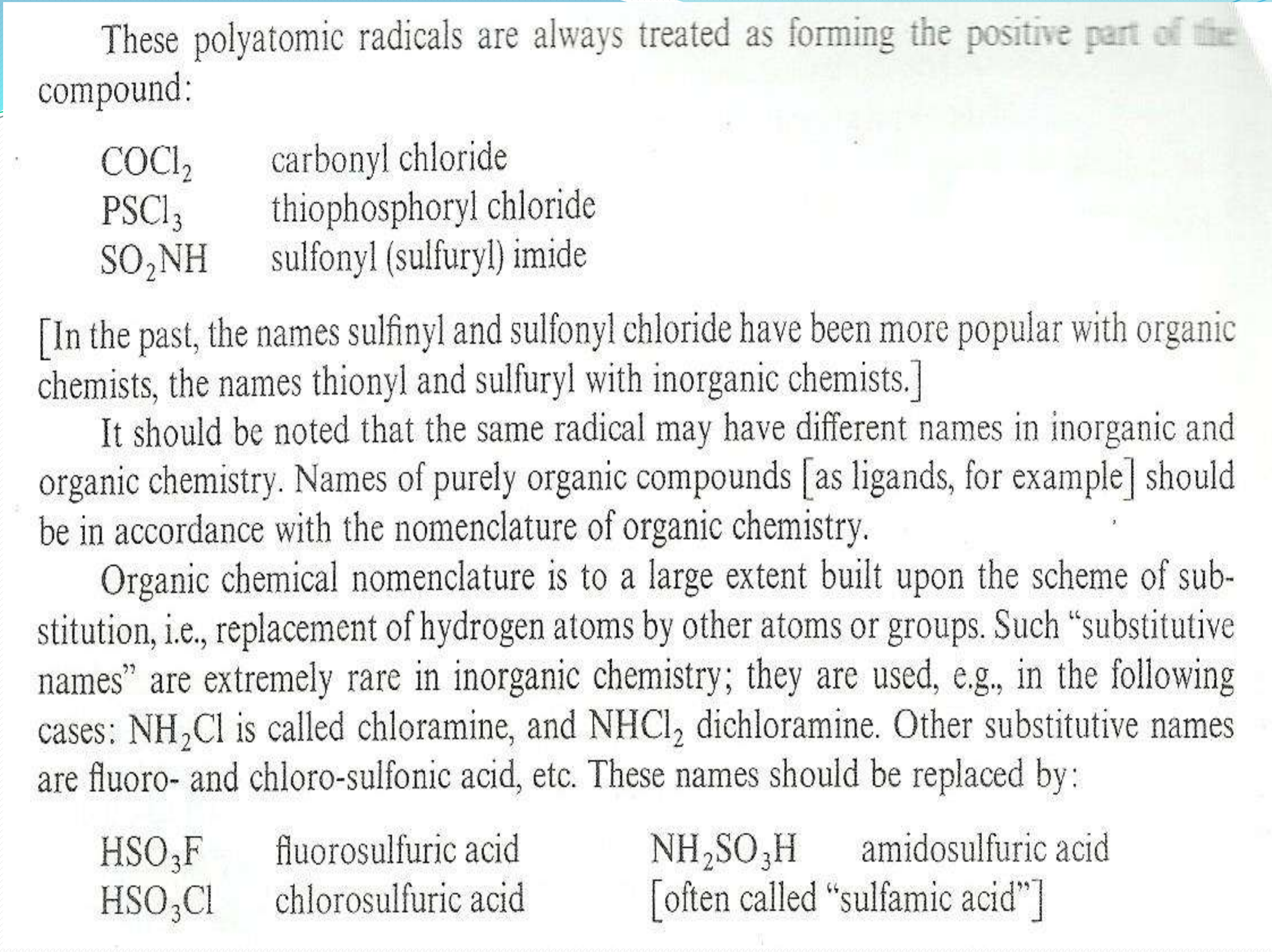


[Without explanation the Commission on the Nomenclature of Inorganic Chemistry dismissed the name phosphite for PO_3^{3-} (while retaining arsenite!) and replaced it with phosphonate, which is already used for $RP(O)(OH)_2$. It is not likely that most American inorganic chemists would agree that this was an improvement.]

A radical is here regarded as a group of atoms which occurs repeatedly in a number of different compounds. Certain neutral and cationic radicals containing oxygen or other chalcogens have, irrespective of charge, special names ending in -yl, and the Commission approves the provisional retention of the following:

HO	hydroxyl	SO	sulfinyl (thionyl)
CO	carbonyl	SO_2	sulfonyl (sulfuryl)
NO	nitrosyl	S_2O_5	disulfuryl
NO_2	nitryl	SeO	seleninyl
PO	phosphoryl	SeO_2	selenonyl
ClO	chlorosyl	CrO_2	chromyl
ClO_2	chloryl	UO_2	uranyl
ClO_3	perchloryl	NpO_2	neptunyl
(similarly for other halogens)		(similarly for other actinides)	

Radicals analogous to the above containing other chalcogens in place of oxygen are named by adding the prefixes thio-, seleno-, etc.



These polyatomic radicals are always treated as forming the positive part of the compound:

$COCl_2$	carbonyl chloride
$PSCl_3$	thiophosphoryl chloride
SO_2NH	sulfonyl (sulfuryl) imide

[In the past, the names sulfinyl and sulfonyl chloride have been more popular with organic chemists, the names thionyl and sulfuryl with inorganic chemists.]

It should be noted that the same radical may have different names in inorganic and organic chemistry. Names of purely organic compounds [as ligands, for example] should be in accordance with the nomenclature of organic chemistry.

Organic chemical nomenclature is to a large extent built upon the scheme of substitution, i.e., replacement of hydrogen atoms by other atoms or groups. Such "substitutive names" are extremely rare in inorganic chemistry; they are used, e.g., in the following cases: NH_2Cl is called chloramine, and $NHCl_2$ dichloramine. Other substitutive names are fluoro- and chloro-sulfonic acid, etc. These names should be replaced by:

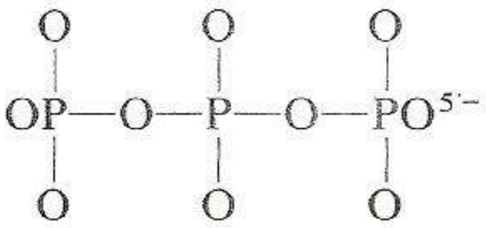
HSO_3F	fluorosulfuric acid	NH_2SO_3H	amidosulfuric acid
HSO_3Cl	chlorosulfuric acid	[often called "sulfamic acid"]	

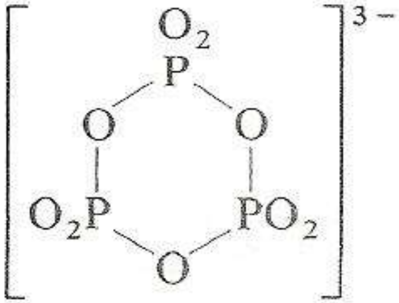
4. ISO- AND HETEROPOLYANIONS

Anions of polyacids derived by condensation of molecules of the same monoacid, containing the characteristic element in the oxidation state corresponding to its Group number, are named by indicating with Greek numeral prefixes the number of atoms of that element:

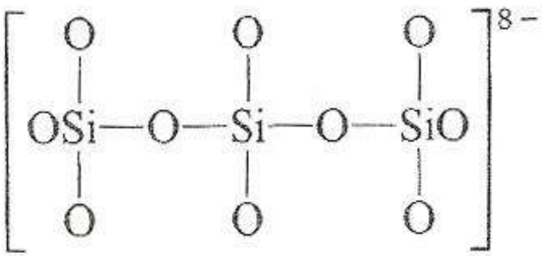
$Na_2B_4O_7$	disodium tetraborate
$Mo_7O_{24}^{6-}$	heptamolybdate

Cyclic and strain-chain structures may be distinguished by means of the prefixes *cyclo* and *catena*, although the latter may usually be omitted:

1. 
$\mathrm{O\overset{O}{\underset{O}{P}}{-}O{-}\overset{O}{\underset{O}{P}}{-}O{-}\overset{O}{\underset{O}{P}}O^{5-}}$ triphosphate

2.  *cyclo*-triphosphate

3. $[O(PO_3)_n]^{(n+2)-}$ *catena*-polyphosphate

4. 

$$\left[\begin{array}{ccccc} O & & O & & O \\ | & & | & & | \\ OSi & -O- & Si & -O- & SiO \\ | & & | & & | \\ O & & O & & O \end{array}\right]^{8-}$$

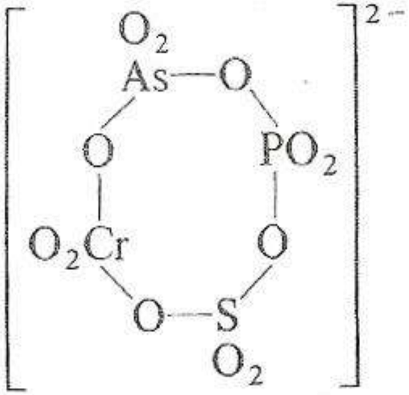
trisilicate

Heteropolyanions with a chain or ring structure

Dinuclear anions are named by treating the anion which comes first in alphabetical order as the ligand on the characteristic atoms of the second:

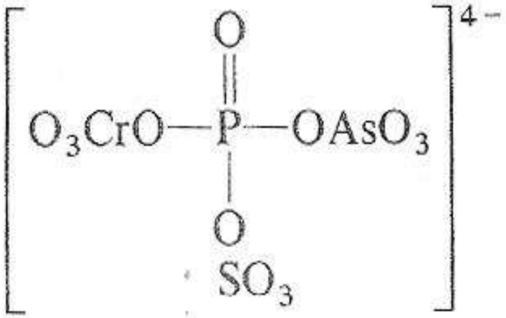
$[O_3P{-}O{-}SO_3]^{3-}$ phosphatosulfate(3−)

Cyclic heteropolyanions are named in a manner similar to those with a chain structure, the starting point and direction of citation of the units being chosen according to alphabetical priority:



cyclo-arsenatochromatosulfatophosphate (2−)

In polyanions with an obvious central atom the peripheral anions are named as ligands on the central atom and cited in alphabetical order:



$$\left[\begin{array}{c} O \\ \| \\ O_3CrO{-}P{-}OAsO_3 \\ | \\ O \\ SO_3 \end{array}\right]^{4-}$$

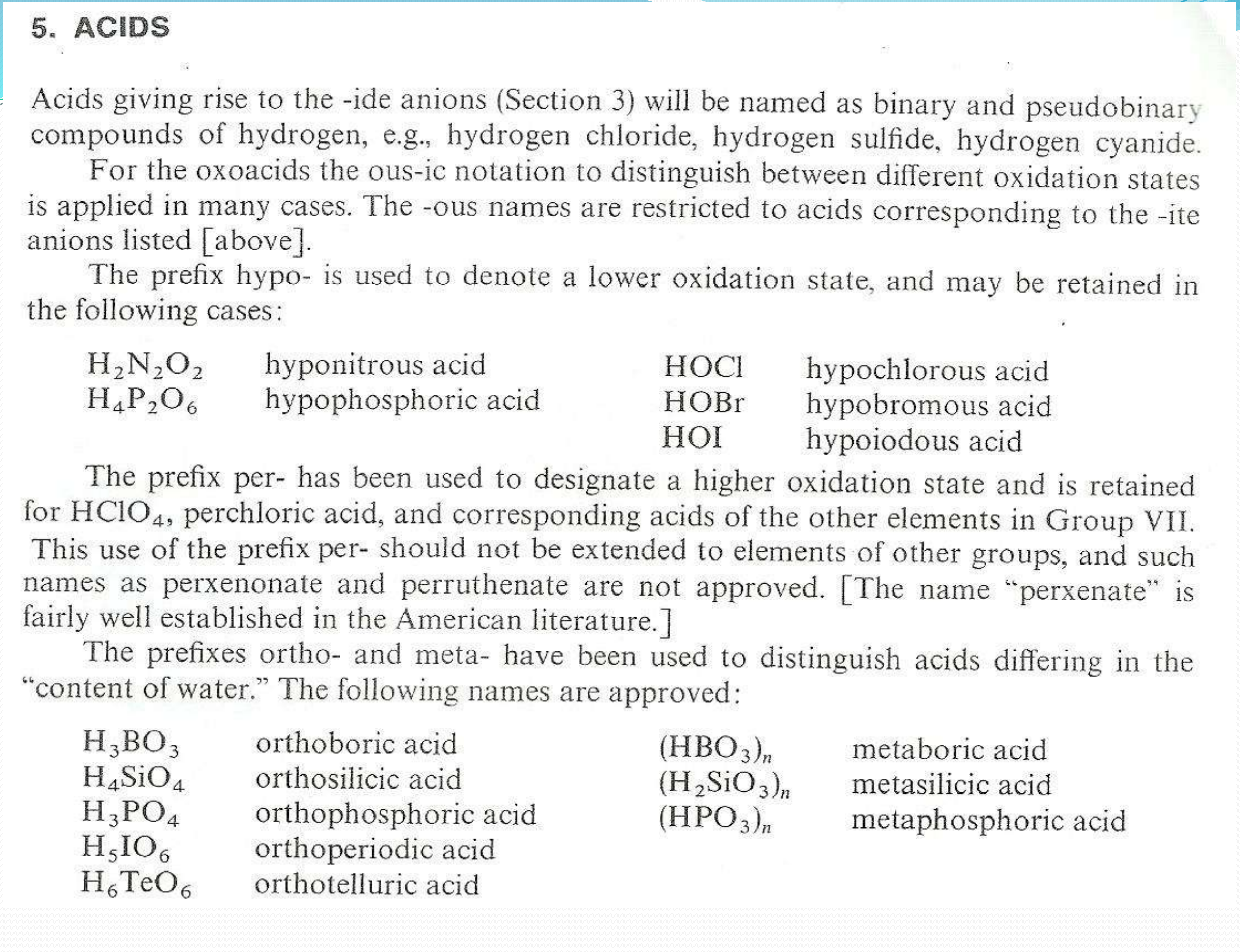
(arsenato)(chromato)(sulfato)phosphate(4−)

Condensed heteropoly anions

The three-dimensional frameworks of linked WO_6, MoO_6, etc., octahedra surrounding a central atom are designated by the prefixes wolframo, molybdo, etc., e.g., wolframophosphate (tungstophosphate), *not* phosphowolframate (phosphotungstate). The numbers of atoms of the characteristic element are indicated by Greek prefixes or numerals.

$[PW_{12}O_{40}]^{3-}$	dodecawolframophosphate(3−) 12-wolframophosphate(3−)
$[P_2Mo_{18}O_{62}]^{6-}$	18-molybdodiphosphate(V)(6−)

[American chemists almost never use the combining form *wolframo-*, preferring the form *tungsto-*.]



5. ACIDS

Acids giving rise to the -ide anions (Section 3) will be named as binary and pseudobinary compounds of hydrogen, e.g., hydrogen chloride, hydrogen sulfide, hydrogen cyanide.

For the oxoacids the ous-ic notation to distinguish between different oxidation states is applied in many cases. The -ous names are restricted to acids corresponding to the -ite anions listed [above].

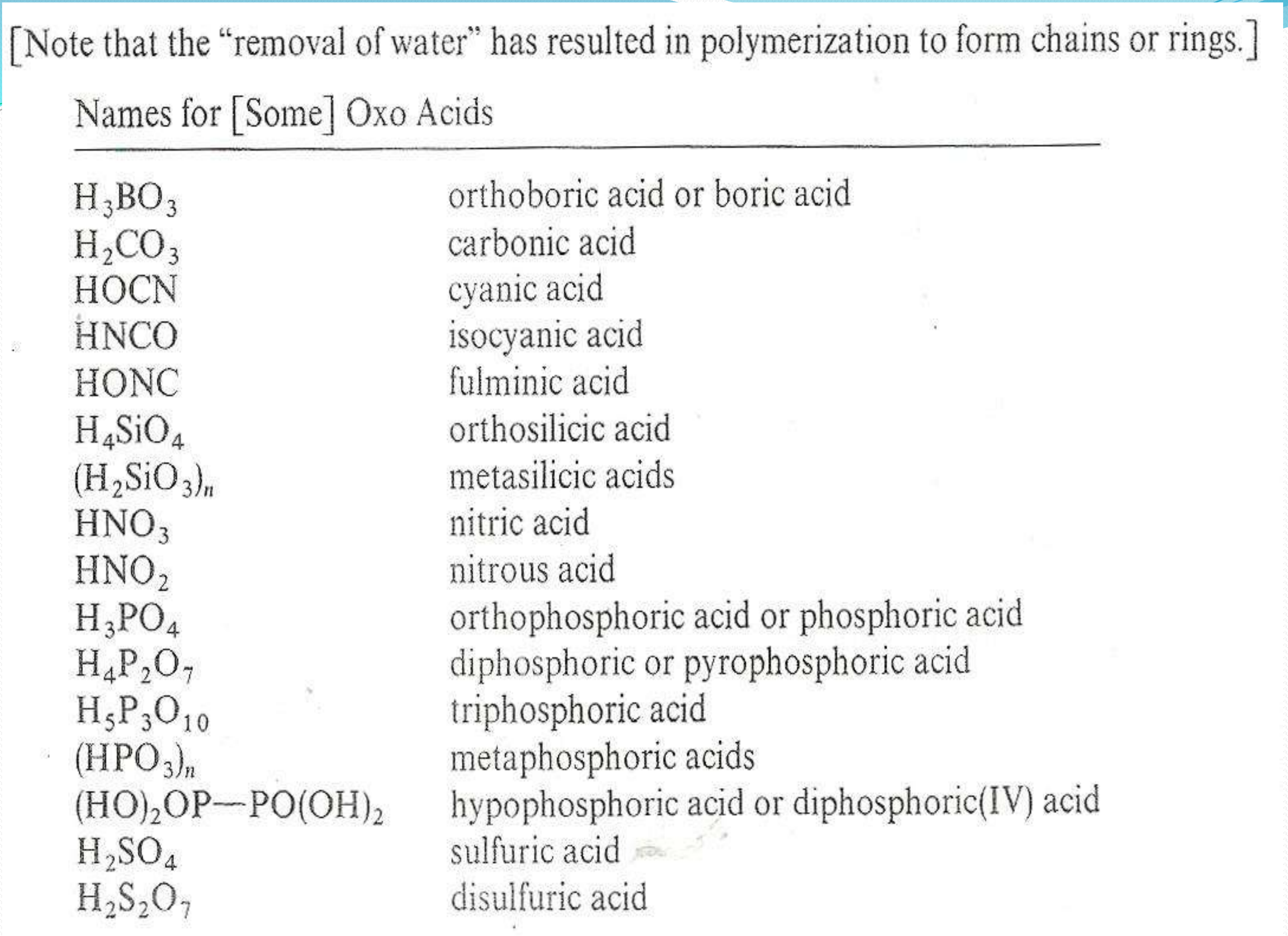
The prefix hypo- is used to denote a lower oxidation state, and may be retained in the following cases:

$H_2N_2O_2$	hyponitrous acid	HOCl	hypochlorous acid
$H_4P_2O_6$	hypophosphoric acid	HOBr	hypobromous acid
		HOI	hypoiodous acid

The prefix per- has been used to designate a higher oxidation state and is retained for $HClO_4$, perchloric acid, and corresponding acids of the other elements in Group VII. This use of the prefix per- should not be extended to elements of other groups, and such names as perxenonate and perruthenate are not approved. [The name "perxenate" is fairly well established in the American literature.]

The prefixes ortho- and meta- have been used to distinguish acids differing in the "content of water." The following names are approved:

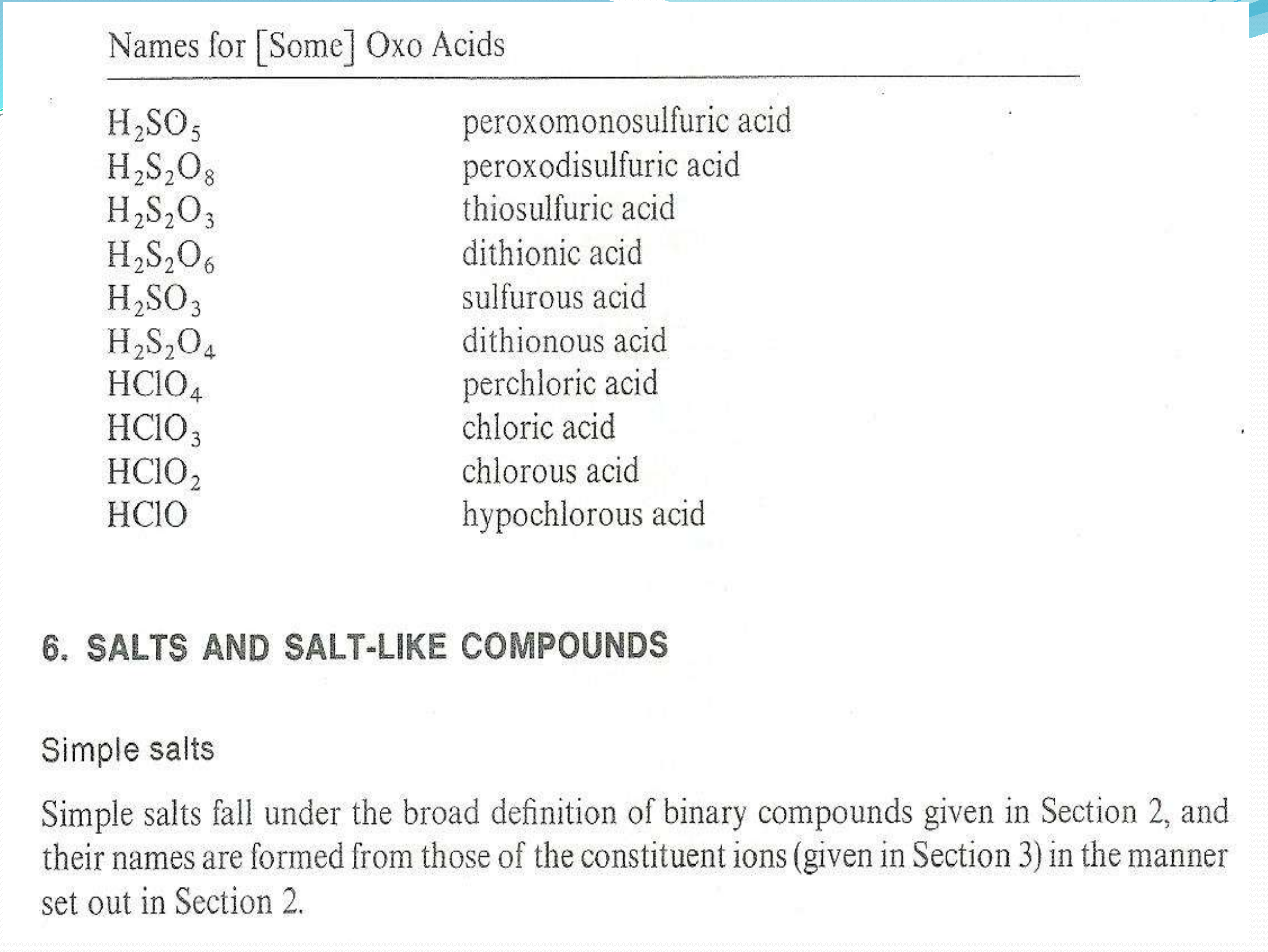
H_3BO_3	orthoboric acid	$(HBO_3)_n$	metaboric acid
H_4SiO_4	orthosilicic acid	$(H_2SiO_3)_n$	metasilicic acid
H_3PO_4	orthophosphoric acid	$(HPO_3)_n$	metaphosphoric acid
H_5IO_6	orthoperiodic acid		
H_6TeO_6	orthotelluric acid		



[Note that the "removal of water" has resulted in polymerization to form chains or rings.]

Names for [Some] Oxo Acids

H_3BO_3	orthoboric acid or boric acid
H_2CO_3	carbonic acid
HOCN	cyanic acid
HNCO	isocyanic acid
HONC	fulminic acid
H_4SiO_4	orthosilicic acid
$(H_2SiO_3)_n$	metasilicic acids
HNO_3	nitric acid
HNO_2	nitrous acid
H_3PO_4	orthophosphoric acid or phosphoric acid
$H_4P_2O_7$	diphosphoric or pyrophosphoric acid
$H_5P_3O_{10}$	triphosphoric acid
$(HPO_3)_n$	metaphosphoric acids
$(HO)_2OP—PO(OH)_2$	hypophosphoric acid or diphosphoric(IV) acid
H_2SO_4	sulfuric acid
$H_2S_2O_7$	disulfuric acid



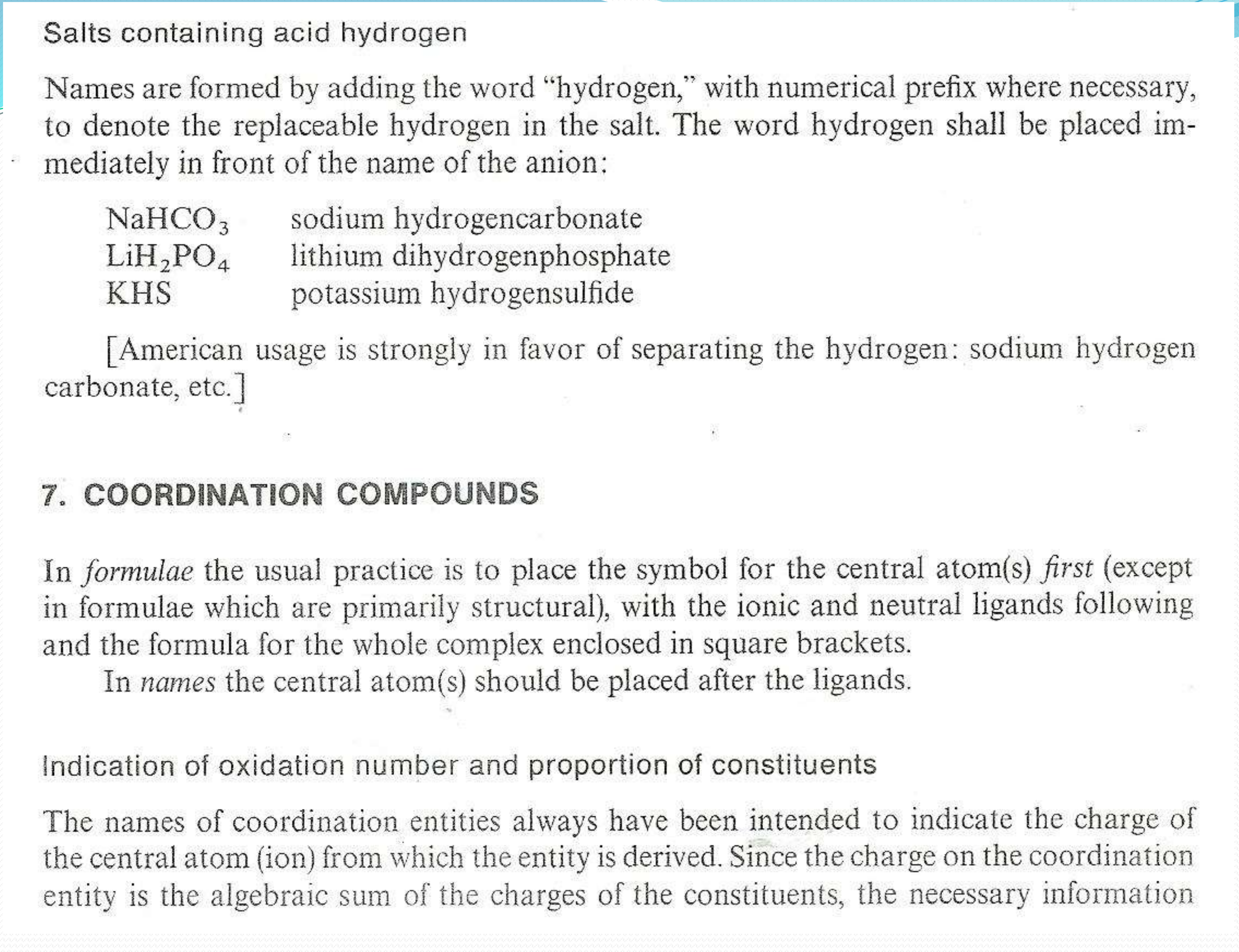
Names for [Some] Oxo Acids

H_2SO_5	peroxomonosulfuric acid
$H_2S_2O_8$	peroxodisulfuric acid
$H_2S_2O_3$	thiosulfuric acid
$H_2S_2O_6$	dithionic acid
H_2SO_3	sulfurous acid
$H_2S_2O_4$	dithionous acid
$HClO_4$	perchloric acid
$HClO_3$	chloric acid
$HClO_2$	chlorous acid
$HClO$	hypochlorous acid

6. SALTS AND SALT-LIKE COMPOUNDS

Simple salts

Simple salts fall under the broad definition of binary compounds given in Section 2, and their names are formed from those of the constituent ions (given in Section 3) in the manner set out in Section 2.



Salts containing acid hydrogen

Names are formed by adding the word "hydrogen," with numerical prefix where necessary, to denote the replaceable hydrogen in the salt. The word hydrogen shall be placed immediately in front of the name of the anion:

$NaHCO_3$	sodium hydrogencarbonate
LiH_2PO_4	lithium dihydrogenphosphate
KHS	potassium hydrogensulfide

[American usage is strongly in favor of separating the hydrogen: sodium hydrogen carbonate, etc.]

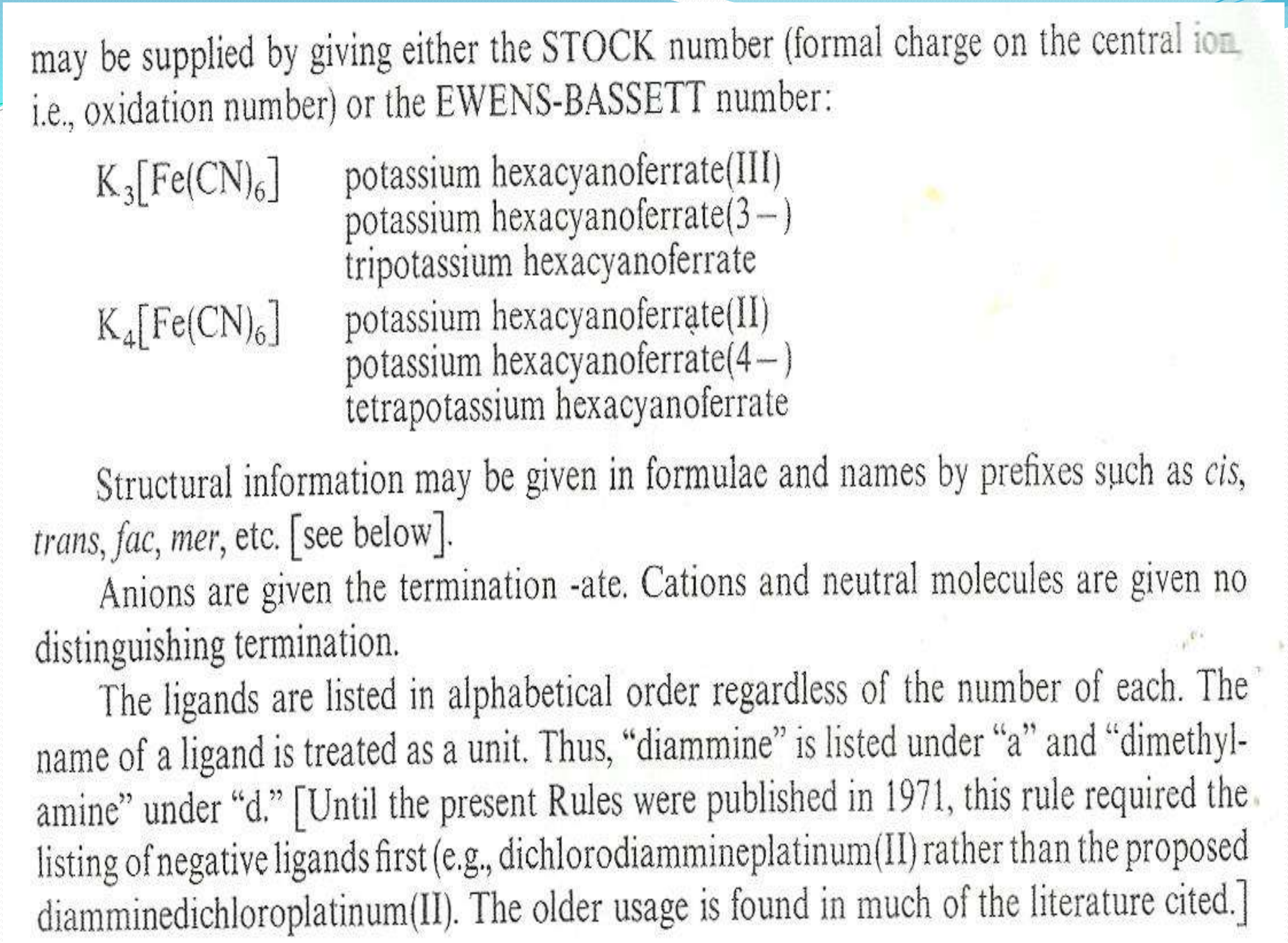
7. COORDINATION COMPOUNDS

In *formulae* the usual practice is to place the symbol for the central atom(s) *first* (except in formulae which are primarily structural), with the ionic and neutral ligands following and the formula for the whole complex enclosed in square brackets.

In *names* the central atom(s) should be placed after the ligands.

Indication of oxidation number and proportion of constituents

The names of coordination entities always have been intended to indicate the charge of the central atom (ion) from which the entity is derived. Since the charge on the coordination entity is the algebraic sum of the charges of the constituents, the necessary information



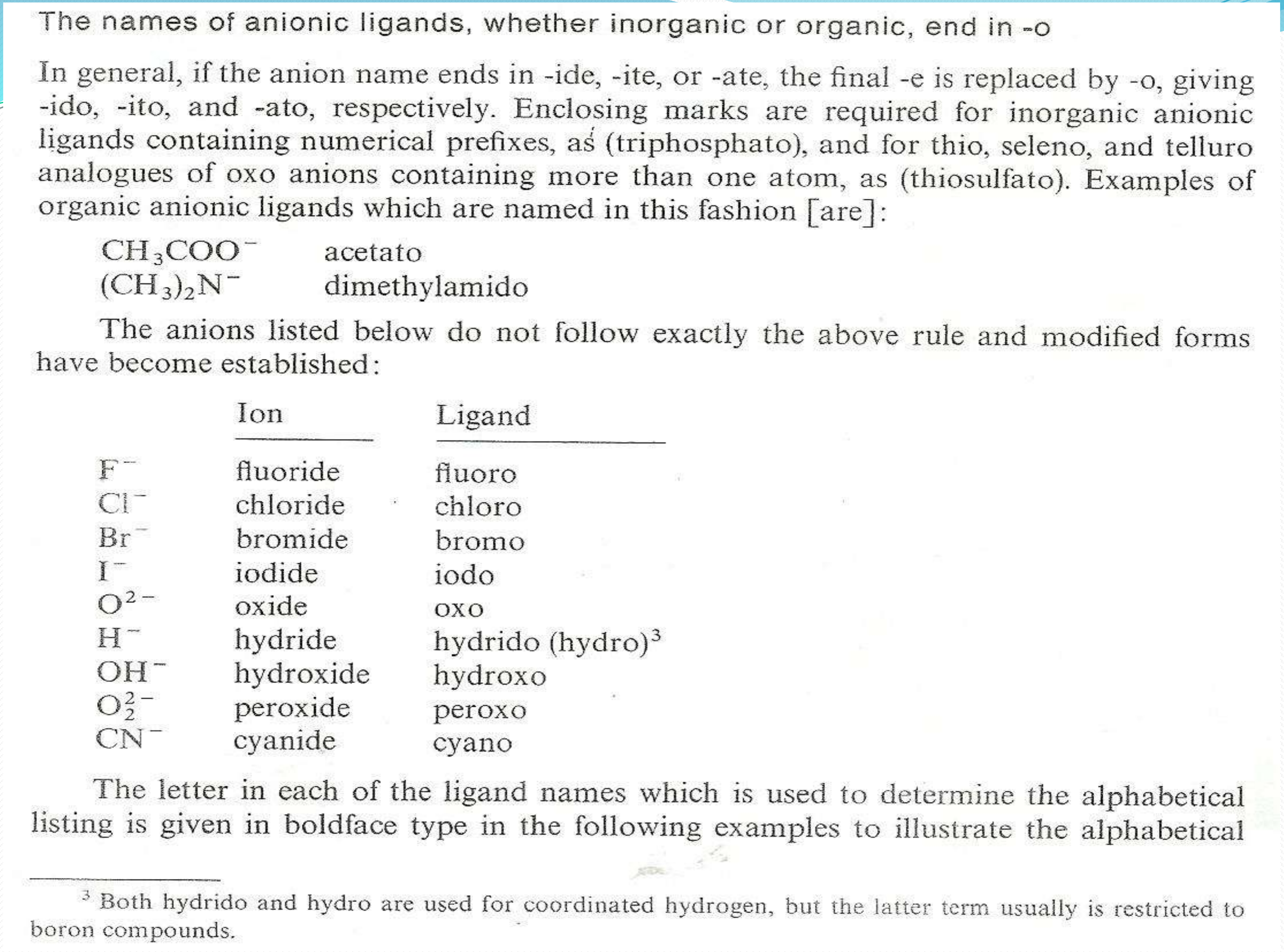
may be supplied by giving either the STOCK number (formal charge on the central ion, i.e., oxidation number) or the EWENS-BASSETT number:

$K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III) potassium hexacyanoferrate(3−) tripotassium hexacyanoferrate
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II) potassium hexacyanoferrate(4−) tetrapotassium hexacyanoferrate

Structural information may be given in formulae and names by prefixes such as *cis*, *trans*, *fac*, *mer*, etc. [see below].

Anions are given the termination -ate. Cations and neutral molecules are given no distinguishing termination.

The ligands are listed in alphabetical order regardless of the number of each. The name of a ligand is treated as a unit. Thus, "diammine" is listed under "a" and "dimethylamine" under "d." [Until the present Rules were published in 1971, this rule required the listing of negative ligands first (e.g., dichlorodiammineplatinum(II) rather than the proposed diamminedichloroplatinum(II). The older usage is found in much of the literature cited.]



The names of anionic ligands, whether inorganic or organic, end in -o

In general, if the anion name ends in -ide, -ite, or -ate, the final -e is replaced by -o, giving -ido, -ito, and -ato, respectively. Enclosing marks are required for inorganic anionic ligands containing numerical prefixes, as (triphosphato), and for thio, seleno, and telluro analogues of oxo anions containing more than one atom, as (thiosulfato). Examples of organic anionic ligands which are named in this fashion [are]:

CH_3COO^-	acetato
$(CH_3)_2N^-$	dimethylamido

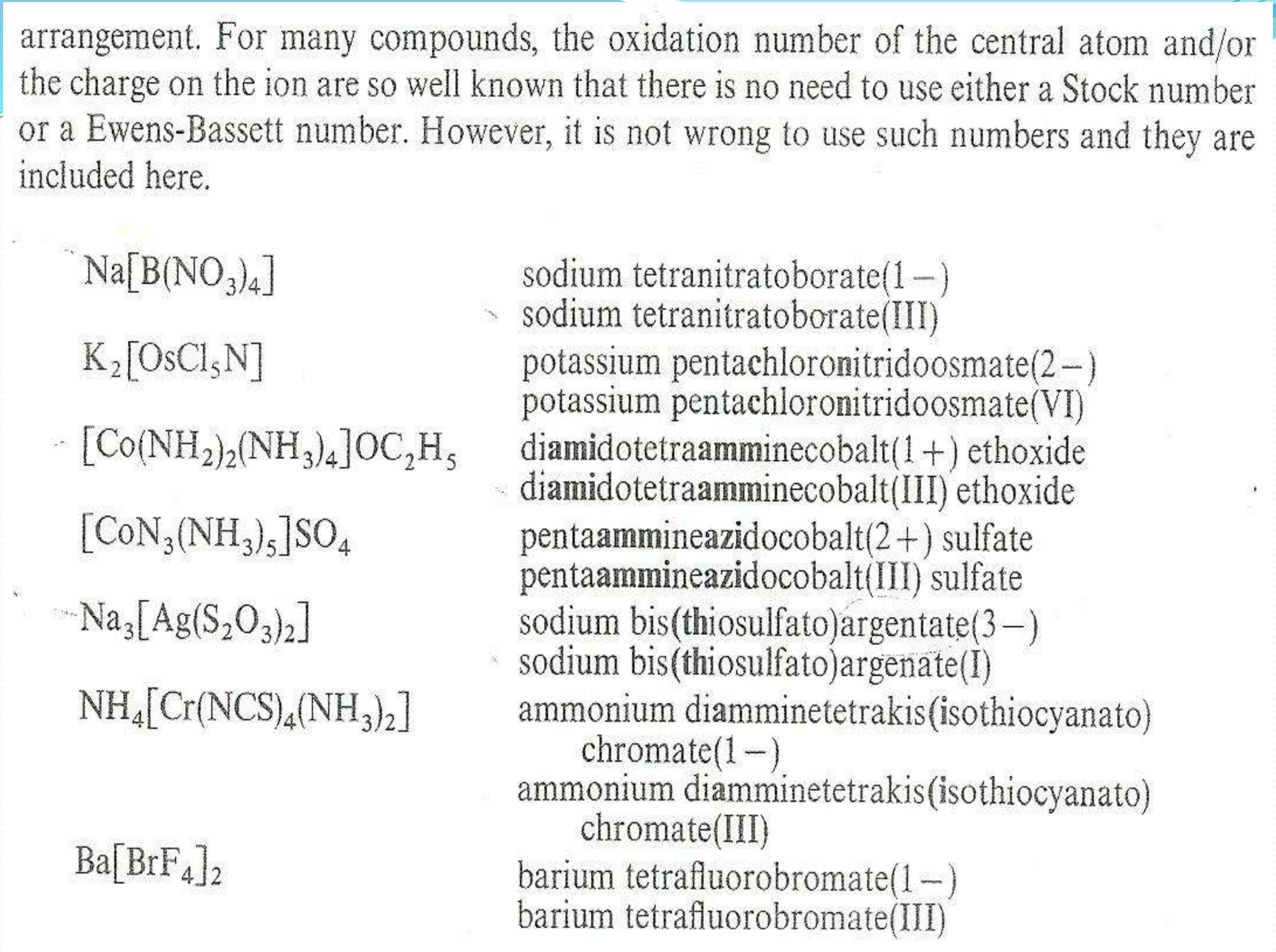
The anions listed below do not follow exactly the above rule and modified forms have become established:

	Ion	Ligand
F^-	fluoride	fluoro
Cl^-	chloride	chloro
Br^-	bromide	bromo
I^-	iodide	iodo
O^{2-}	oxide	oxo
H^-	hydride	hydrido (hydro)[3]
OH^-	hydroxide	hydroxo
O_2^{2-}	peroxide	peroxo
CN^-	cyanide	cyano

The letter in each of the ligand names which is used to determine the alphabetical listing is given in boldface type in the following examples to illustrate the alphabetical

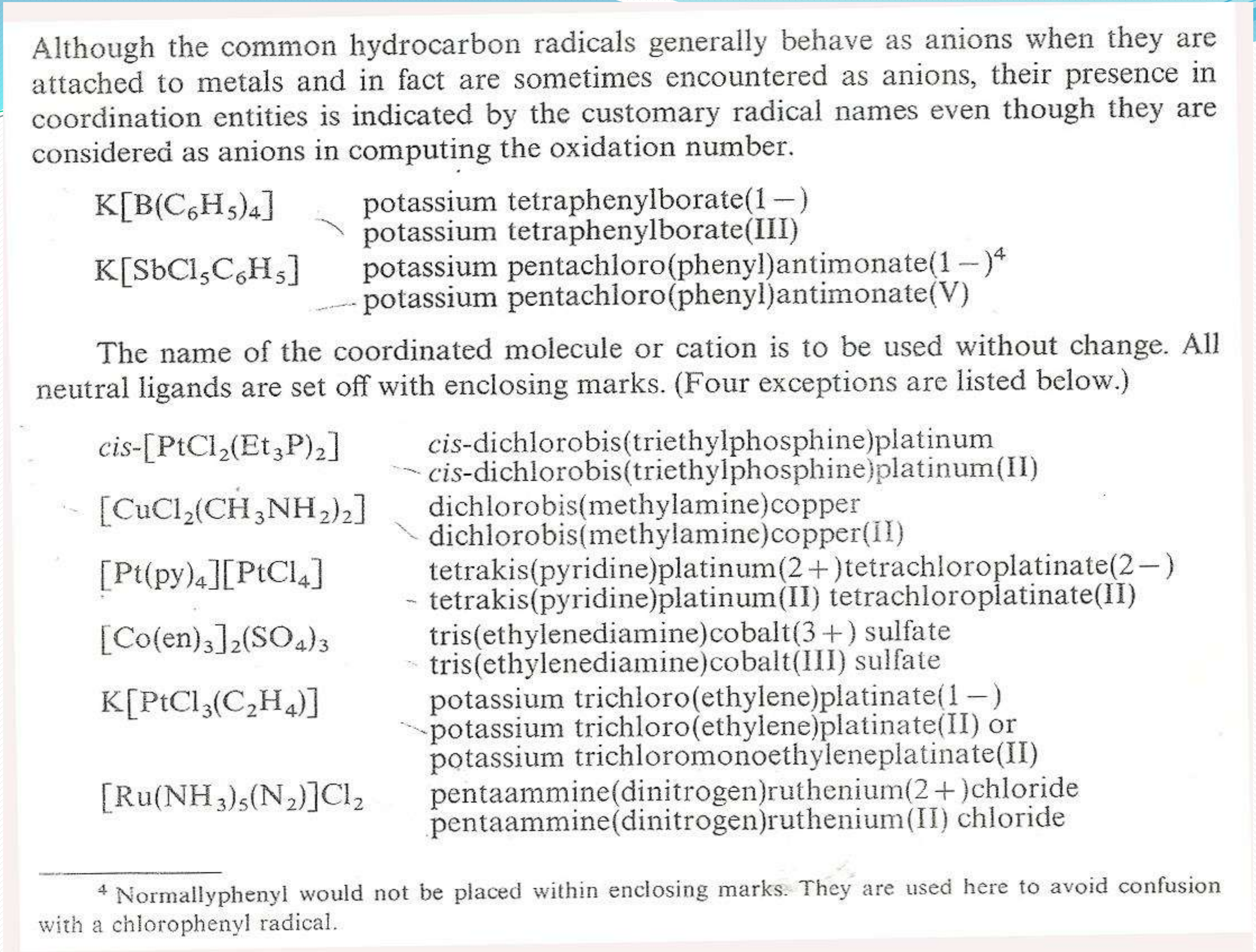
---

[3] Both hydrido and hydro are used for coordinated hydrogen, but the latter term usually is restricted to boron compounds.



arrangement. For many compounds, the oxidation number of the central atom and/or the charge on the ion are so well known that there is no need to use either a Stock number or a Ewens-Bassett number. However, it is not wrong to use such numbers and they are included here.

$Na[B(NO_3)_4]$	sodium tetranitratoborate(1 –) sodium tetranitratoborate(III)
$K_2[OsCl_5N]$	potassium pentachloronitridoosmate(2 –) potassium pentachloronitridoosmate(VI)
$[Co(NH_2)_2(NH_3)_4]OC_2H_5$	diamidotetraamminecobalt(1 +) ethoxide diamidotetraamminecobalt(III) ethoxide
$[CoN_3(NH_3)_5]SO_4$	pentaammineazidocobalt(2 +) sulfate pentaammineazidocobalt(III) sulfate
$Na_3[Ag(S_2O_3)_2]$	sodium bis(thiosulfato)argentate(3 –) sodium bis(thiosulfato)argenate(I)
$NH_4[Cr(NCS)_4(NH_3)_2]$	ammonium diamminetetrakis(isothiocyanato) chromate(1 –) ammonium diamminetetrakis(isothiocyanato) chromate(III)
$Ba[BrF_4]_2$	barium tetrafluorobromate(1 –) barium tetrafluorobromate(III)



Although the common hydrocarbon radicals generally behave as anions when they are attached to metals and in fact are sometimes encountered as anions, their presence in coordination entities is indicated by the customary radical names even though they are considered as anions in computing the oxidation number.

$K[B(C_6H_5)_4]$	potassium tetraphenylborate(1 −) potassium tetraphenylborate(III)
$K[SbCl_5C_6H_5]$	potassium pentachloro(phenyl)antimonate(1 −)[4] potassium pentachloro(phenyl)antimonate(V)

The name of the coordinated molecule or cation is to be used without change. All neutral ligands are set off with enclosing marks. (Four exceptions are listed below.)

cis-$[PtCl_2(Et_3P)_2]$	*cis*-dichlorobis(triethylphosphine)platinum *cis*-dichlorobis(triethylphosphine)platinum(II)
$[CuCl_2(CH_3NH_2)_2]$	dichlorobis(methylamine)copper dichlorobis(methylamine)copper(II)
$[Pt(py)_4][PtCl_4]$	tetrakis(pyridine)platinum(2 +)tetrachloroplatinate(2 −) tetrakis(pyridine)platinum(II) tetrachloroplatinate(II)
$[Co(en)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(3 +) sulfate tris(ethylenediamine)cobalt(III) sulfate
$K[PtCl_3(C_2H_4)]$	potassium trichloro(ethylene)platinate(1 −) potassium trichloro(ethylene)platinate(II) or potassium trichloromonoethyleneplatinate(II)
$[Ru(NH_3)_5(N_2)]Cl_2$	pentaammine(dinitrogen)ruthenium(2 +)chloride pentaammine(dinitrogen)ruthenium(II) chloride

---

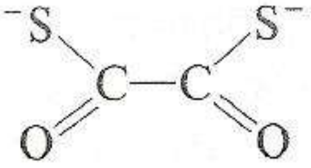
[4] Normallyphenyl would not be placed within enclosing marks. They are used here to avoid confusion with a chlorophenyl radical.

Water and ammonia as neutral ligands in coordination complexes are called "aqua" (formerly "aquo") and "ammine," respectively. The groups NO and CO, when linked directly to a metal atom, are called "nitrosyl" and "carbonyl," respectively. In computing the oxidation number these ligands are treated as neutral.

$[Cr(H_2O)_6]Cl_3$	hexaaquachromium(3+) chloride hexaaquachromium trichloride
$Na_2[Fe(CN)_5NO]$	sodium pentacyanonitrosylferrate(2−) sodium pentacyanonitrosylferrate(III)
$K_3[Fe(CN)_5CO]$	potassium carbonylpentacyanoferrate(3−) potassium carbonylpentacyanoferrate(II)

Alternative modes of linkage of some ligands

The different points of attachment of a ligand may be denoted by adding the italicized symbol(s) for the atom or atoms through which attachment occurs at the end of the name of the ligand. Thus the dithiooxalato anion



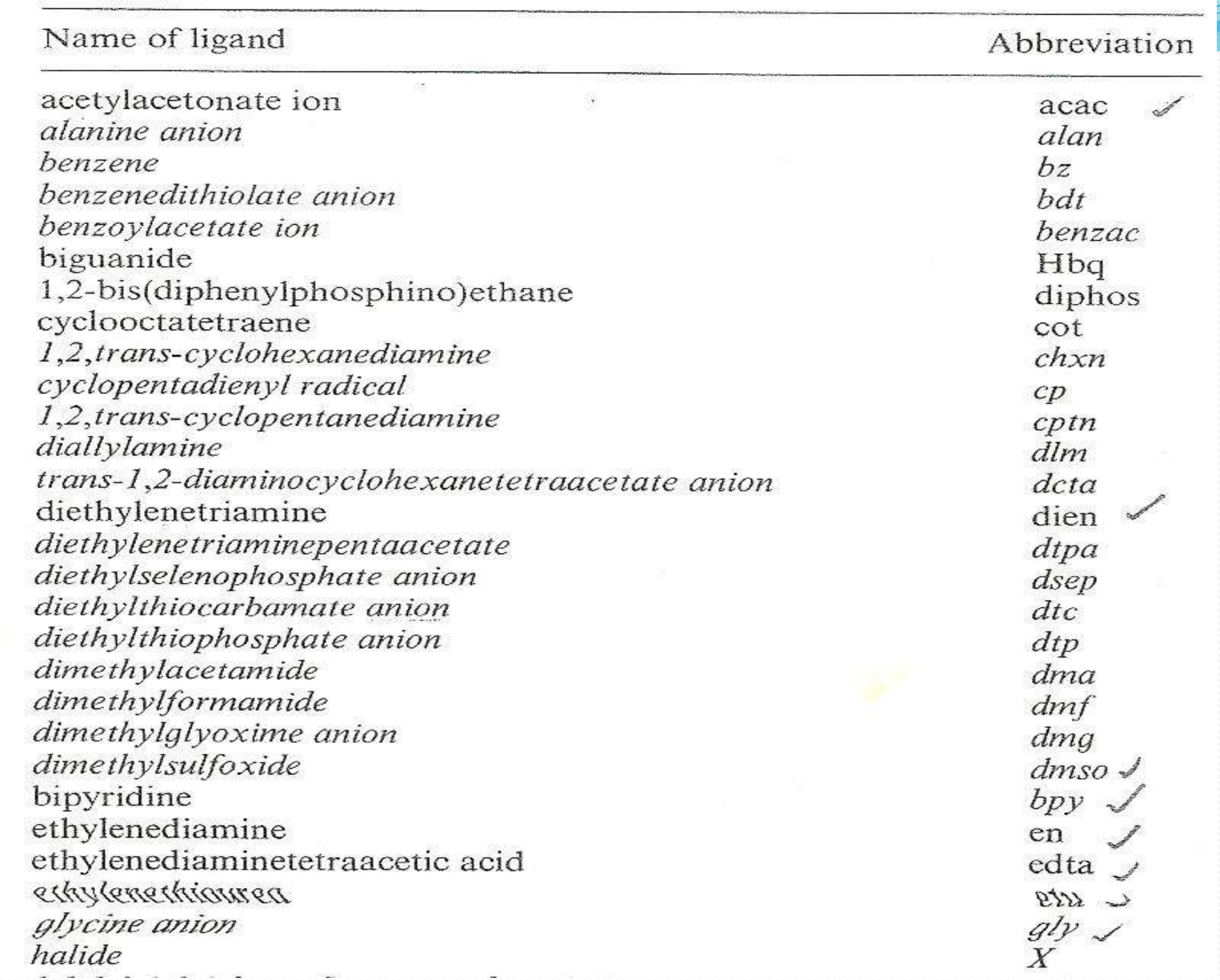
conceivably may be attached through S or O, and these are distinguished as dithiooxalato-*S,S′* and dithiooxalato-*O,O′*, respectively.

In some cases different names are already in use for alternative modes of attachment as, for example, thiocyanato (—SCN) and isothiocyanato (—NCS), nitro (—NO_2), and nitrito (—ONO).

$Na_3[Co(NO_2)_6]$	sodium hexanitrocobaltate(3−) sodium hexanitrocobaltate(III)
$[Co(ONO)(NH_3)_5]SO_4$	pentaamminenitritocobalt(2+) sulfate pentaamminenitritocobalt(III) sulfate
$[Co(NCS)(NH_3)_5]Cl_2$	pentaammineisothiocyanatocobalt(2+) chloride pentaammineisothiocyanatocobalt(III) chloride

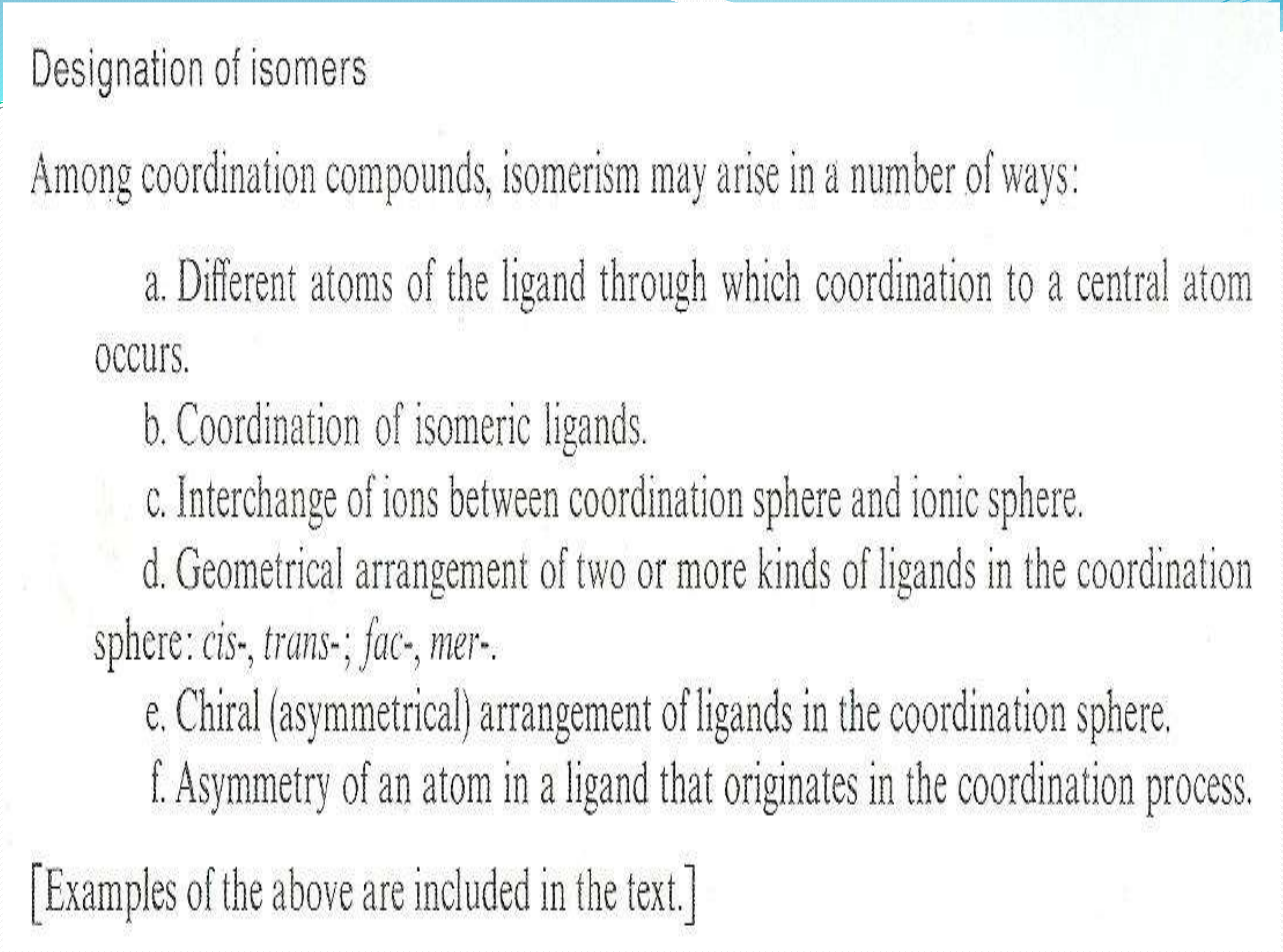
Use of abbreviations

In the literature of coordination compounds, abbreviations for ligand names are used extensively, especially in formulae. A list of common abbreviations is given below. [The IUPAC list is rather short. Additional abbreviations used in this book or in the current literature are included in the following list (italicized). It should be noted that often these are used as capital letters (e.g., EDTA) but should be lower case (edta) according to the Rules.]



Name of ligand	Abbreviation
acetylacetonate ion	acac ✓
alanine anion	*alan*
benzene	*bz*
benzenedithiolate anion	*bdt*
benzoylacetate ion	*benzac*
biguanide	Hbq
1,2-bis(diphenylphosphino)ethane	diphos
cyclooctatetraene	cot
1,2,trans-cyclohexanediamine	*chxn*
cyclopentadienyl radical	*cp*
1,2,trans-cyclopentanediamine	*cptn*
diallylamine	*dlm*
trans-1,2-diaminocyclohexanetetraacetate anion	*dcta*
diethylenetriamine	dien ✓
diethylenetriaminepentaacetate	*dtpa*
diethylselenophosphate anion	*dsep*
diethylthiocarbamate anion	*dtc*
diethylthiophosphate anion	*dtp*
dimethylacetamide	*dma*
dimethylformamide	*dmf*
dimethylglyoxime anion	*dmg*
dimethylsulfoxide	*dmso* ✓
bipyridine	*bpy* ✓
ethylenediamine	en ✓
ethylenediaminetetraacetic acid	edta ✓
ethylenethiourea	etu ✓
glycine anion	*gly* ✓
halide	*X*

1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione	*fod*
N-hydroxyethylethylenediaminetriacetate anion	*hedta*
any unspecified ligand	*L*
maleonitriledithiolate anion	*mnt*
methylbis(3-dimethy arsinopropyl)arsine	*tas*
nitrilotriacetate anion	*nta*
oxalate dibasic anion	ox
1,10-phenanthroline	phen
o-phenylenebis(dimethylarsine)	diars
1-phosphabicyclo[2.2.2]octane	*phosph*
phthalocyanine (dinegative group)	*pc*
propylenediamine (1,2-diaminopropane)	pn
pyridine	py ✓
stilbenediamine (1,2-diphenylethylenediamine)	*stien*
2,2,6,6-tetramethylheptane-3,5-dione	*thd*
2,2′,2″,2‴-tetrapyridyl	*tetrpy*
thenoyltrifluoroacetone	*tta*
thiourea	*tu*
toluene-3,4-dithiolate anion	*tdt*
1,2,3-triaminopropane	*tn*
2,2′,2″-triaminotriethylamine	tren
trimethylenetetramine	trien
trimethylenediamine	*trim*



Designation of isomers

Among coordination compounds, isomerism may arise in a number of ways:

a. Different atoms of the ligand through which coordination to a central atom occurs.

b. Coordination of isomeric ligands.

c. Interchange of ions between coordination sphere and ionic sphere.

d. Geometrical arrangement of two or more kinds of ligands in the coordination sphere: *cis*-, *trans*-; *fac*-, *mer*-.

e. Chiral (asymmetrical) arrangement of ligands in the coordination sphere.

f. Asymmetry of an atom in a ligand that originates in the coordination process.

[Examples of the above are included in the text.]

Compounds with bridging atoms or groups

a. A bridging group is indicated by adding the Greek letter μ immediately before its name and separating the name from the rest of the complex by hyphens.

b. Two or more bridging groups of the same kind are indicated by di-μ- (or bis-μ-), etc.

c. The bridging groups are listed with the other groups in alphabetical order *unless the symmetry of the molecule permits simpler names by the use of multiplicative prefixes.*

d. Where the same ligand is present as a bridging ligand and as a non-bridging ligand, it is cited first as a bridging ligand.

Bridging groups between two centers of coordination are of two types: (1) the two centers are attached to the same atom of the bridging group and (2) the two centers are attached to different atoms of the bridging group. For bridging groups of the first type it is often desirable to indicate the bridging atom. This is done by adding the italicized symbol for the atom at the end of the name of the ligand. For bridging groups of the second type, the symbols of all coordinated atoms are added.

$[(NH_3)_5Cr{-}OH{-}Cr(NH_3)_5]Cl_5$	μ-hydroxobis(pentaamminechromium)(5+) chloride μ-hydroxobis[pentaamminechromium(III)] chloride
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	tri-μ-carbonylbis(tricarbonyliron)
$[Br_2Pt(SMe_2)_2PtBr_2]$	bis(μ-dimethylsulfide)bis-[dibromoplatinum(II)]

Di- and polynuclear compounds without bridging groups; direct linking between centers of coordination

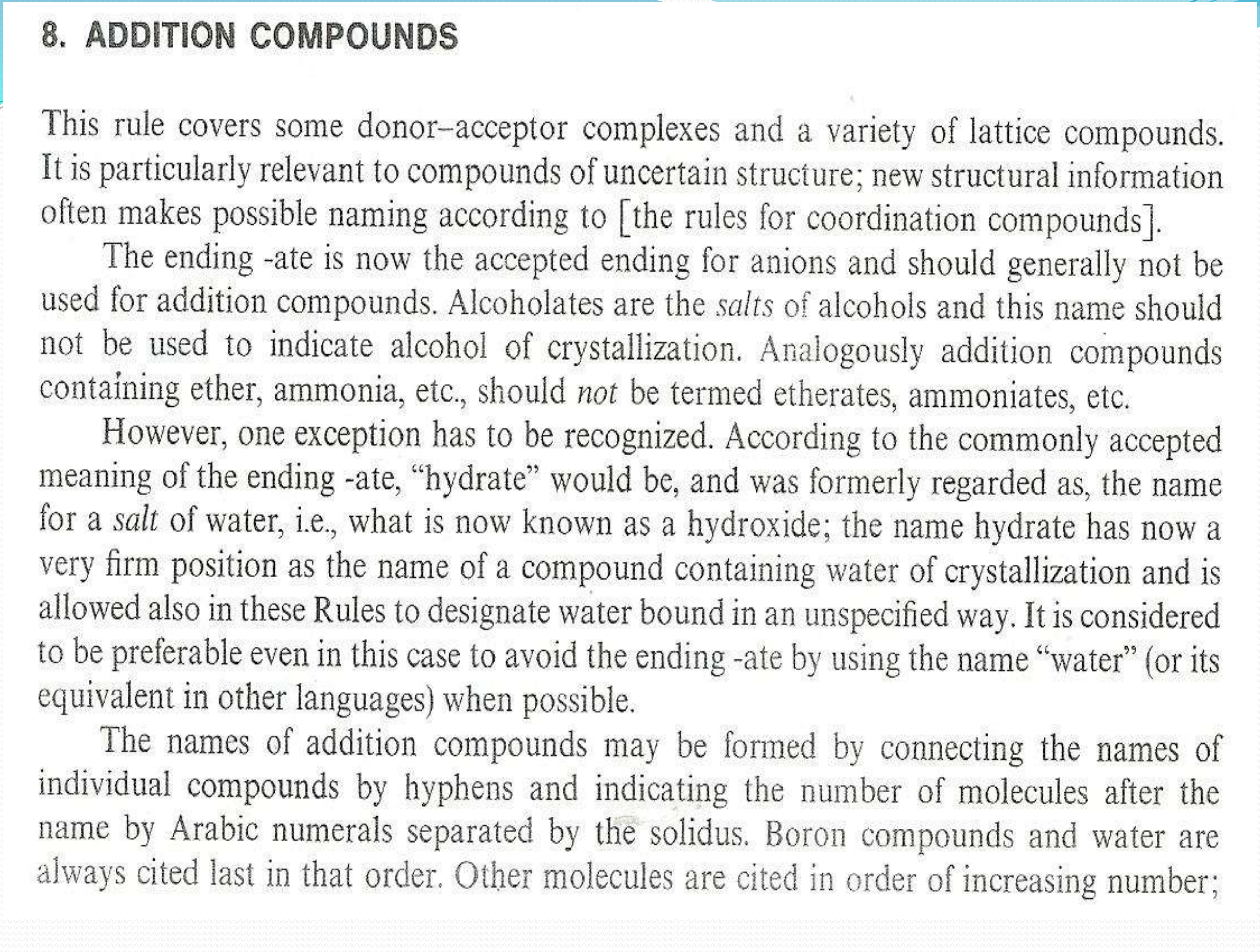
There are a number of compounds containing metal–metal bonds. Such compounds, when symmetrical, are named by the use of multiplicative prefixes; when unsymmetrical, one central atom and its attached ligands shall be treated as a ligand on the other center.

$[\mathrm{Br_4Re{-}ReBr_4}]^{2-}$	bis(tetrabromorhenate)(2−) bis[tetrabromorhenate(II)]
$[\mathrm{(CO)_5Mn{-}Mn(CO)_5}]$	bis(pentacarbonylmanganese)
$[\mathrm{(CO)_4Co{-}Re(CO)_5}]$	pentacarbonyl(tetracarbonylcobaltio)rhenium
$[\eta\text{-}\mathrm{C_5H_5(CO)_3Mo{-}Mo(CO)_3}\text{-}\eta\text{-}\mathrm{C_5H_5}]$	bis(tricarbonyl-η-cyclopentadienylmolybdenum)
$[\mathrm{(Cl_3Sn)_2RhCl_2Rh(SnCl_3)_2}]^{4-}$	di-μ-chloro-bis[bis(trichlorostannyl)rhodate](4−) ion di-μ-chloro-bis[bis(trichlorostannyl)rhodate(I)] ion

Homoatomic aggregates

There are several instances of a finite group of metal atoms with bonds directly between the metal atoms but also with some nonmetal atoms or groups (ligands) intimately associated with the *cluster*. The geometrical shape of the cluster is designated by *triangulo*, *quadro*, *tetrahedro*, *octahedro*, etc., and the nature of the bonds to the ligands by the conventions for bridging bonds and simple bonds. Numbers are used as locant designators as they are for homoatomic chains and boron clusters (cf. Rules for Boron Compounds).

$\mathrm{Os_3(CO)_{12}}$	dodecacarbonyl-*triangulo*-triosmium
$\mathrm{Cs_3[Re_3Cl_{12}]}$	cesium dodecachloro-*triangulo*-trirhenate(3−) tricesium dodecachloro-*triangulo*-trirhenate
$\mathrm{B_4Cl_4}$	tetrachloro-*tetrahedro*-tetraboron
$[\mathrm{Nb_6Cl_{12}}]^{2+}$	dodeca-μ-chloro-*octahedro*-hexaniobium(2+) ion



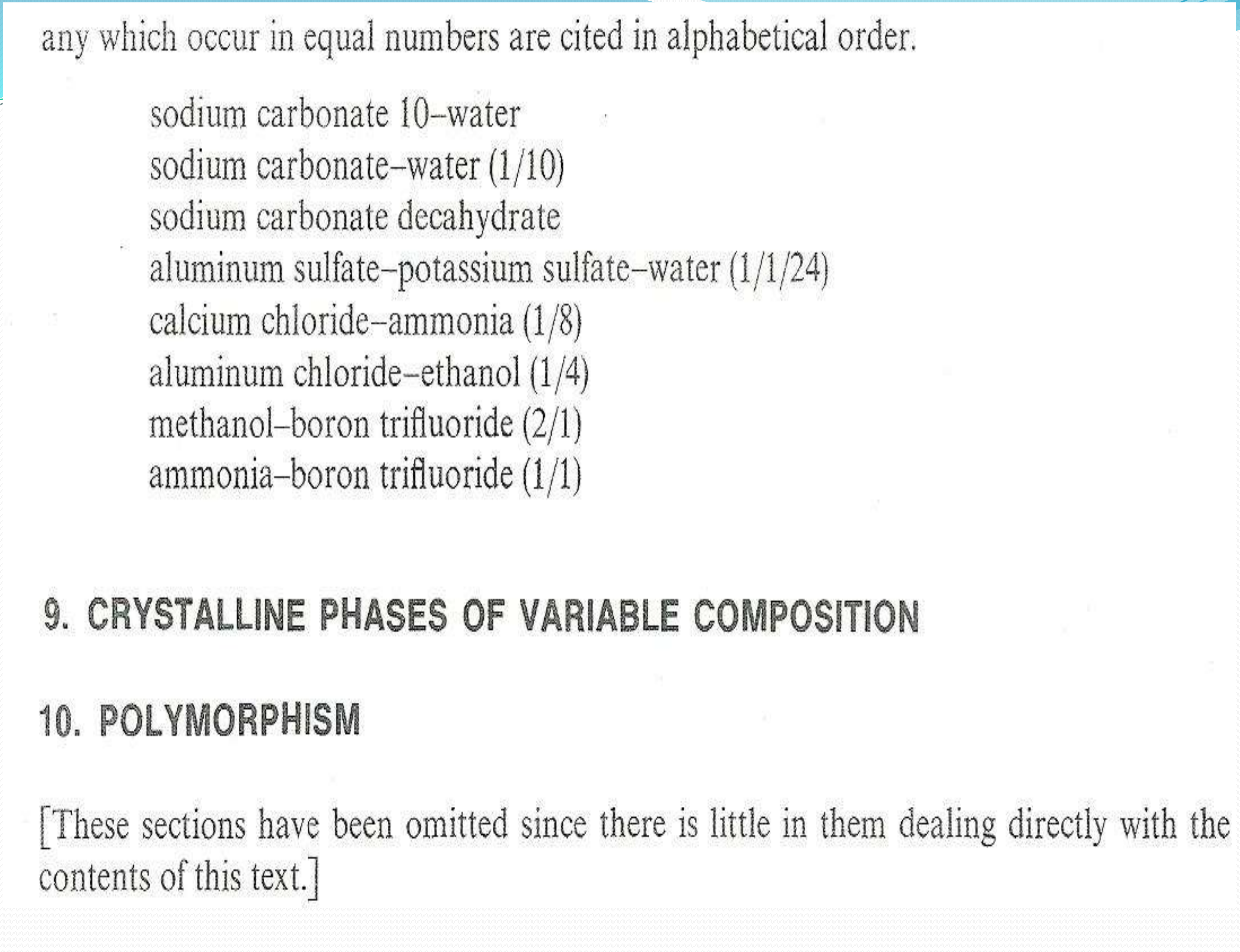
8. ADDITION COMPOUNDS

This rule covers some donor–acceptor complexes and a variety of lattice compounds. It is particularly relevant to compounds of uncertain structure; new structural information often makes possible naming according to [the rules for coordination compounds].

The ending -ate is now the accepted ending for anions and should generally not be used for addition compounds. Alcoholates are the *salts* of alcohols and this name should not be used to indicate alcohol of crystallization. Analogously addition compounds containing ether, ammonia, etc., should *not* be termed etherates, ammoniates, etc.

However, one exception has to be recognized. According to the commonly accepted meaning of the ending -ate, "hydrate" would be, and was formerly regarded as, the name for a *salt* of water, i.e., what is now known as a hydroxide; the name hydrate has now a very firm position as the name of a compound containing water of crystallization and is allowed also in these Rules to designate water bound in an unspecified way. It is considered to be preferable even in this case to avoid the ending -ate by using the name "water" (or its equivalent in other languages) when possible.

The names of addition compounds may be formed by connecting the names of individual compounds by hyphens and indicating the number of molecules after the name by Arabic numerals separated by the solidus. Boron compounds and water are always cited last in that order. Other molecules are cited in order of increasing number;



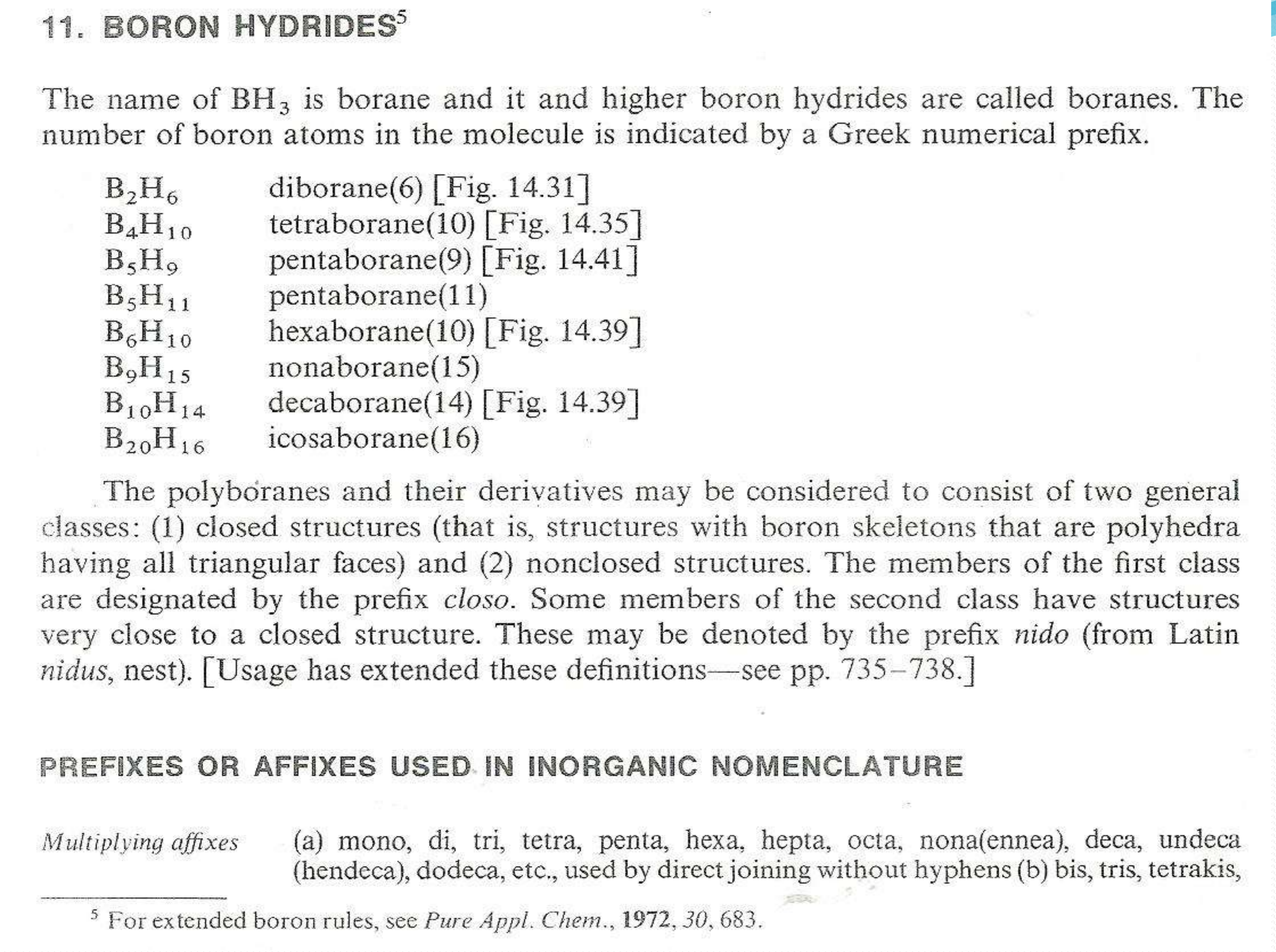
any which occur in equal numbers are cited in alphabetical order.

sodium carbonate 10–water
sodium carbonate–water (1/10)
sodium carbonate decahydrate
aluminum sulfate–potassium sulfate–water (1/1/24)
calcium chloride–ammonia (1/8)
aluminum chloride–ethanol (1/4)
methanol–boron trifluoride (2/1)
ammonia–boron trifluoride (1/1)

9. CRYSTALLINE PHASES OF VARIABLE COMPOSITION

10. POLYMORPHISM

[These sections have been omitted since there is little in them dealing directly with the contents of this text.]



11. BORON HYDRIDES[5]

The name of BH_3 is borane and it and higher boron hydrides are called boranes. The number of boron atoms in the molecule is indicated by a Greek numerical prefix.

B_2H_6	diborane(6) [Fig. 14.31]
B_4H_{10}	tetraborane(10) [Fig. 14.35]
B_5H_9	pentaborane(9) [Fig. 14.41]
B_5H_{11}	pentaborane(11)
B_6H_{10}	hexaborane(10) [Fig. 14.39]
B_9H_{15}	nonaborane(15)
$B_{10}H_{14}$	decaborane(14) [Fig. 14.39]
$B_{20}H_{16}$	icosaborane(16)

The polyboranes and their derivatives may be considered to consist of two general classes: (1) closed structures (that is, structures with boron skeletons that are polyhedra having all triangular faces) and (2) nonclosed structures. The members of the first class are designated by the prefix *closo*. Some members of the second class have structures very close to a closed structure. These may be denoted by the prefix *nido* (from Latin *nidus*, nest). [Usage has extended these definitions—see pp. 735–738.]

PREFIXES OR AFFIXES USED IN INORGANIC NOMENCLATURE

Multiplying affixes	(a) mono, di, tri, tetra, penta, hexa, hepta, octa, nona(ennea), deca, undeca (hendeca), dodeca, etc., used by direct joining without hyphens (b) bis, tris, tetrakis,

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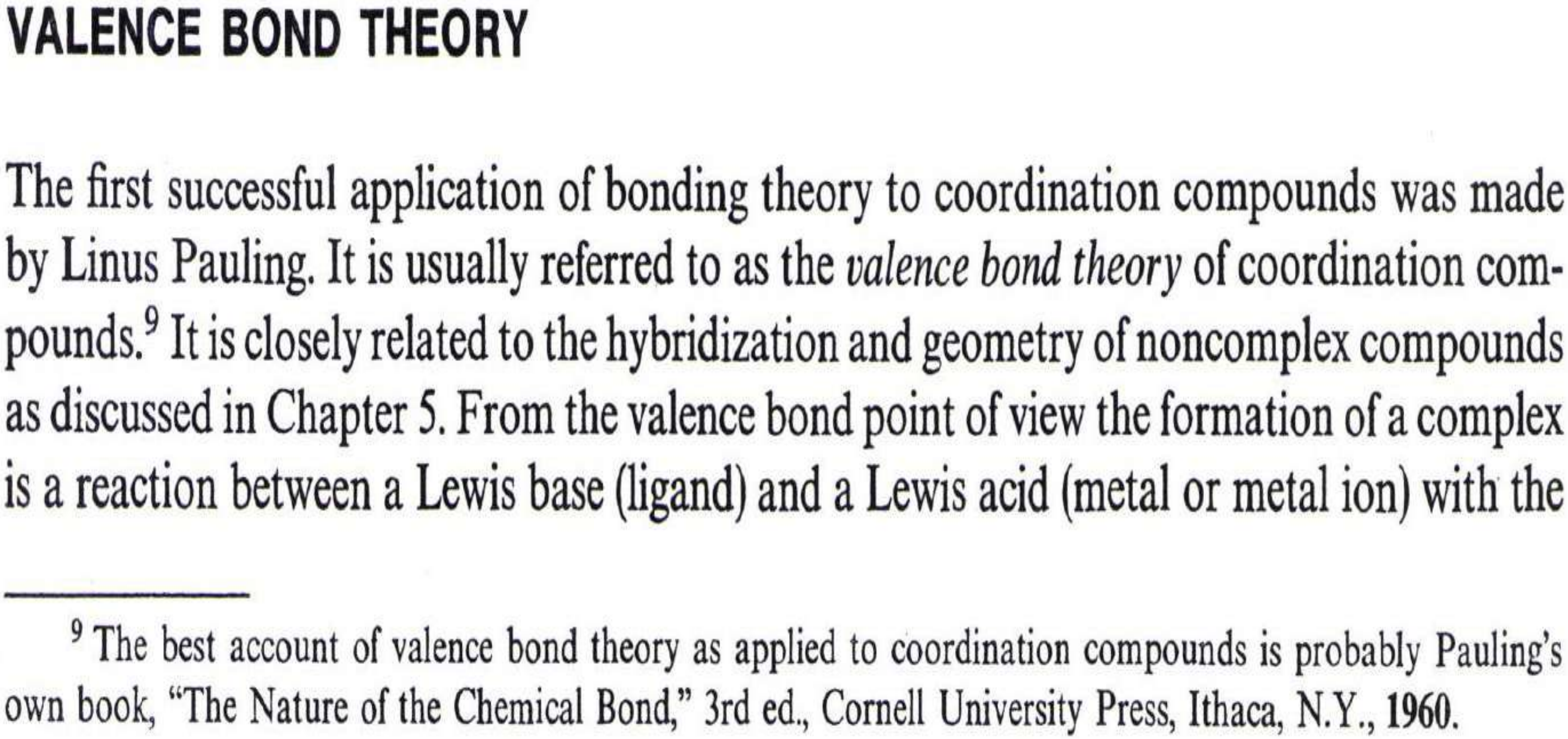
[5] For extended boron rules, see *Pure Appl. Chem.*, **1972**, *30*, 683.

	pentakis, etc., used by direct joining without hyphens but usually with enclosing marks around each whole expression to which the prefix applies
Structural affixes	italicized and separated from the rest of the name by hyphens
antiprismo	eight atoms bound into a rectangular antiprism
asym	asymmetrical
catena	a chain structure; often used to designate linear polymeric substances
cis	two groups occupying adjacent positions; sometimes used in the sense of *fac*
closo	a cage or closed structure, especially a boron skeleton that is a polyhedron having all triangular faces
cyclo	a ring structure[6]
dodecahedro	eight atoms bound into a dodecahedron with triangular faces
fac	three groups occupying the corners of the same face of an octahedron
hexahedro	eight atoms bound into a hexahedron (e.g., cube)
hexaprismo	twelve atoms bound into a hexagonal prism
icosahedro	twelve atoms bound into a triangular icosahedron
mer	meridional; three groups on an octahedron in such a relationship that one is *cis* to the two others which are themselves *trans*
nido	a nest-like structure, especially a boron skeleton that is very close to a closed or closo structure
octahedro	six atoms bound into an octahedron
pentaprismo	ten atoms bound into a pentagonal prism
quadro	four atoms bound into a quadrangle (e.g., square)
sym	symmetrical
tetrahedro	four atoms bound into a tetrahedron
trans	two groups directly across a central atom from each other; i.e., in the polar position on a sphere
triangulo	three atoms bound into a triangle
triprismo	six atoms bound into a triangular prism
η	signifies that two or more contiguous atoms of the group are attached to a metal
μ	signifies that the group so designated bridges two centers of coordination
σ	signifies that one atom of the group is attached to a metal

VALANCE BOND THEORY



VALENCE BOND THEORY

The first successful application of bonding theory to coordination compounds was made by Linus Pauling. It is usually referred to as the *valence bond theory* of coordination compounds.[9] It is closely related to the hybridization and geometry of noncomplex compounds as discussed in Chapter 5. From the valence bond point of view the formation of a complex is a reaction between a Lewis base (ligand) and a Lewis acid (metal or metal ion) with the

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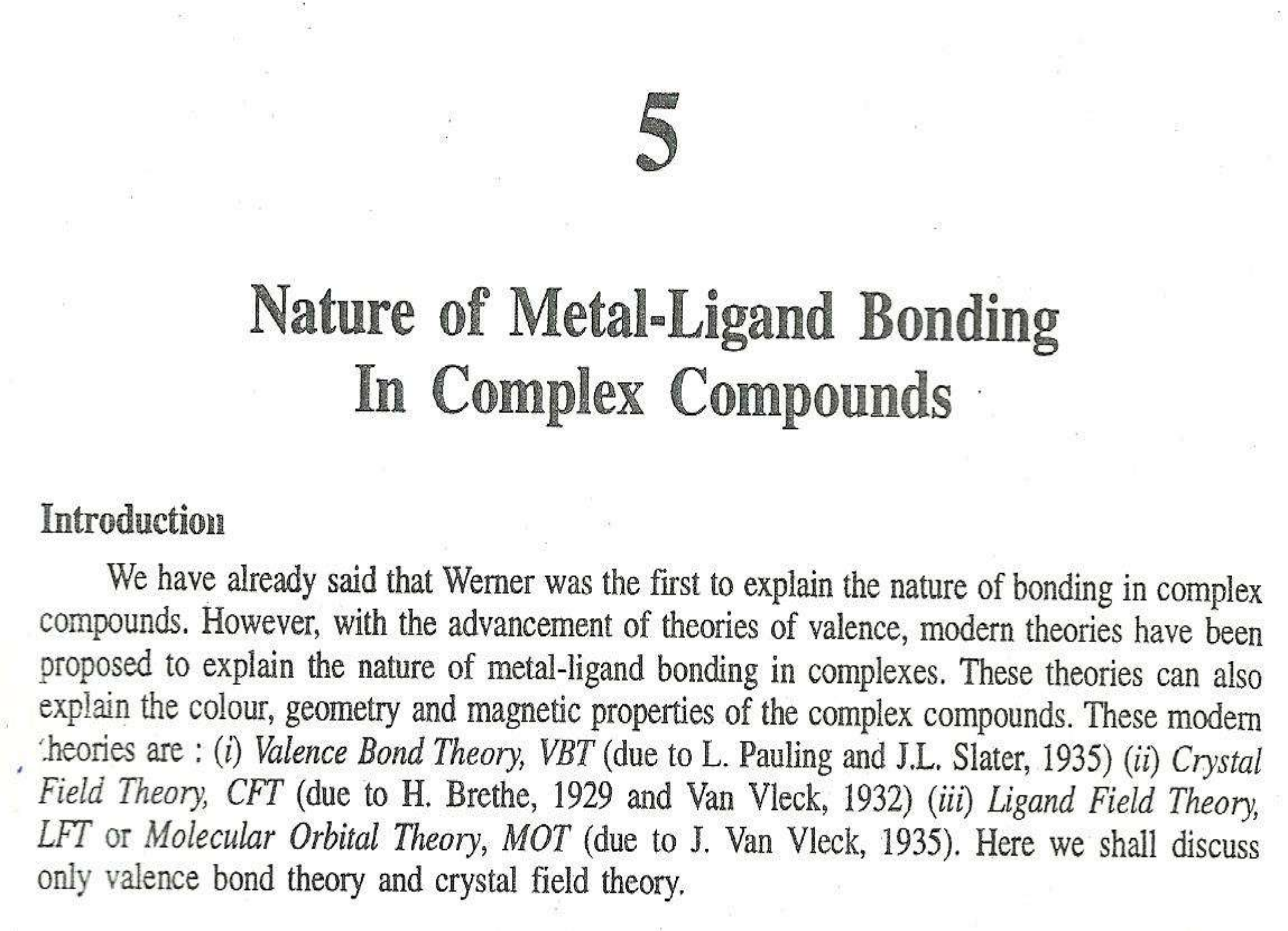
[9] The best account of valence bond theory as applied to coordination compounds is probably Pauling's own book, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N.Y., **1960**.

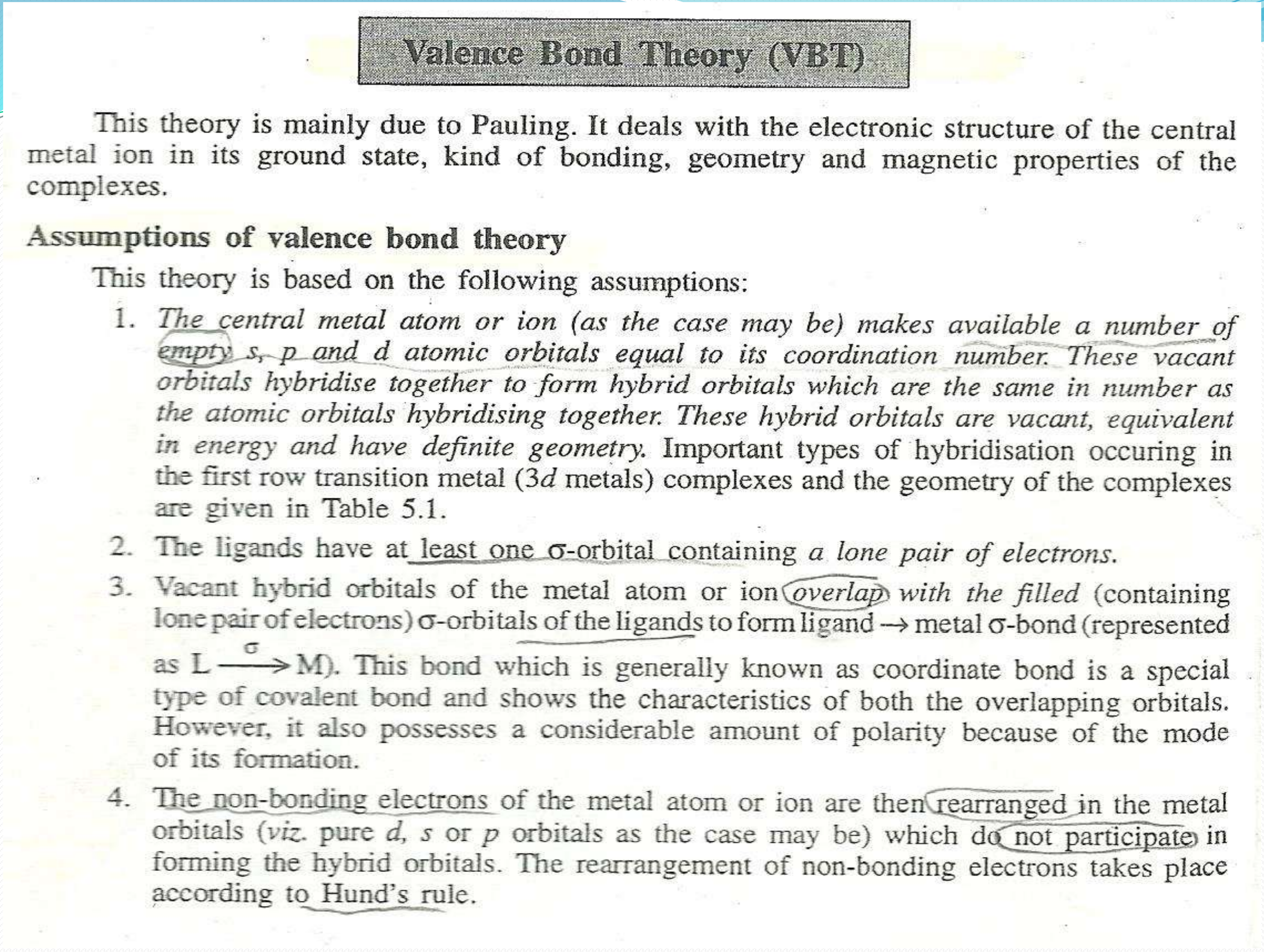


5

Nature of Metal-Ligand Bonding In Complex Compounds

Introduction

We have already said that Werner was the first to explain the nature of bonding in complex compounds. However, with the advancement of theories of valence, modern theories have been proposed to explain the nature of metal-ligand bonding in complexes. These theories can also explain the colour, geometry and magnetic properties of the complex compounds. These modern theories are : (*i*) *Valence Bond Theory, VBT* (due to L. Pauling and J.L. Slater, 1935) (*ii*) *Crystal Field Theory, CFT* (due to H. Brethe, 1929 and Van Vleck, 1932) (*iii*) *Ligand Field Theory, LFT* or *Molecular Orbital Theory, MOT* (due to J. Van Vleck, 1935). Here we shall discuss only valence bond theory and crystal field theory.



Valence Bond Theory (VBT)

This theory is mainly due to Pauling. It deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

Assumptions of valence bond theory

This theory is based on the following assumptions:

1. *The central metal atom or ion (as the case may be) makes available a number of empty s, p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry.* Important types of hybridisation occuring in the first row transition metal (3*d* metals) complexes and the geometry of the complexes are given in Table 5.1.
2. The ligands have at least one σ-orbital containing *a lone pair of electrons.*
3. Vacant hybrid orbitals of the metal atom or ion *overlap with the filled* (containing lone pair of electrons) σ-orbitals of the ligands to form ligand → metal σ-bond (represented as $L \xrightarrow{\sigma} M$). This bond which is generally known as coordinate bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.
4. The non-bonding electrons of the metal atom or ion are then rearranged in the metal orbitals (*viz.* pure *d*, *s* or *p* orbitals as the case may be) which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's rule.

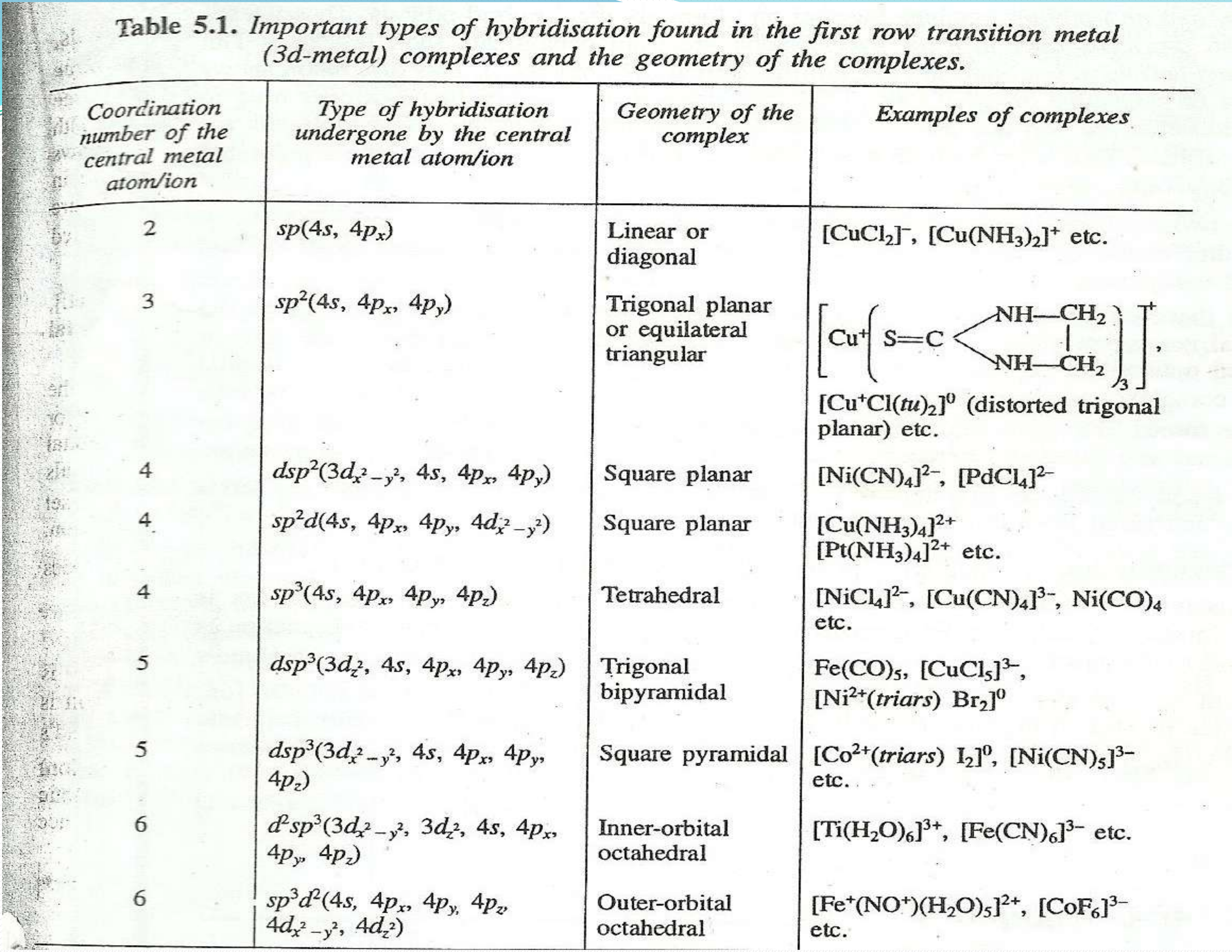
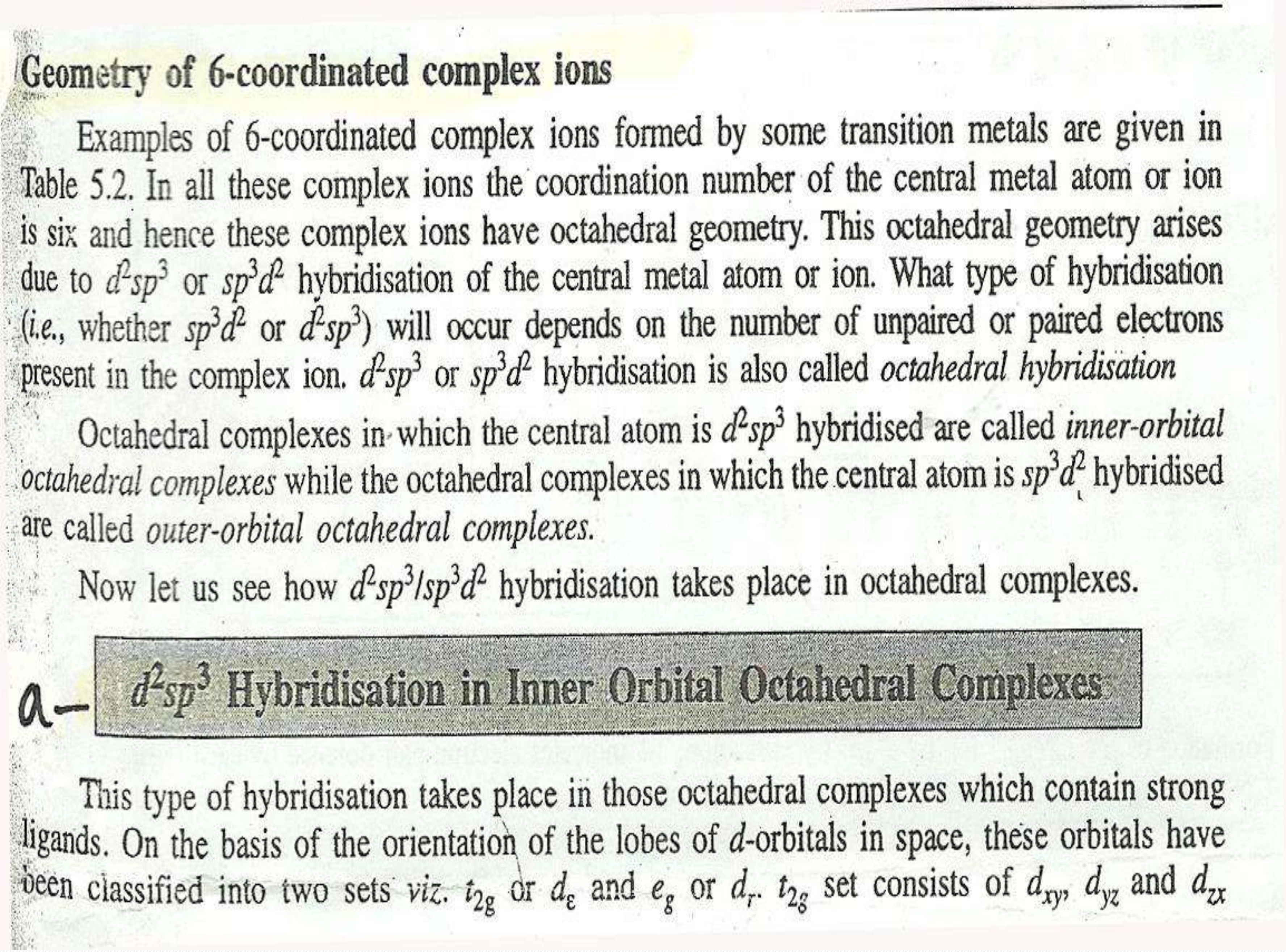


Table 5.1. *Important types of hybridisation found in the first row transition metal (3d-metal) complexes and the geometry of the complexes.*

Coordination number of the central metal atom/ion	*Type of hybridisation undergone by the central metal atom/ion*	*Geometry of the complex*	*Examples of complexes*
2	$sp(4s, 4p_x)$	Linear or diagonal	$[CuCl_2]^-$, $[Cu(NH_3)_2]^+$ etc.
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar or equilateral triangular	$\left[Cu^+\left(S{=}C\langle{NH-CH_2 \atop NH-CH_2}\right)_3\right]^+$, $[Cu^+Cl(tu)_2]^0$ (distorted trigonal planar) etc.
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$
4	$sp^2d(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$	Square planar	$[Cu(NH_3)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$ etc.
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $Ni(CO)_4$ etc.
5	$dsp^3(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$, $[Ni^{2+}(triars)\ Br_2]^0$
5	$dsp^3(3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$	Square pyramidal	$[Co^{2+}(triars)\ I_2]^0$, $[Ni(CN)_5]^{3-}$ etc.
6	$d^2sp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2})$	Outer-orbital octahedral	$[Fe^+(NO^+)(H_2O)_5]^{2+}$, $[CoF_6]^{3-}$ etc.



Geometry of 6-coordinated complex ions

Examples of 6-coordinated complex ions formed by some transition metals are given in Table 5.2. In all these complex ions the coordination number of the central metal atom or ion is six and hence these complex ions have octahedral geometry. This octahedral geometry arises due to d^2sp^3 or sp^3d^2 hybridisation of the central metal atom or ion. What type of hybridisation (*i.e.*, whether sp^3d^2 or d^2sp^3) will occur depends on the number of unpaired or paired electrons present in the complex ion. d^2sp^3 or sp^3d^2 hybridisation is also called *octahedral hybridisation*

Octahedral complexes in which the central atom is d^2sp^3 hybridised are called *inner-orbital octahedral complexes* while the octahedral complexes in which the central atom is sp^3d^2 hybridised are called *outer-orbital octahedral complexes.*

Now let us see how d^2sp^3/sp^3d^2 hybridisation takes place in octahedral complexes.

a– d^2sp^3 Hybridisation in Inner Orbital Octahedral Complexes

This type of hybridisation takes place in those octahedral complexes which contain strong ligands. On the basis of the orientation of the lobes of *d*-orbitals in space, these orbitals have been classified into two sets *viz.* t_{2g} or d_ε and e_g or d_γ. t_{2g} set consists of d_{xy}, d_{yz} and d_{zx}

orbitals while e_g set has d_{z^2} and $d_{x^2-y^2}$ orbitals. In the formation of six d^2sp^3 hybrid orbitals, *two* $(n-1)$ *d*-orbitals of e_g set [*i.e.*, $(n-1)d_{z^2}$ and $(n-1)$ $d_{x^2-y^2}$ orbitals], *one ns* and *three np* (np_x, np_y and np_z) orbitals combine together and form six d^2sp^3 hybrid orbitals. Thus we see that the two *d*-orbitals used in d^2sp^3 hybridisation are from penultimate shell [*i.e.* $(n-1)$th shell] while *s* and three *p*-orbitals are from ultimate shell (*i.e.*, *n*th shell). This discussion shows that in case of octahedral complex ions of 3*d* transition series elements, two *d*-orbitals used in d^2sp^3 hybridisation are $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals (e_g set of orbitals) while *s*- and *p*-orbitals are 4*s* and 4*p* orbitals. Thus d^2sp^3 hybridisation taking place in such complexes can be represented as $3d_{x^2-y^2}.3d_{z^2}.4s.4p_x.4p_y\ 4p_z(d^2sp^3)$.

Since two *d*-orbitals used in d^2sp^3 hybridisation belong to inner shell [*i.e.*, $(n-1)$th shell], the octahedral complex compounds resulted from d^2sp^3 hybridisation are called **inner orbital octahedral complexes.**

Since these complexes have comparatively lesser number of unpaired electrons than the outer-orbital octahedral complexes (see later on), these complexes are also called **low spin** or **spin paired octahedral complexes.** It is due to the presence of strong ligands in inner-orbital octahedral complexes of 3*d* transition series that the electrons present in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals (e_g set) are forced to occupy $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals (t_{2g} set) and thus 3*d* orbitals of e_g set become vacant and hence can be used in $3d_{x^2-y^2}$. $3d_{z^2}$. 4*s*. $4p_x$. $4p_y$. $4p_z$ (d^2sp^3) hybridisation.

Now let us discuss the structure of some octahedral complex ions of 3*d* transition series elements which result from d^2sp^3 hybridisation.

1. Ferricyanide ion, $[Fe(CN)_6]^{3-}$ [Also called hexacynoferrate (III) ion]

In this ion the coordination number of Fe is six and hence the given complex ion is octahedral in shape. In this ion, Fe is present as Fe^{3+} ion whose valence-shell configuration is $3d^5$ or $t_{2g}^3\ e_g^2$ (Fe = $3d^6 4s^2 4p^0$, $Fe^{3+} = 3d^5 = t_{2g}^3\ e_g^2$) as shown in Fig. 5.1. According to Hund's rule, each of the five electrons in 3*d* orbitals is unpaired in free Fe^{3+} ion (uncomplexed ion) and hence the number of unpaired electrons (*n*) is equal to 5 (see Fig. 5.1). However, magnetic study of $[Fe(CN)_6]^{3-}$ ion has shown that this ion has one unpaired electron ($n = 1$) and hence

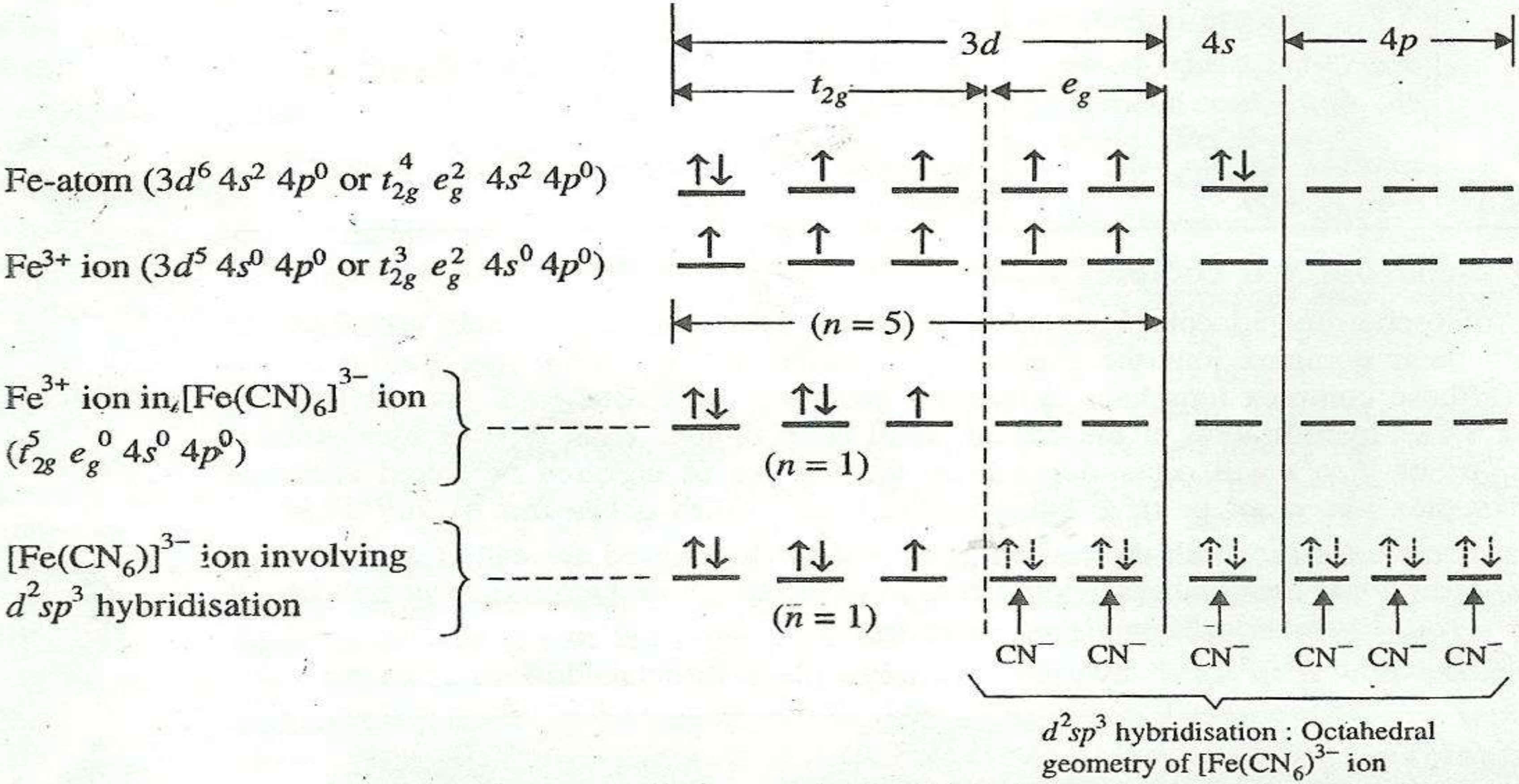
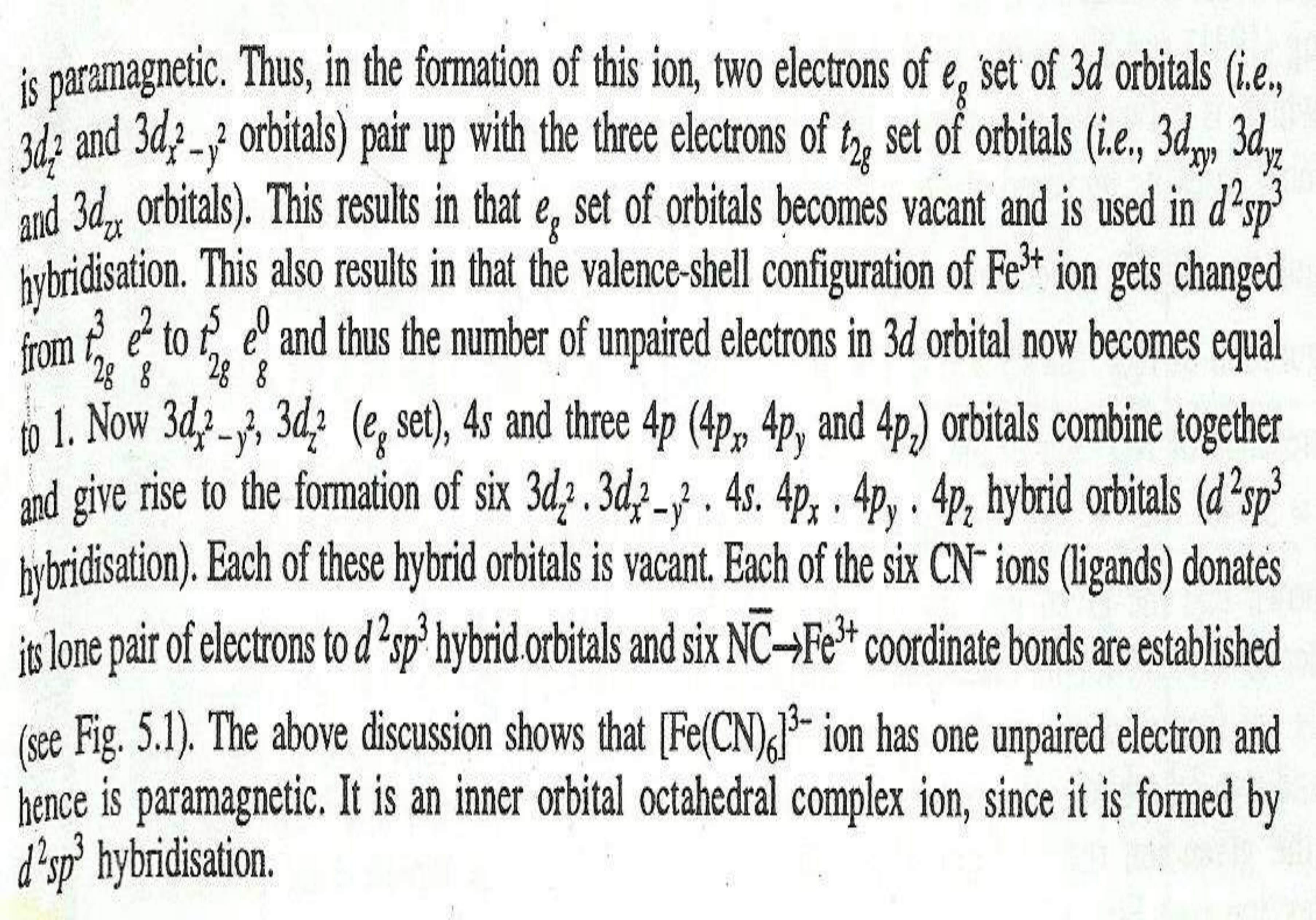
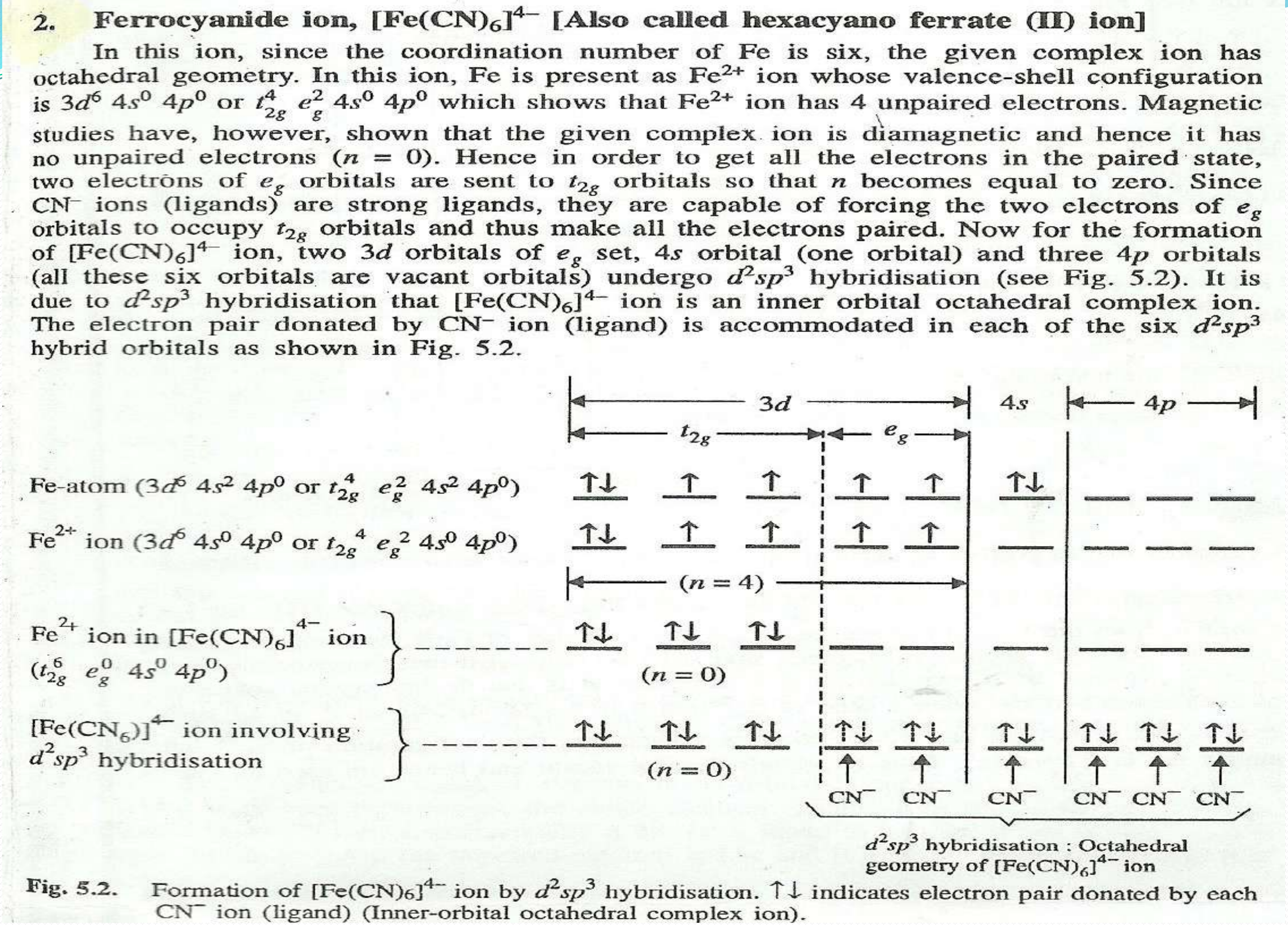


Fig. 5.1. Formation of $[Fe(CN)_6]^{3-}$ ion by d^2sp^3 hybridisation. ↑↓ indicates electron pair donated by each CN^- ion (ligand). (Inner-orbital octahedral complex ion).



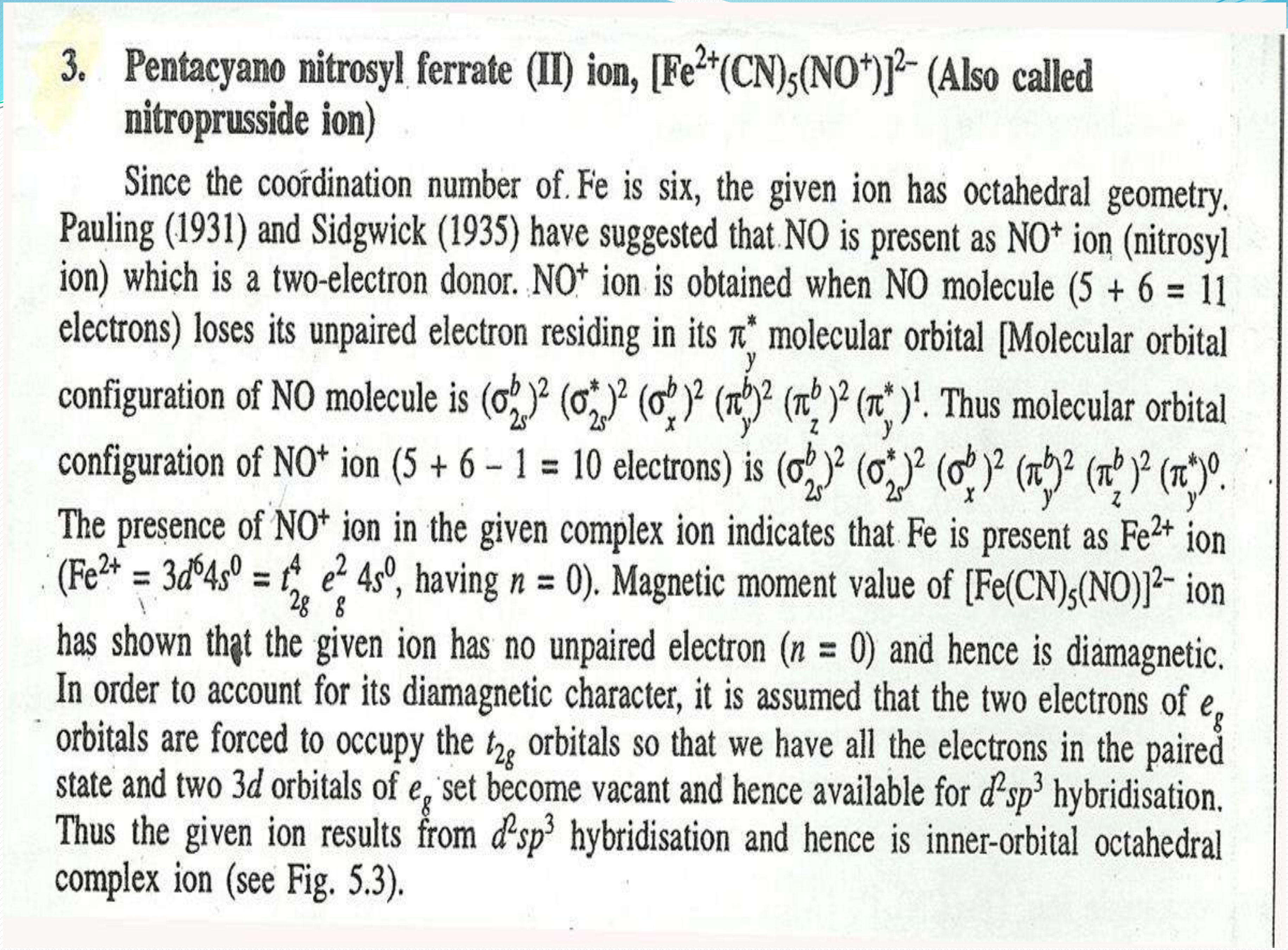
is paramagnetic. Thus, in the formation of this ion, two electrons of e_g set of 3*d* orbitals (*i.e.*, $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals) pair up with the three electrons of t_{2g} set of orbitals (*i.e.*, $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ orbitals). This results in that e_g set of orbitals becomes vacant and is used in d^2sp^3 hybridisation. This also results in that the valence-shell configuration of Fe^{3+} ion gets changed from $t_{2g}^3\ e_g^2$ to $t_{2g}^5\ e_g^0$ and thus the number of unpaired electrons in 3*d* orbital now becomes equal to 1. Now $3d_{x^2-y^2}$, $3d_{z^2}$ (e_g set), 4*s* and three 4*p* ($4p_x$, $4p_y$ and $4p_z$) orbitals combine together and give rise to the formation of six $3d_{z^2} . 3d_{x^2-y^2} . 4s. 4p_x . 4p_y . 4p_z$ hybrid orbitals (d^2sp^3 hybridisation). Each of these hybrid orbitals is vacant. Each of the six CN^- ions (ligands) donates its lone pair of electrons to d^2sp^3 hybrid orbitals and six $N\overline{C} \to Fe^{3+}$ coordinate bonds are established (see Fig. 5.1). The above discussion shows that $[Fe(CN)_6]^{3-}$ ion has one unpaired electron and hence is paramagnetic. It is an inner orbital octahedral complex ion, since it is formed by d^2sp^3 hybridisation.



2. Ferrocyanide ion, $[Fe(CN)_6]^{4-}$ [Also called hexacyano ferrate (II) ion]

In this ion, since the coordination number of Fe is six, the given complex ion has octahedral geometry. In this ion, Fe is present as Fe^{2+} ion whose valence-shell configuration is $3d^6\ 4s^0\ 4p^0$ or $t_{2g}^4\ e_g^2\ 4s^0\ 4p^0$ which shows that Fe^{2+} ion has 4 unpaired electrons. Magnetic studies have, however, shown that the given complex ion is diamagnetic and hence it has no unpaired electrons ($n = 0$). Hence in order to get all the electrons in the paired state, two electrons of e_g orbitals are sent to t_{2g} orbitals so that n becomes equal to zero. Since CN^- ions (ligands) are strong ligands, they are capable of forcing the two electrons of e_g orbitals to occupy t_{2g} orbitals and thus make all the electrons paired. Now for the formation of $[Fe(CN)_6]^{4-}$ ion, two $3d$ orbitals of e_g set, $4s$ orbital (one orbital) and three $4p$ orbitals (all these six orbitals are vacant orbitals) undergo d^2sp^3 hybridisation (see Fig. 5.2). It is due to d^2sp^3 hybridisation that $[Fe(CN)_6]^{4-}$ ion is an inner orbital octahedral complex ion. The electron pair donated by CN^- ion (ligand) is accommodated in each of the six d^2sp^3 hybrid orbitals as shown in Fig. 5.2.

Fig. 5.2. Formation of $[Fe(CN)_6]^{4-}$ ion by d^2sp^3 hybridisation. ↑↓ indicates electron pair donated by each CN^- ion (ligand) (Inner-orbital octahedral complex ion).



3. Pentacyano nitrosyl ferrate (II) ion, $[Fe^{2+}(CN)_5(NO^+)]^{2-}$ (Also called nitroprusside ion)

Since the coordination number of Fe is six, the given ion has octahedral geometry. Pauling (1931) and Sidgwick (1935) have suggested that NO is present as NO^+ ion (nitrosyl ion) which is a two-electron donor. NO^+ ion is obtained when NO molecule (5 + 6 = 11 electrons) loses its unpaired electron residing in its π^*_y molecular orbital [Molecular orbital configuration of NO molecule is $(\sigma^b_{2s})^2 (\sigma^*_{2s})^2 (\sigma^b_x)^2 (\pi^b_y)^2 (\pi^b_z)^2 (\pi^*_y)^1$. Thus molecular orbital configuration of NO^+ ion (5 + 6 − 1 = 10 electrons) is $(\sigma^b_{2s})^2 (\sigma^*_{2s})^2 (\sigma^b_x)^2 (\pi^b_y)^2 (\pi^b_z)^2 (\pi^*_y)^0$. The presence of NO^+ ion in the given complex ion indicates that Fe is present as Fe^{2+} ion ($Fe^{2+} = 3d^6 4s^0 = t^4_{2g}\ e^2_g\ 4s^0$, having $n = 0$). Magnetic moment value of $[Fe(CN)_5(NO)]^{2-}$ ion has shown that the given ion has no unpaired electron ($n = 0$) and hence is diamagnetic. In order to account for its diamagnetic character, it is assumed that the two electrons of e_g orbitals are forced to occupy the t_{2g} orbitals so that we have all the electrons in the paired state and two 3*d* orbitals of e_g set become vacant and hence available for d^2sp^3 hybridisation. Thus the given ion results from d^2sp^3 hybridisation and hence is inner-orbital octahedral complex ion (see Fig. 5.3).

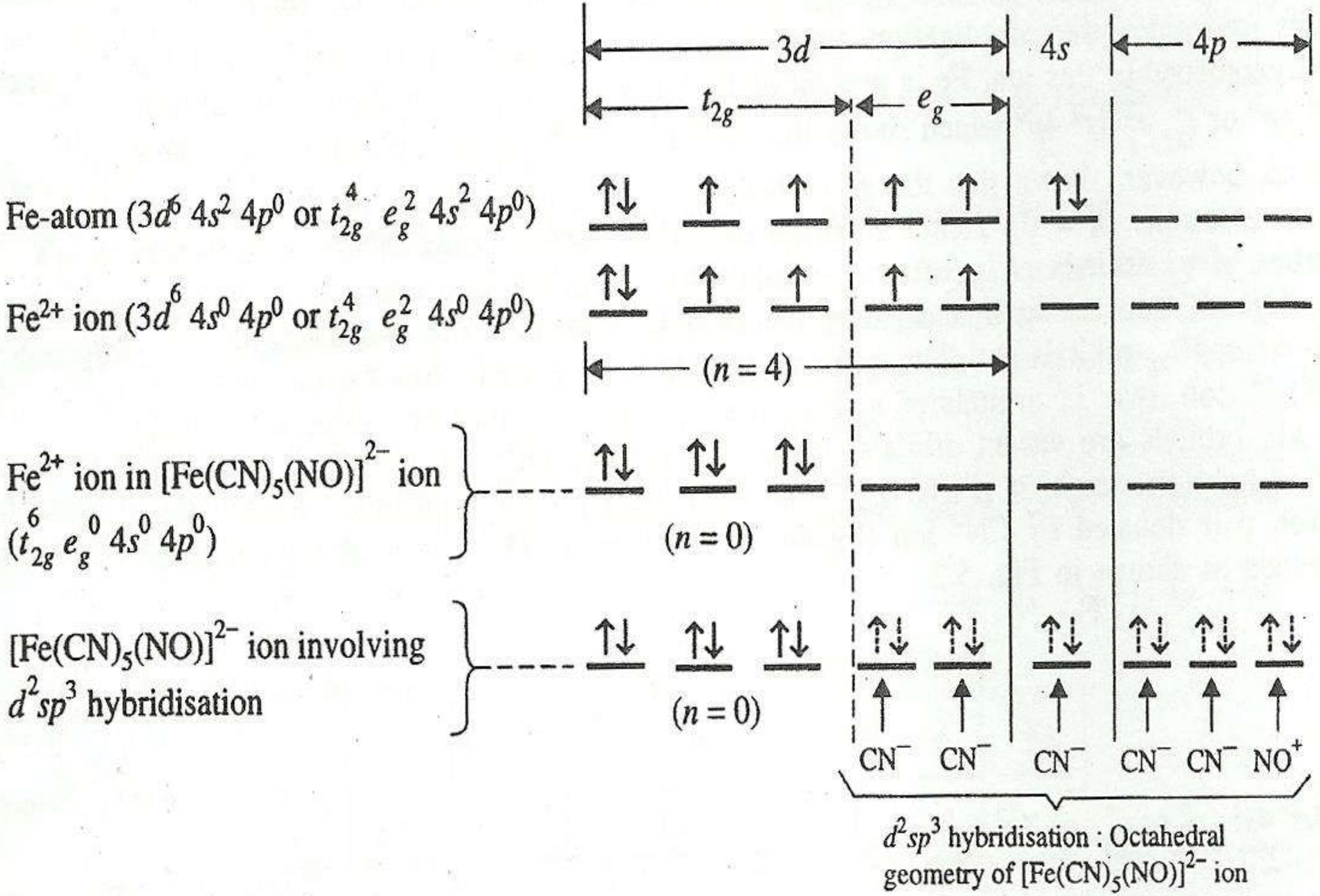
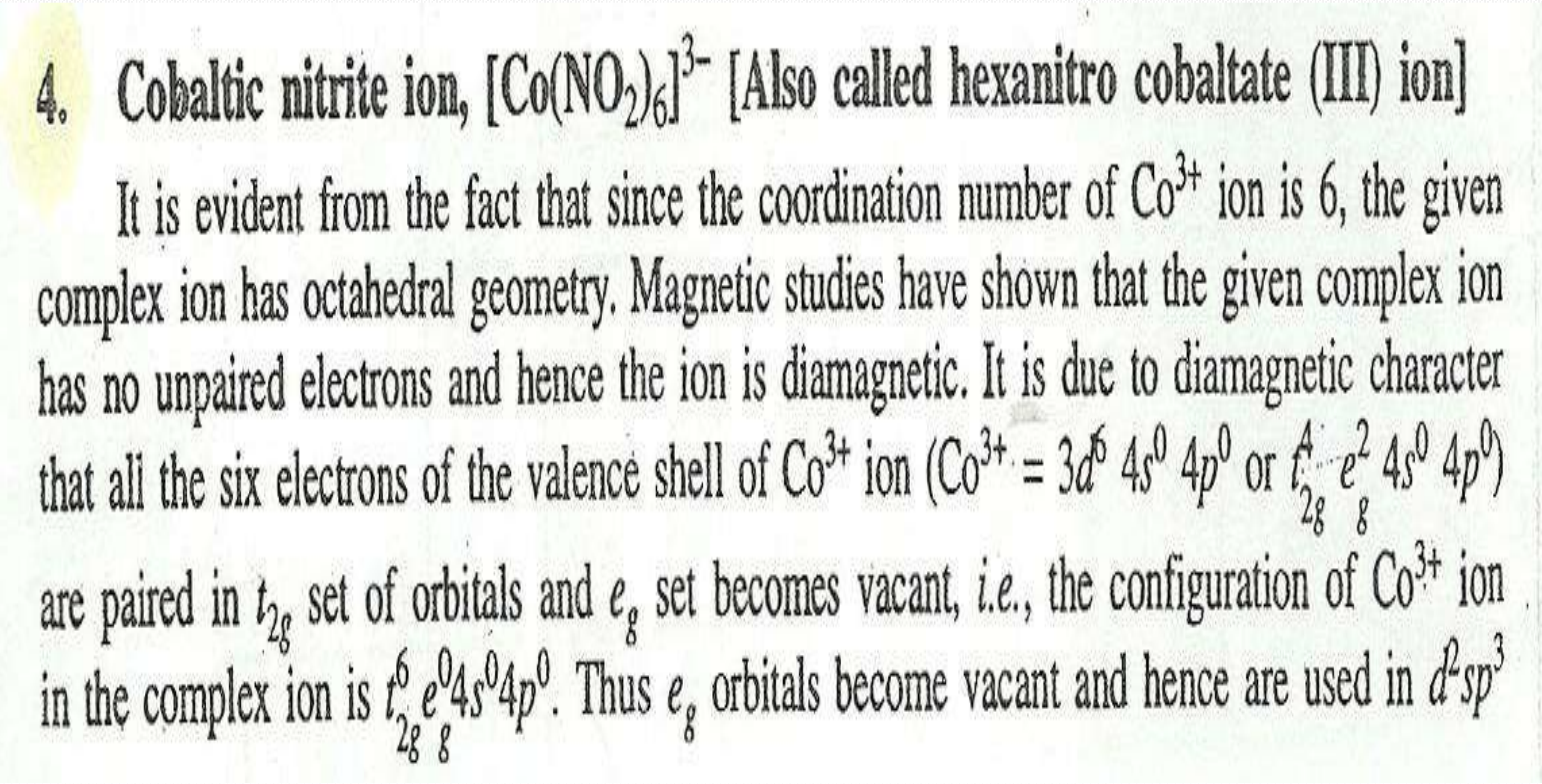


Fig. 5.3. Formation of $[\mathrm{Fe(CN)_5(NO)}]^{2-}$ ion by d^2sp^3 hybridisation (Inner-orbital octahedral complex ion).



4. Cobaltic nitrite ion, $[Co(NO_2)_6]^{3-}$ [Also called hexanitro cobaltate (III) ion]

It is evident from the fact that since the coordination number of Co^{3+} ion is 6, the given complex ion has octahedral geometry. Magnetic studies have shown that the given complex ion has no unpaired electrons and hence the ion is diamagnetic. It is due to diamagnetic character that all the six electrons of the valence shell of Co^{3+} ion ($Co^{3+} = 3d^6\ 4s^0\ 4p^0$ or $t_{2g}^4\ e_g^2\ 4s^0\ 4p^0$) are paired in t_{2g} set of orbitals and e_g set becomes vacant, *i.e.*, the configuration of Co^{3+} ion in the complex ion is $t_{2g}^6 e_g^0 4s^0 4p^0$. Thus e_g orbitals become vacant and hence are used in d^2sp^3

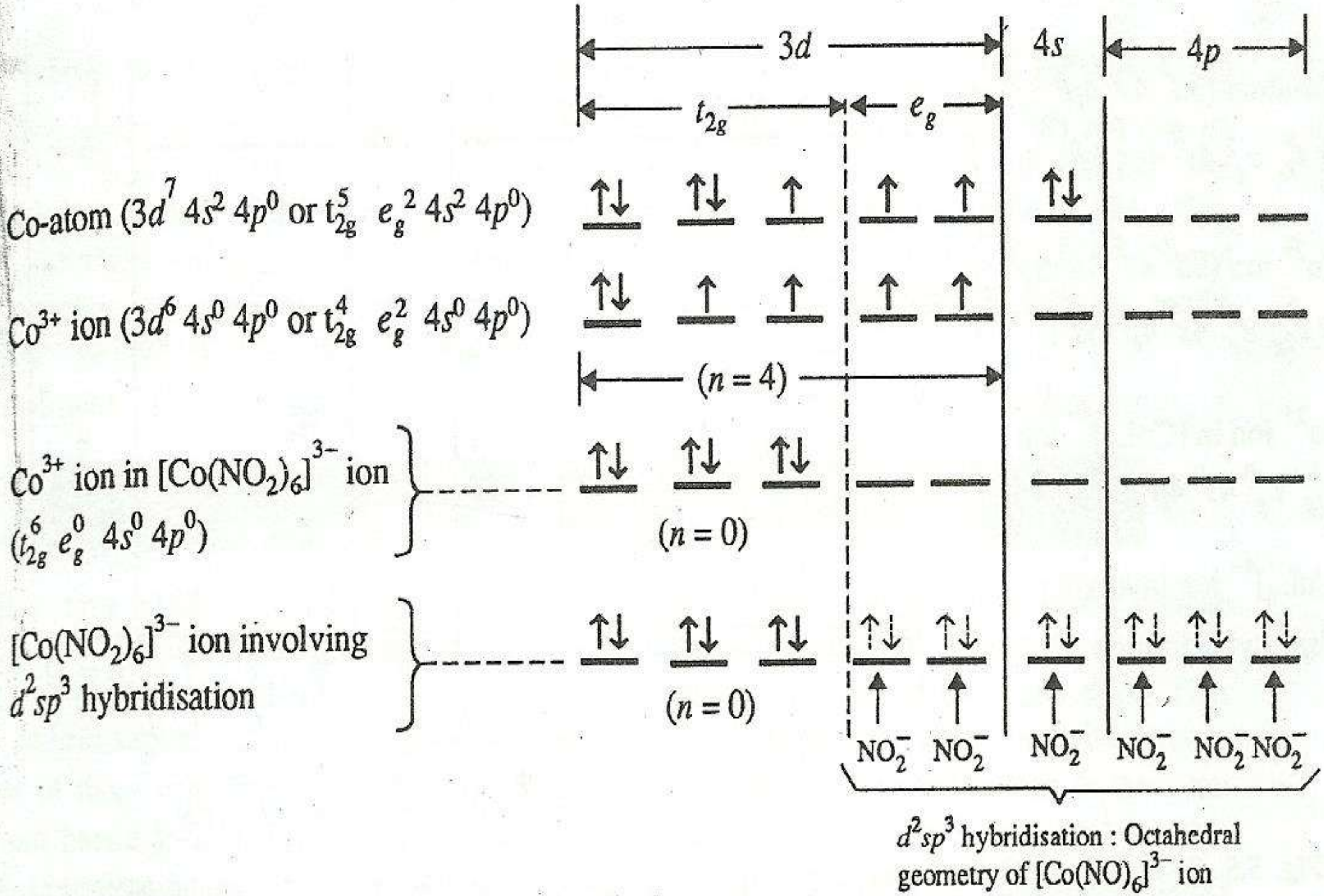
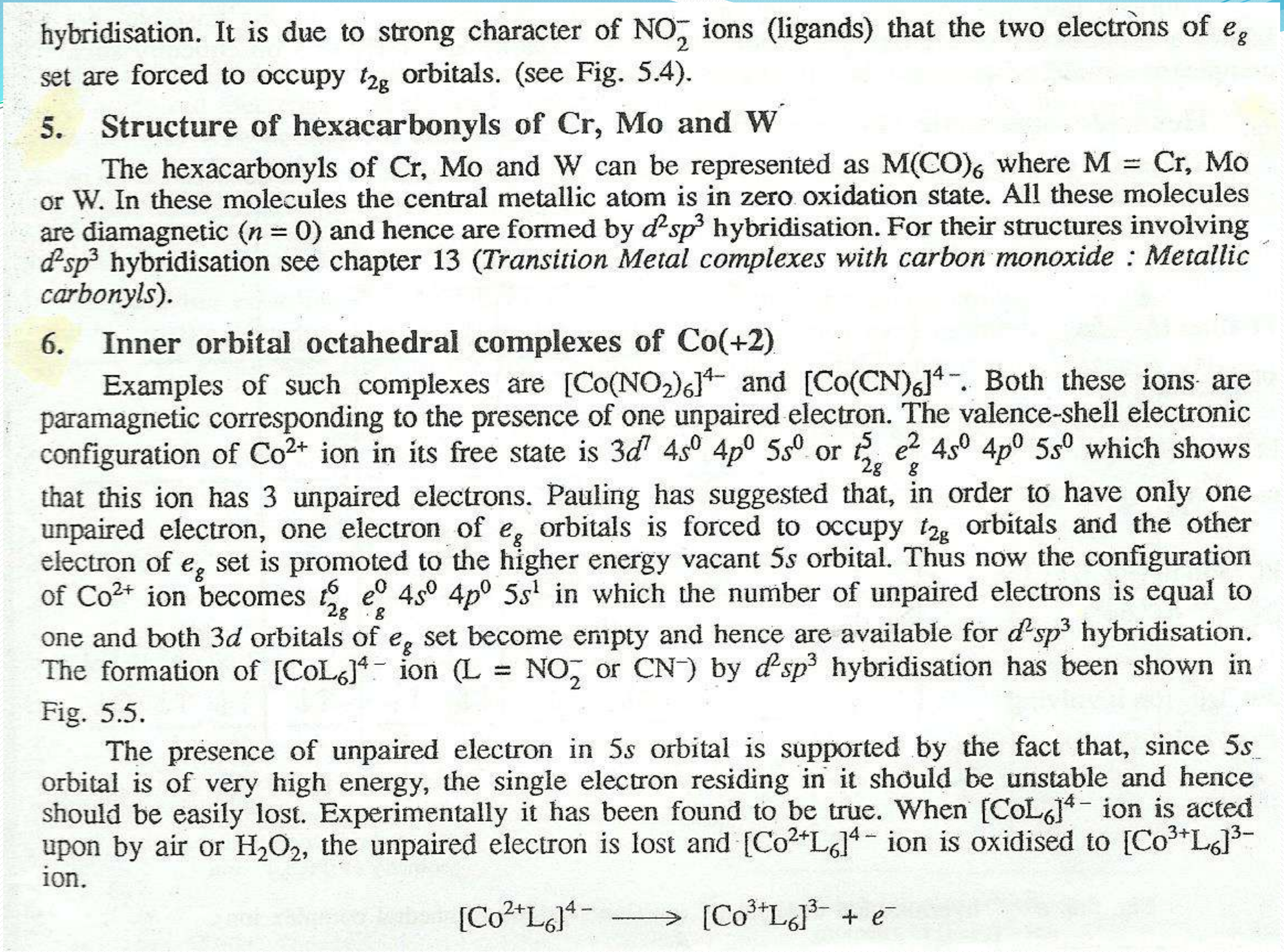


Fig. 5.4. Formation of $[Co(NO2)_6]^{3-}$ ion by d^2sp^3 hybridisation (Inner-orbital octahedral complex ion).



hybridisation. It is due to strong character of NO_2^- ions (ligands) that the two electrons of e_g set are forced to occupy t_{2g} orbitals. (see Fig. 5.4).

5. Structure of hexacarbonyls of Cr, Mo and W

The hexacarbonyls of Cr, Mo and W can be represented as $M(CO)_6$ where M = Cr, Mo or W. In these molecules the central metallic atom is in zero oxidation state. All these molecules are diamagnetic ($n = 0$) and hence are formed by d^2sp^3 hybridisation. For their structures involving d^2sp^3 hybridisation see chapter 13 (*Transition Metal complexes with carbon monoxide : Metallic carbonyls*).

6. Inner orbital octahedral complexes of Co(+2)

Examples of such complexes are $[Co(NO_2)_6]^{4-}$ and $[Co(CN)_6]^{4-}$. Both these ions are paramagnetic corresponding to the presence of one unpaired electron. The valence-shell electronic configuration of Co^{2+} ion in its free state is $3d^7\ 4s^0\ 4p^0\ 5s^0$ or $t_{2g}^5\ e_g^2\ 4s^0\ 4p^0\ 5s^0$ which shows that this ion has 3 unpaired electrons. Pauling has suggested that, in order to have only one unpaired electron, one electron of e_g orbitals is forced to occupy t_{2g} orbitals and the other electron of e_g set is promoted to the higher energy vacant 5s orbital. Thus now the configuration of Co^{2+} ion becomes $t_{2g}^6\ e_g^0\ 4s^0\ 4p^0\ 5s^1$ in which the number of unpaired electrons is equal to one and both 3d orbitals of e_g set become empty and hence are available for d^2sp^3 hybridisation. The formation of $[CoL_6]^{4-}$ ion (L = NO_2^- or CN^-) by d^2sp^3 hybridisation has been shown in Fig. 5.5.

The presence of unpaired electron in 5s orbital is supported by the fact that, since 5s orbital is of very high energy, the single electron residing in it should be unstable and hence should be easily lost. Experimentally it has been found to be true. When $[CoL_6]^{4-}$ ion is acted upon by air or H_2O_2, the unpaired electron is lost and $[Co^{2+}L_6]^{4-}$ ion is oxidised to $[Co^{3+}L_6]^{3-}$ ion.

$$[Co^{2+}L_6]^{4-} \longrightarrow [Co^{3+}L_6]^{3-} + e^-$$

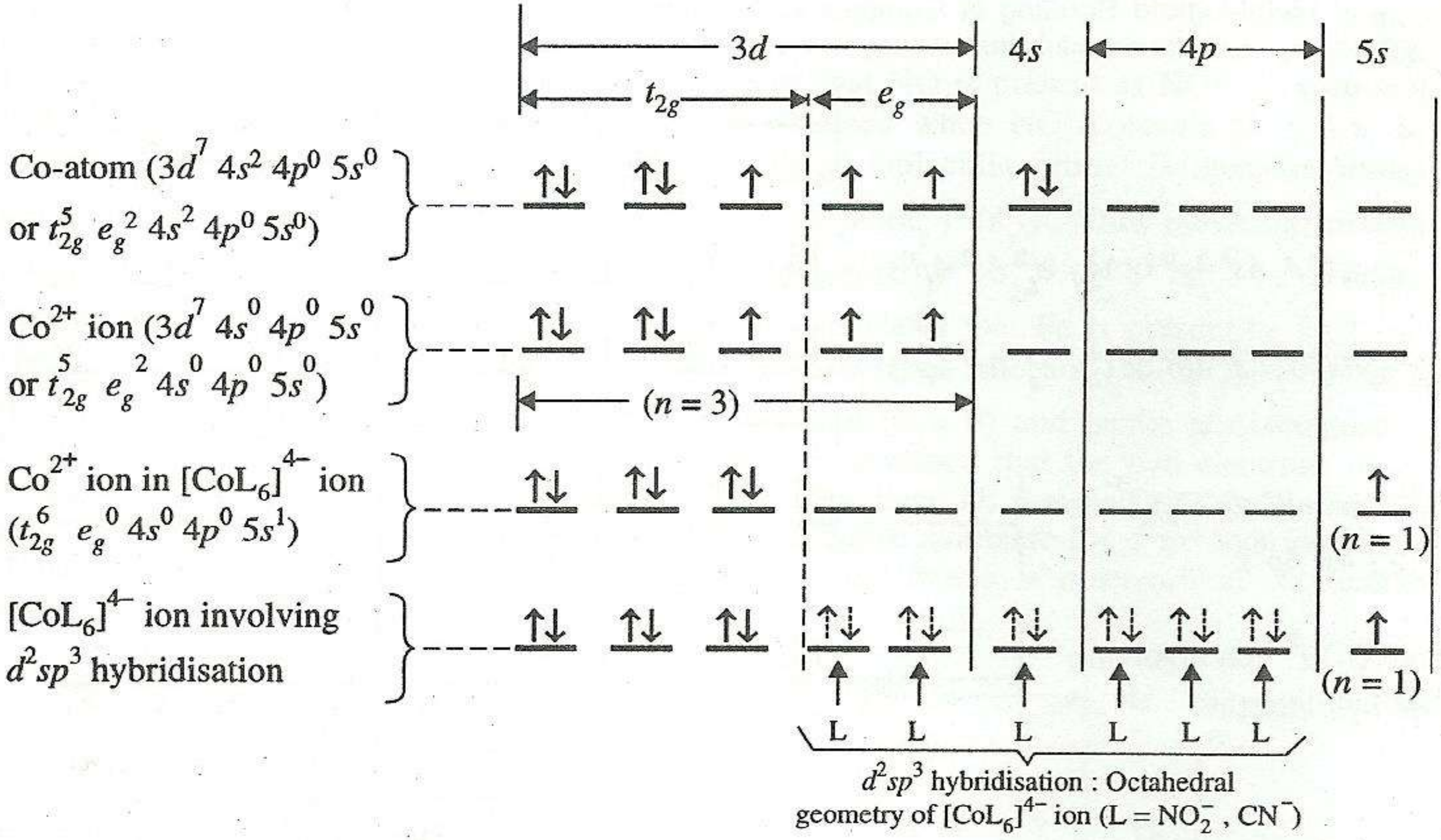


Fig. 5.5. Formation of $[CoL_6]^{4-}$ ion ($L = NO_2^-$ or CN^-) by d^2sp^3 hybridisation (Inner-orbital octahedral complex ion).

Thus we find that Co(+2) low spin (inner orbital) octahedral complexes are unstable (are labile) and hence are easily oxidised to Co (+3) complexes by air or H_2O_2. Consequently such complexes should be prepared in an inert atmosphere.

7. Hexachloroplatinate (IV) ion, $[PtCl_6]^{2-}$

Since the coordination number of Pt^{4+} ion is six, the given complex ion is octahedral in

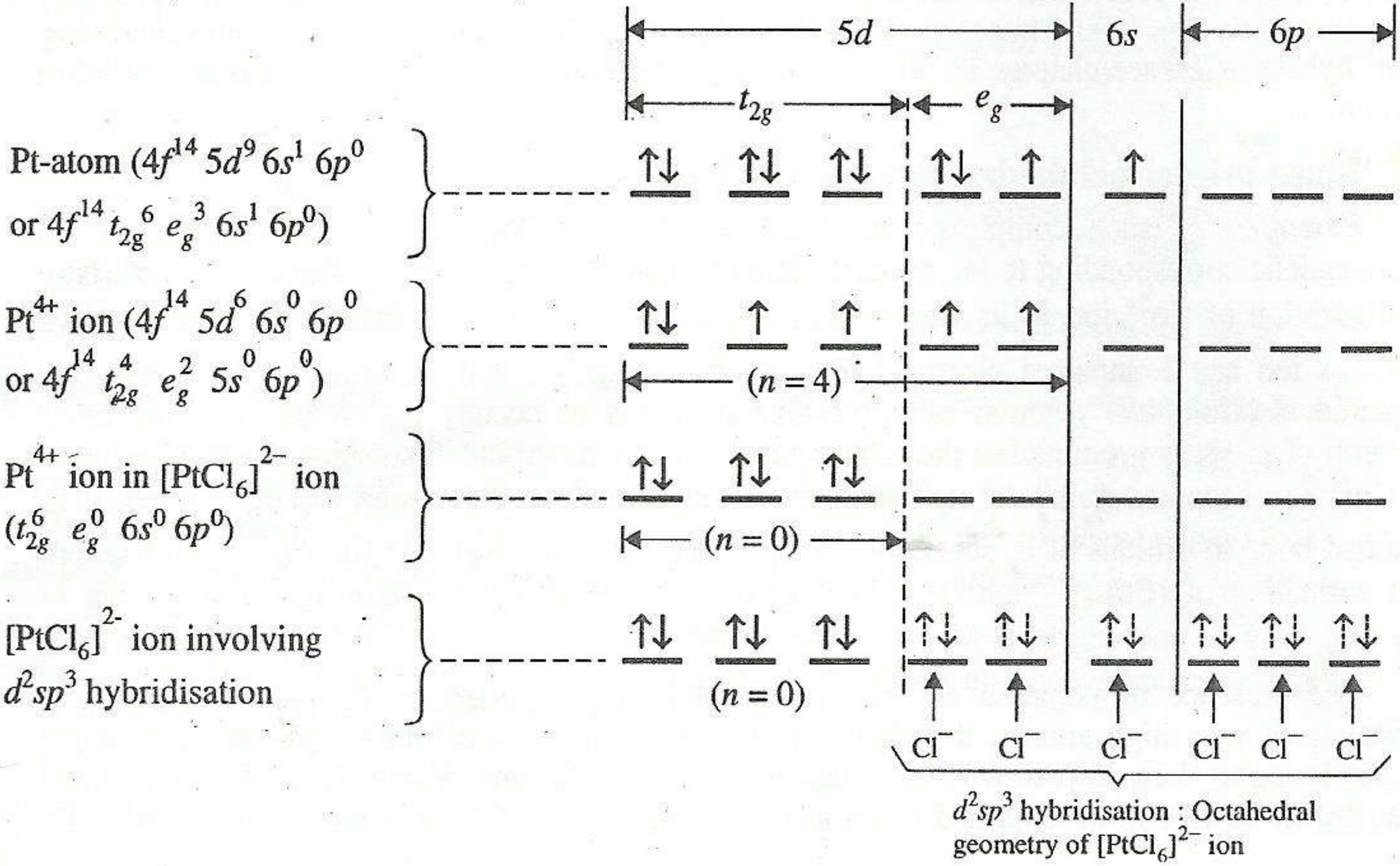
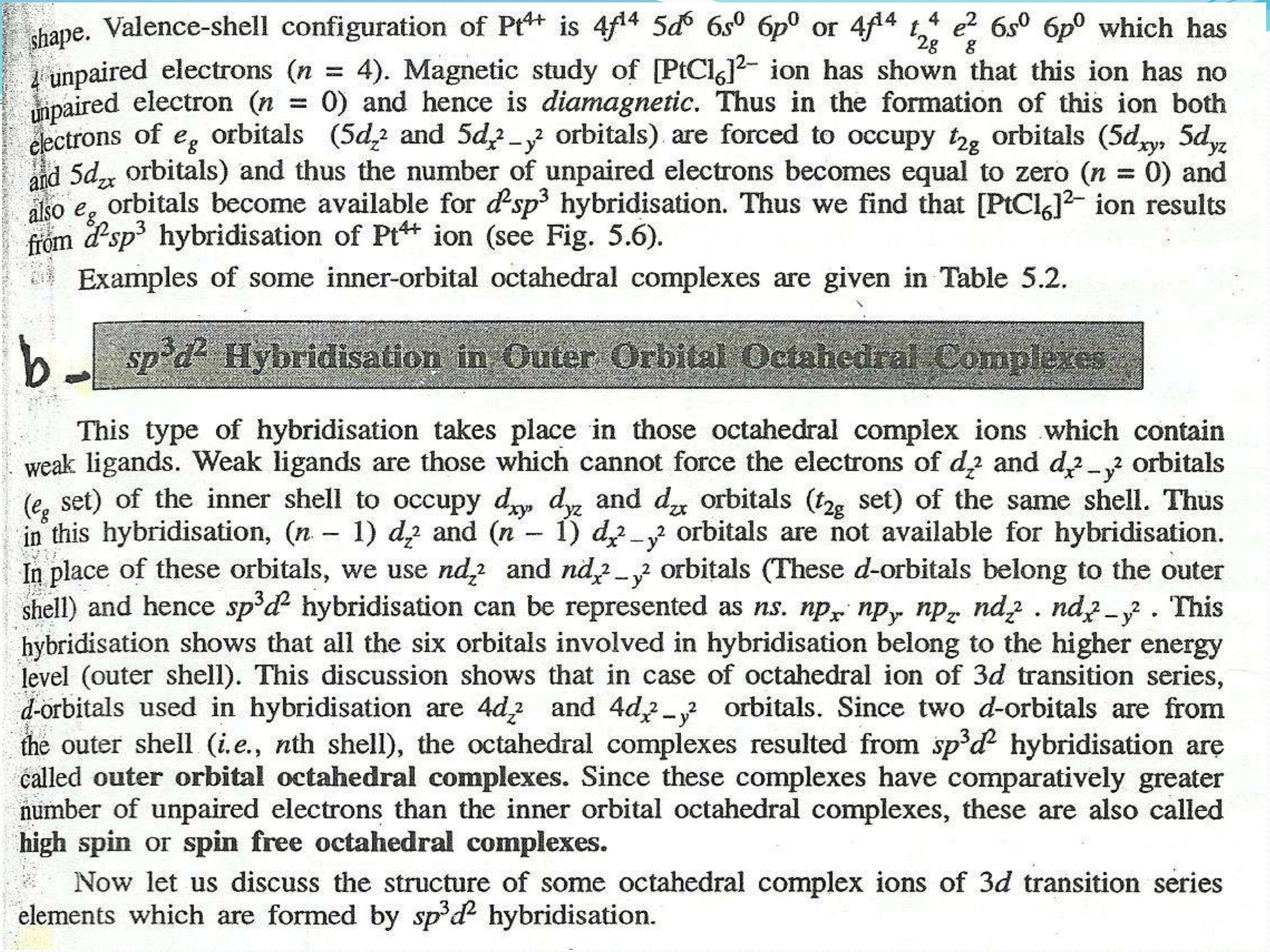


Fig. 5.6. d^2sp^3 hybridisation in $[PtCl6]^{2-}$ ion (Inner-orbital octahedral complex ion).



shape. Valence-shell configuration of Pt^{4+} is $4f^{14}\ 5d^6\ 6s^0\ 6p^0$ or $4f^{14}\ t_{2g}^4\ e_g^2\ 6s^0\ 6p^0$ which has 4 unpaired electrons ($n = 4$). Magnetic study of $[PtCl_6]^{2-}$ ion has shown that this ion has no unpaired electron ($n = 0$) and hence is *diamagnetic*. Thus in the formation of this ion both electrons of e_g orbitals ($5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals) are forced to occupy t_{2g} orbitals ($5d_{xy}$, $5d_{yz}$ and $5d_{zx}$ orbitals) and thus the number of unpaired electrons becomes equal to zero ($n = 0$) and also e_g orbitals become available for d^2sp^3 hybridisation. Thus we find that $[PtCl_6]^{2-}$ ion results from d^2sp^3 hybridisation of Pt^{4+} ion (see Fig. 5.6).

Examples of some inner-orbital octahedral complexes are given in Table 5.2.

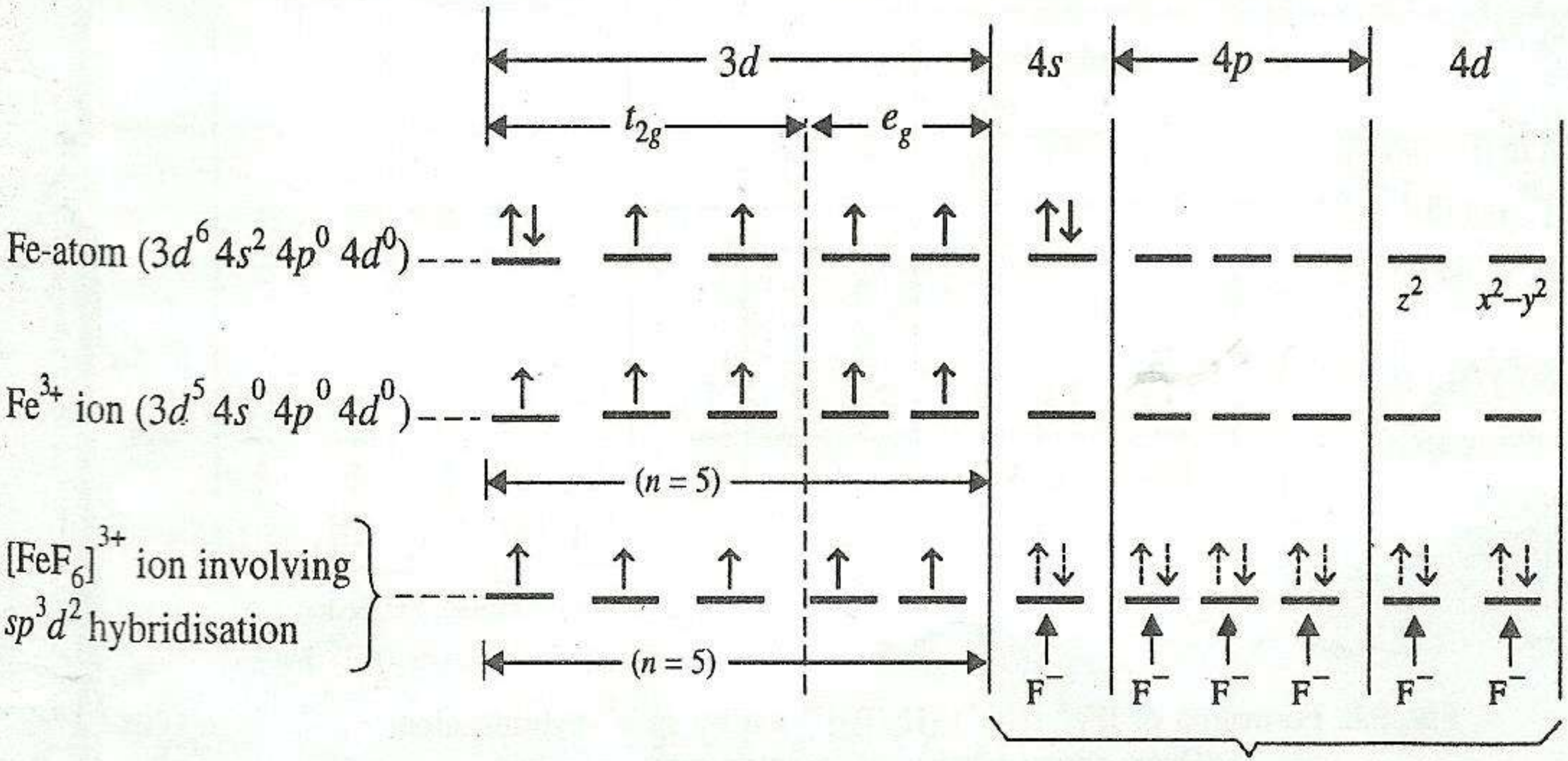
b - sp^3d^2 Hybridisation in Outer Orbital Octahedral Complexes

This type of hybridisation takes place in those octahedral complex ions which contain weak ligands. Weak ligands are those which cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals (e_g set) of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals (t_{2g} set) of the same shell. Thus in this hybridisation, $(n-1)\ d_{z^2}$ and $(n-1)\ d_{x^2-y^2}$ orbitals are not available for hybridisation. In place of these orbitals, we use nd_{z^2} and $nd_{x^2-y^2}$ orbitals (These *d*-orbitals belong to the outer shell) and hence sp^3d^2 hybridisation can be represented as $ns.\ np_x.\ np_y.\ np_z.\ nd_{z^2}\ .\ nd_{x^2-y^2}$. This hybridisation shows that all the six orbitals involved in hybridisation belong to the higher energy level (outer shell). This discussion shows that in case of octahedral ion of 3*d* transition series, *d*-orbitals used in hybridisation are $4d_{z^2}$ and $4d_{x^2-y^2}$ orbitals. Since two *d*-orbitals are from the outer shell (*i.e.*, *n*th shell), the octahedral complexes resulted from sp^3d^2 hybridisation are called **outer orbital octahedral complexes.** Since these complexes have comparatively greater number of unpaired electrons than the inner orbital octahedral complexes, these are also called **high spin** or **spin free octahedral complexes.**

Now let us discuss the structure of some octahedral complex ions of 3*d* transition series elements which are formed by sp^3d^2 hybridisation.

1. Hexafluroferrate (III) ion, $[FeF_6]^{3-}$

In this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry. Here iron is present as Fe^{3+} whose valence shell electronic configuration is $3d^5 4s^0 4p^0$ or $t_{2g}^3\ e_g^2\ 4s^0\ 4p^0$. Each of the five electrons is unpaired and hence $n = 5$. Magnetic



sp^3d^2 hybridisation : Octahedral geometry of $[FeF_6]^{3-}$ ion

Fig. 5.7. Formation of $[FeF_6]^{3-}$ ion by sp^3d^2 hybridisation. (Outer-orbital octahedral complex ion).

shape. Valence-shell configuration of Pt^{4+} is $4f^{14}\ 5d^6\ 6s^0\ 6p^0$ or $4f^{14}\ t_{2g}^4\ e_g^2\ 6s^0\ 6p^0$ which has 4 unpaired electrons ($n = 4$). Magnetic study of $[PtCl_6]^{2-}$ ion has shown that this ion has no unpaired electron ($n = 0$) and hence is *diamagnetic*. Thus in the formation of this ion both electrons of e_g orbitals ($5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals) are forced to occupy t_{2g} orbitals ($5d_{xy}$, $5d_{yz}$ and $5d_{zx}$ orbitals) and thus the number of unpaired electrons becomes equal to zero ($n = 0$) and also e_g orbitals become available for d^2sp^3 hybridisation. Thus we find that $[PtCl_6]^{2-}$ ion results from d^2sp^3 hybridisation of Pt^{4+} ion (see Fig. 5.6).

Examples of some inner-orbital octahedral complexes are given in Table 5.2.

b - sp^3d^2 Hybridisation in Outer Orbital Octahedral Complexes

This type of hybridisation takes place in those octahedral complex ions which contain weak ligands. Weak ligands are those which cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals (e_g set) of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals (t_{2g} set) of the same shell. Thus in this hybridisation, $(n-1)\ d_{z^2}$ and $(n-1)\ d_{x^2-y^2}$ orbitals are not available for hybridisation. In place of these orbitals, we use nd_{z^2} and $nd_{x^2-y^2}$ orbitals (These *d*-orbitals belong to the outer shell) and hence sp^3d^2 hybridisation can be represented as $ns.\ np_x.\ np_y.\ np_z.\ nd_{z^2}\ .\ nd_{x^2-y^2}$. This hybridisation shows that all the six orbitals involved in hybridisation belong to the higher energy level (outer shell). This discussion shows that in case of octahedral ion of 3*d* transition series, *d*-orbitals used in hybridisation are $4d_{z^2}$ and $4d_{x^2-y^2}$ orbitals. Since two *d*-orbitals are from the outer shell (*i.e.*, *n*th shell), the octahedral complexes resulted from sp^3d^2 hybridisation are called **outer orbital octahedral complexes.** Since these complexes have comparatively greater number of unpaired electrons than the inner orbital octahedral complexes, these are also called **high spin** or **spin free octahedral complexes.**

Now let us discuss the structure of some octahedral complex ions of 3*d* transition series elements which are formed by sp^3d^2 hybridisation.

1. **Hexafluroferrate (III) ion, $[FeF_6]^{3-}$**

In this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry. Here iron is present as Fe^{3+} whose valence shell electronic configuration is $3d^5 4s^0 4p^0$ or $t_{2g}^3\, e_g^2\, 4s^0\, 4p^0$. Each of the five electrons is unpaired and hence $n = 5$. Magnetic

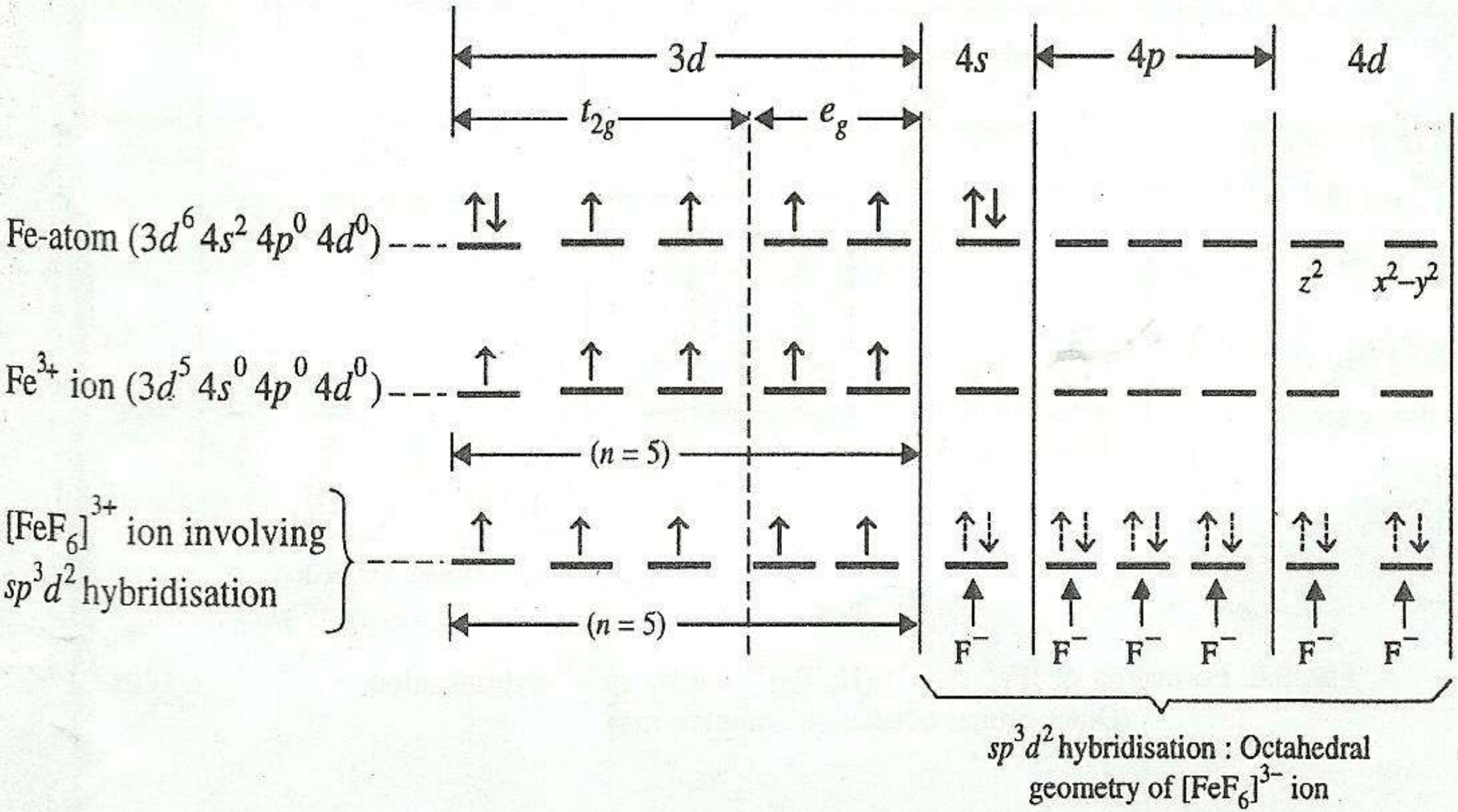


Fig. 5.7. Formation of $[FeF_6]^{3-}$ ion by sp^3d^2 hybridisation. (Outer-orbital octahedral complex ion).

3. Outer-orbital octahedral complexes of Ni(+2)

Octahedral complexes of Ni^{2+} ion are outer-orbital octahedral complexes (sp^3d^2 hybridisation). The formation of inner-orbital octahedral complexes of Ni^{2+} ion ($Ni^{2+} = 3d^8 = t_{2g}^6\ e_g^2$) is not possible, since the two unpaired electrons present in e_g set of orbitals cannot be sent to t_{2g} orbitals which are already completely-filled. Thus e_g orbitals cannot be made empty for d^2sp^3 hybridisation. Outer orbital complexes of Ni^{2+} ion are paramagnetic corresponding to the presence of two unpaired electrons present in e_g orbitals.

As an example let us see how sp^3d^2 hybridisation takes place in $[Ni(NH_3)_6]^{2+}$ ion. (See Fig. 5.9).

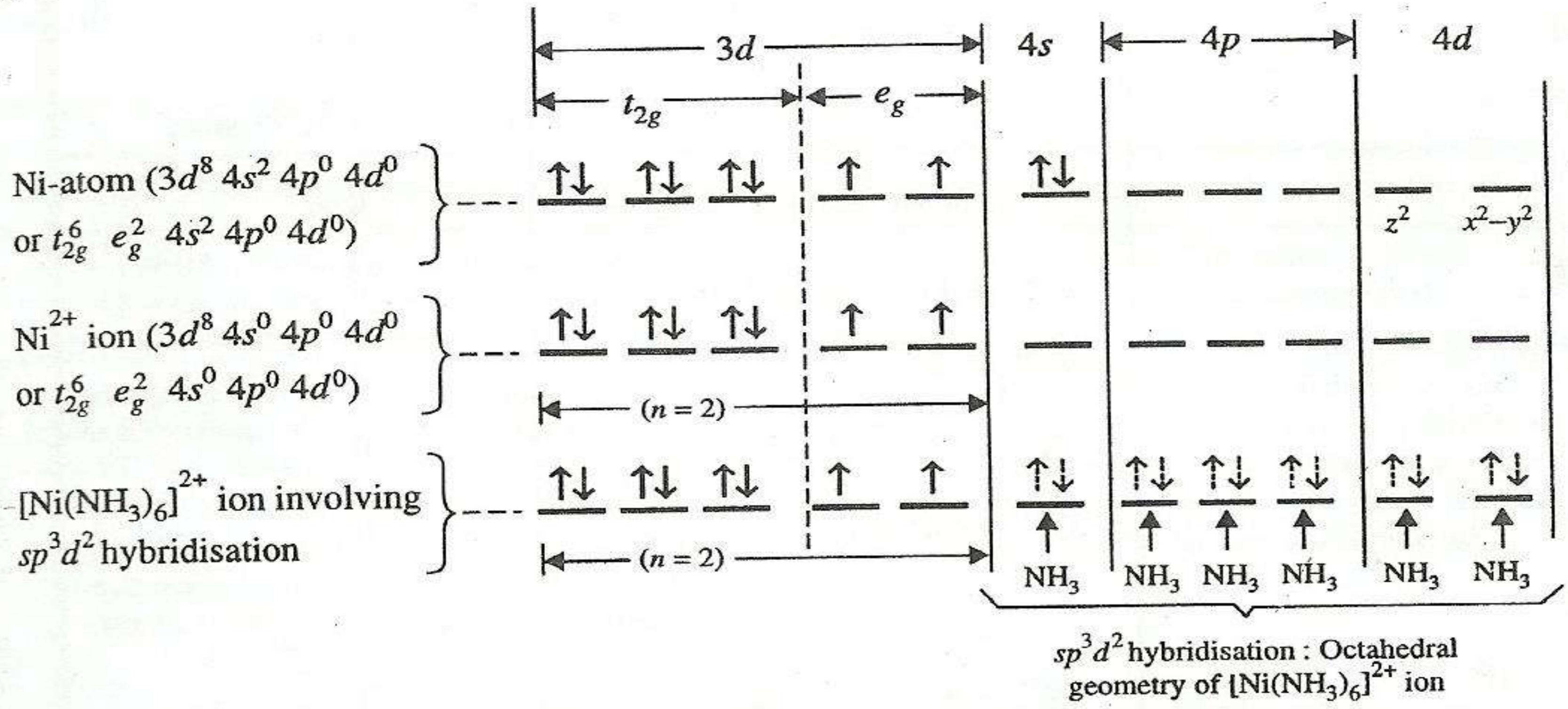
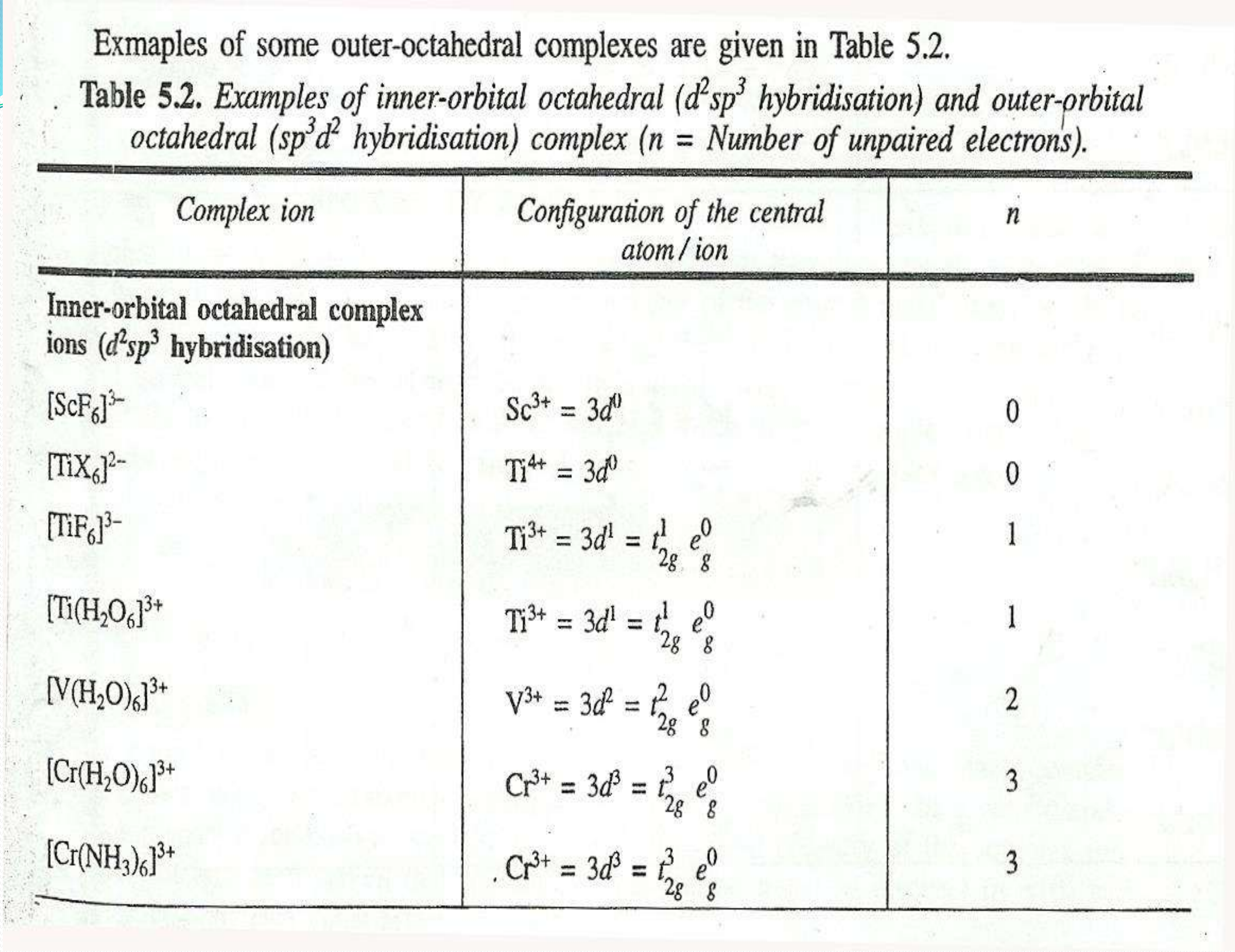


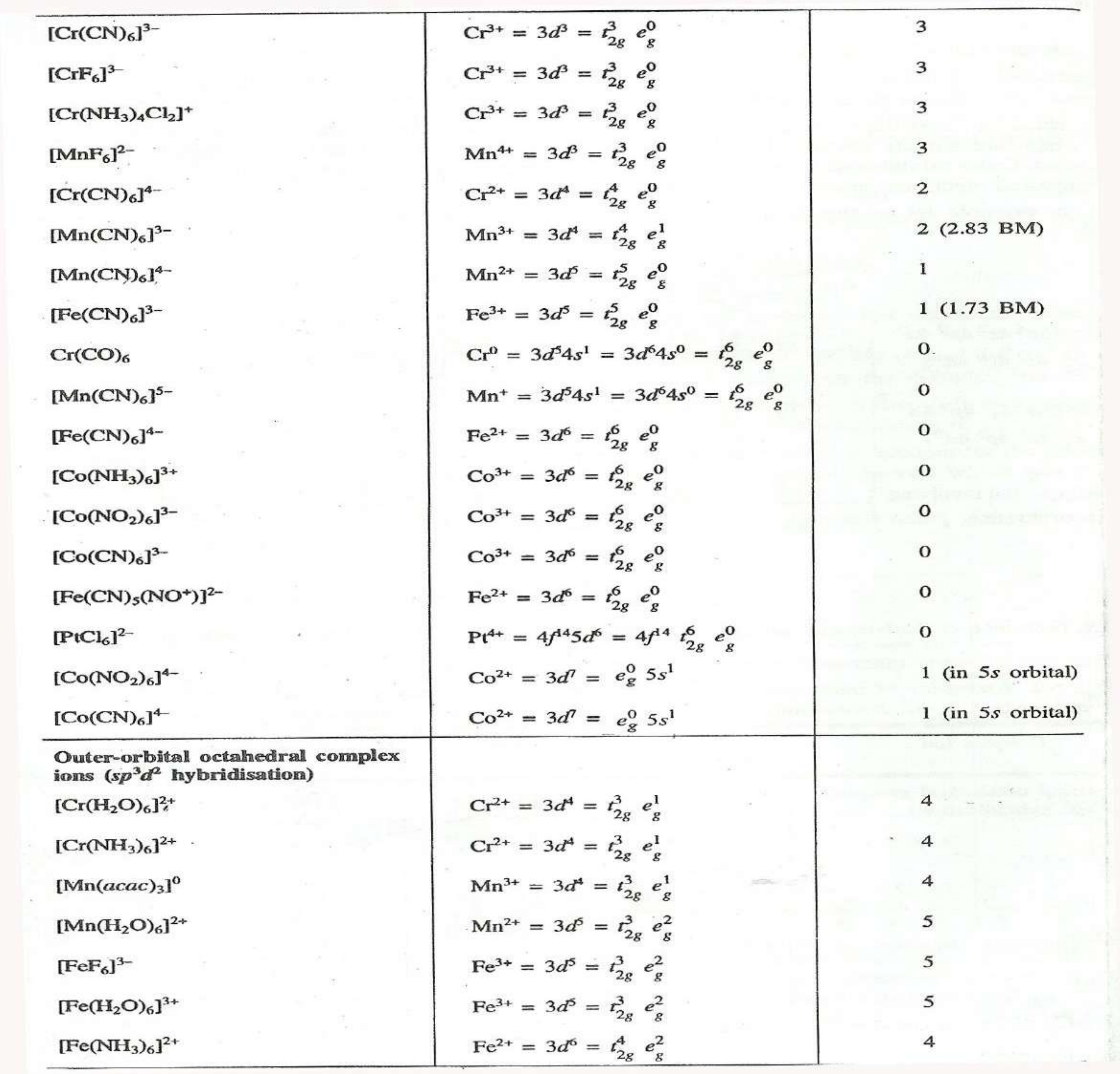
Fig. 5.9. Formation of $[Ni(NH_3)_6]^{2+}$ ion by sp^3d^2 hybridisation (Outer-orbital octahedral complex ion).



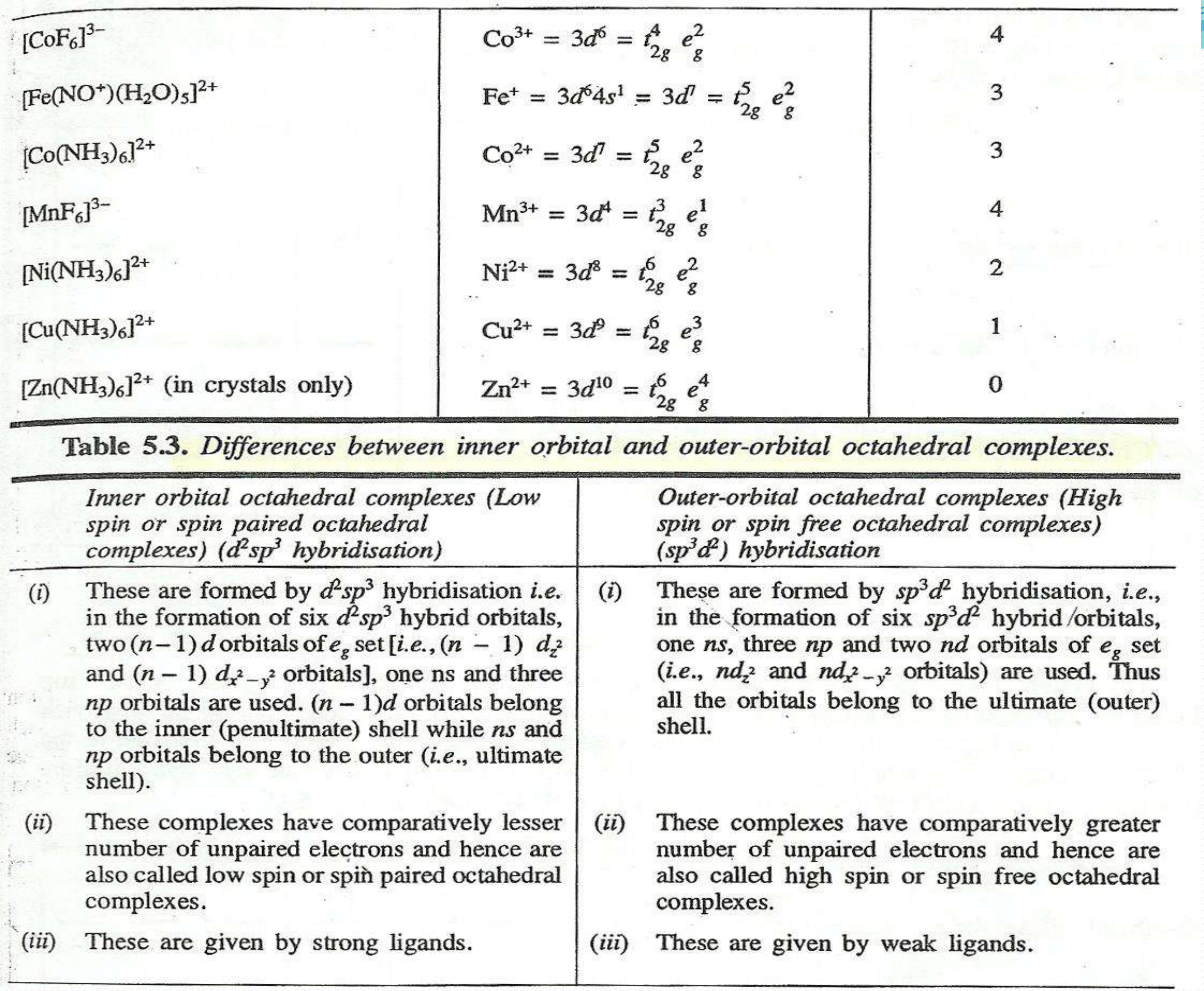
Exmaples of some outer-octahedral complexes are given in Table 5.2.

Table 5.2. *Examples of inner-orbital octahedral (d^2sp^3 hybridisation) and outer-orbital octahedral (sp^3d^2 hybridisation) complex (n = Number of unpaired electrons).*

Complex ion	*Configuration of the central atom / ion*	*n*
Inner-orbital octahedral complex ions (d^2sp^3 hybridisation)		
$[ScF_6]^{3-}$	$Sc^{3+} = 3d^0$	0
$[TiX_6]^{2-}$	$Ti^{4+} = 3d^0$	0
$[TiF_6]^{3-}$	$Ti^{3+} = 3d^1 = t_{2g}^1\ e_g^0$	1
$[Ti(H_2O_6]^{3+}$	$Ti^{3+} = 3d^1 = t_{2g}^1\ e_g^0$	1
$[V(H_2O)_6]^{3+}$	$V^{3+} = 3d^2 = t_{2g}^2\ e_g^0$	2
$[Cr(H_2O)_6]^{3+}$	$Cr^{3+} = 3d^3 = t_{2g}^3\ e_g^0$	3
$[Cr(NH_3)_6]^{3+}$	$Cr^{3+} = 3d^3 = t_{2g}^3\ e_g^0$	3



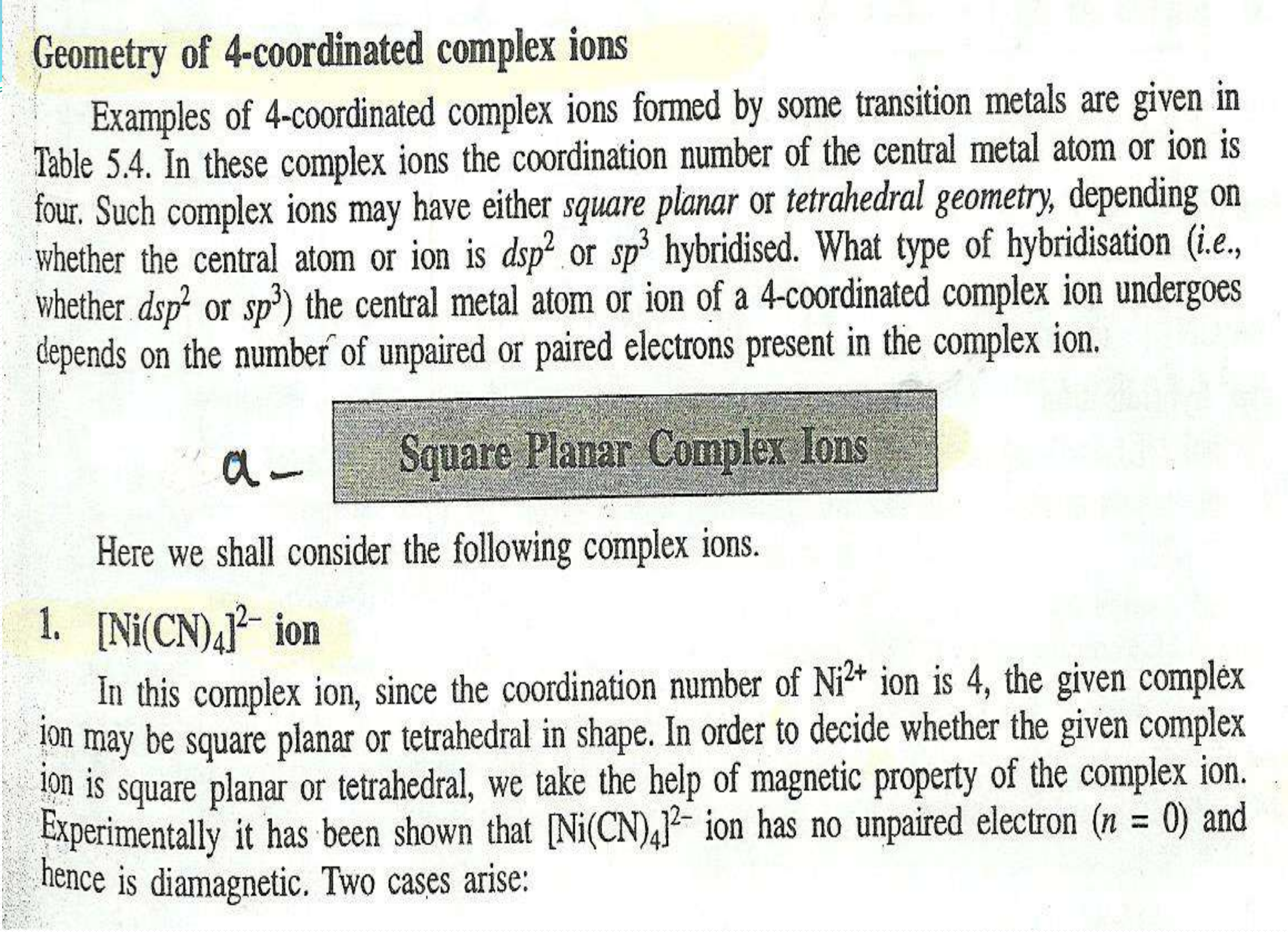
$[Cr(CN)_6]^{3-}$	$Cr^{3+} = 3d^3 = t_{2g}^3\ e_g^0$	3
$[CrF_6]^{3-}$	$Cr^{3+} = 3d^3 = t_{2g}^3\ e_g^0$	3
$[Cr(NH_3)_4Cl_2]^+$	$Cr^{3+} = 3d^3 = t_{2g}^3\ e_g^0$	3
$[MnF_6]^{2-}$	$Mn^{4+} = 3d^3 = t_{2g}^3\ e_g^0$	3
$[Cr(CN)_6]^{4-}$	$Cr^{2+} = 3d^4 = t_{2g}^4\ e_g^0$	2
$[Mn(CN)_6]^{3-}$	$Mn^{3+} = 3d^4 = t_{2g}^4\ e_g^1$	2 (2.83 BM)
$[Mn(CN)_6]^{4-}$	$Mn^{2+} = 3d^5 = t_{2g}^5\ e_g^0$	1
$[Fe(CN)_6]^{3-}$	$Fe^{3+} = 3d^5 = t_{2g}^5\ e_g^0$	1 (1.73 BM)
$Cr(CO)_6$	$Cr^0 = 3d^5 4s^1 = 3d^6 4s^0 = t_{2g}^6\ e_g^0$	0
$[Mn(CN)_6]^{5-}$	$Mn^+ = 3d^5 4s^1 = 3d^6 4s^0 = t_{2g}^6\ e_g^0$	0
$[Fe(CN)_6]^{4-}$	$Fe^{2+} = 3d^6 = t_{2g}^6\ e_g^0$	0
$[Co(NH_3)_6]^{3+}$	$Co^{3+} = 3d^6 = t_{2g}^6\ e_g^0$	0
$[Co(NO_2)_6]^{3-}$	$Co^{3+} = 3d^6 = t_{2g}^6\ e_g^0$	0
$[Co(CN)_6]^{3-}$	$Co^{3+} = 3d^6 = t_{2g}^6\ e_g^0$	0
$[Fe(CN)_5(NO^+)]^{2-}$	$Fe^{2+} = 3d^6 = t_{2g}^6\ e_g^0$	0
$[PtCl_6]^{2-}$	$Pt^{4+} = 4f^{14}5d^6 = 4f^{14}\ t_{2g}^6\ e_g^0$	0
$[Co(NO_2)_6]^{4-}$	$Co^{2+} = 3d^7 = e_g^0\ 5s^1$	1 (in 5*s* orbital)
$[Co(CN)_6]^{4-}$	$Co^{2+} = 3d^7 = e_g^0\ 5s^1$	1 (in 5*s* orbital)
Outer-orbital octahedral complex ions (sp^3d^2 hybridisation)		
$[Cr(H_2O)_6]^{2+}$	$Cr^{2+} = 3d^4 = t_{2g}^3\ e_g^1$	4
$[Cr(NH_3)_6]^{2+}$	$Cr^{2+} = 3d^4 = t_{2g}^3\ e_g^1$	4
$[Mn(acac)_3]^0$	$Mn^{3+} = 3d^4 = t_{2g}^3\ e_g^1$	4
$[Mn(H_2O)_6]^{2+}$	$Mn^{2+} = 3d^5 = t_{2g}^3\ e_g^2$	5
$[FeF_6]^{3-}$	$Fe^{3+} = 3d^5 = t_{2g}^3\ e_g^2$	5
$[Fe(H_2O)_6]^{3+}$	$Fe^{3+} = 3d^5 = t_{2g}^3\ e_g^2$	5
$[Fe(NH_3)_6]^{2+}$	$Fe^{2+} = 3d^6 = t_{2g}^4\ e_g^2$	4



$[CoF_6]^{3-}$	$Co^{3+} = 3d^6 = t_{2g}^4\ e_g^2$	4
$[Fe(NO^+)(H_2O)_5]^{2+}$	$Fe^+ = 3d^6 4s^1 = 3d^7 = t_{2g}^5\ e_g^2$	3
$[Co(NH_3)_6]^{2+}$	$Co^{2+} = 3d^7 = t_{2g}^5\ e_g^2$	3
$[MnF_6]^{3-}$	$Mn^{3+} = 3d^4 = t_{2g}^3\ e_g^1$	4
$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} = 3d^8 = t_{2g}^6\ e_g^2$	2
$[Cu(NH_3)_6]^{2+}$	$Cu^{2+} = 3d^9 = t_{2g}^6\ e_g^3$	1
$[Zn(NH_3)_6]^{2+}$ (in crystals only)	$Zn^{2+} = 3d^{10} = t_{2g}^6\ e_g^4$	0

Table 5.3. *Differences between inner orbital and outer-orbital octahedral complexes.*

Inner orbital octahedral complexes (Low spin or spin paired octahedral complexes) (d^2sp^3 hybridisation)	*Outer-orbital octahedral complexes (High spin or spin free octahedral complexes) (sp^3d^2) hybridisation*
(*i*) These are formed by d^2sp^3 hybridisation *i.e.* in the formation of six d^2sp^3 hybrid orbitals, two $(n-1)\,d$ orbitals of e_g set [*i.e.*, $(n-1)\ d_{z^2}$ and $(n-1)\ d_{x^2-y^2}$ orbitals], one ns and three *np* orbitals are used. $(n-1)d$ orbitals belong to the inner (penultimate) shell while *ns* and *np* orbitals belong to the outer (*i.e.*, ultimate shell).	(*i*) These are formed by sp^3d^2 hybridisation, *i.e.*, in the formation of six sp^3d^2 hybrid /orbitals, one *ns*, three *np* and two *nd* orbitals of e_g set (*i.e.*, nd_{z^2} and $nd_{x^2-y^2}$ orbitals) are used. Thus all the orbitals belong to the ultimate (outer) shell.
(*ii*) These complexes have comparatively lesser number of unpaired electrons and hence are also called low spin or spin paired octahedral complexes.	(*ii*) These complexes have comparatively greater number of unpaired electrons and hence are also called high spin or spin free octahedral complexes.
(*iii*) These are given by strong ligands.	(*iii*) These are given by weak ligands.



Geometry of 4-coordinated complex ions

Examples of 4-coordinated complex ions formed by some transition metals are given in Table 5.4. In these complex ions the coordination number of the central metal atom or ion is four. Such complex ions may have either *square planar* or *tetrahedral geometry*, depending on whether the central atom or ion is dsp^2 or sp^3 hybridised. What type of hybridisation (*i.e.*, whether dsp^2 or sp^3) the central metal atom or ion of a 4-coordinated complex ion undergoes depends on the number of unpaired or paired electrons present in the complex ion.

a –

Square Planar Complex Ions

Here we shall consider the following complex ions.

1. $[Ni(CN)_4]^{2-}$ ion

In this complex ion, since the coordination number of Ni^{2+} ion is 4, the given complex ion may be square planar or tetrahedral in shape. In order to decide whether the given complex ion is square planar or tetrahedral, we take the help of magnetic property of the complex ion. Experimentally it has been shown that $[Ni(CN)_4]^{2-}$ ion has no unpaired electron ($n = 0$) and hence is diamagnetic. Two cases arise:

(a) When $[Ni(CN)_4]^{2-}$ ion has tetrahedral geometry. In this case Ni^{2+} ion is sp^3 hybridised as shown in Fig. 5.10. sp^3 hybridisation scheme given in Fig. 5.10 shows that $[Ni(CN)_4]^{2-}$ ion has two unpaired electrons ($n = 2$).

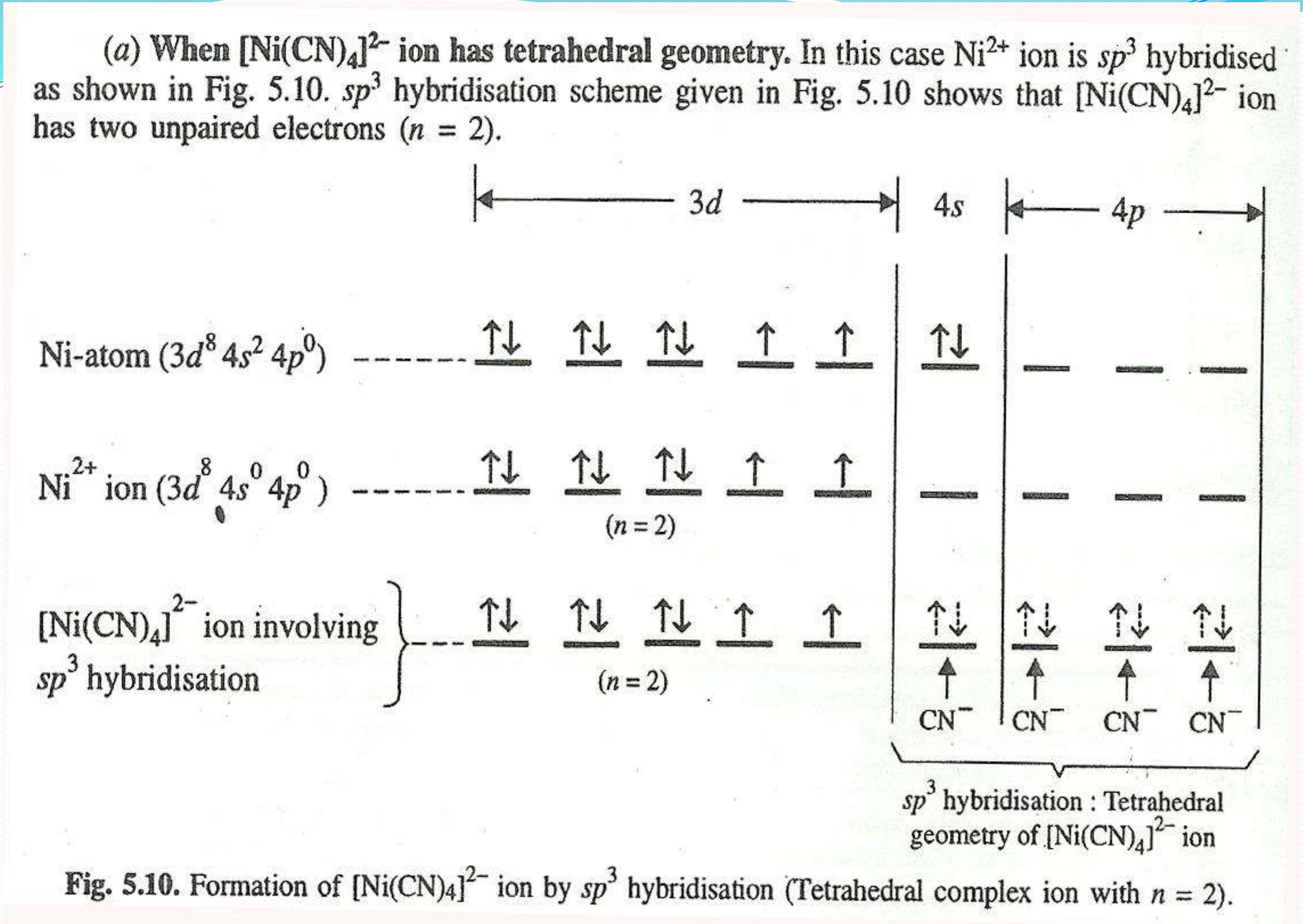
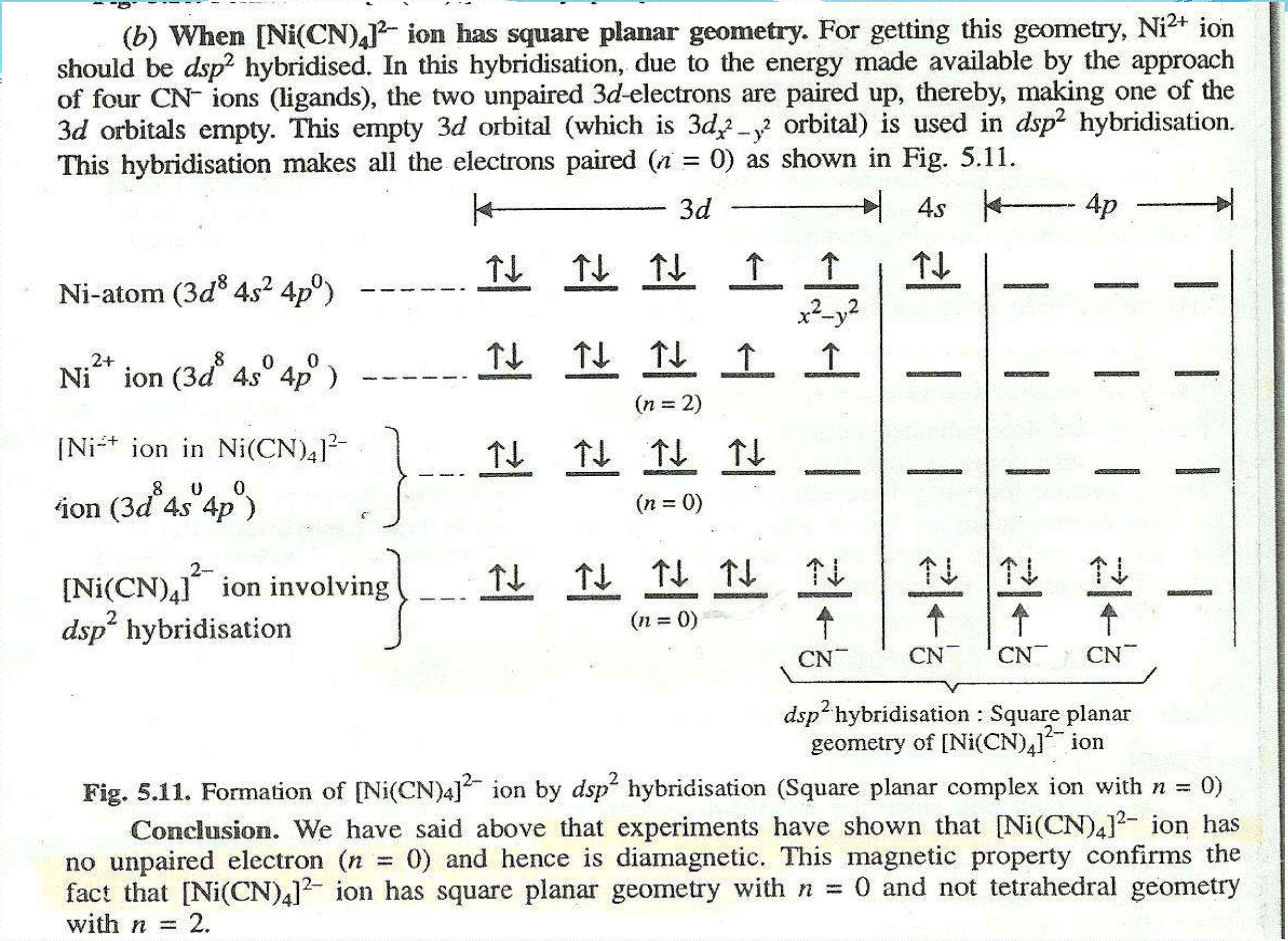


Fig. 5.10. Formation of $[Ni(CN)_4]^{2-}$ ion by sp^3 hybridisation (Tetrahedral complex ion with $n = 2$).



(*b*) **When $[Ni(CN)_4]^{2-}$ ion has square planar geometry.** For getting this geometry, Ni^{2+} ion should be dsp^2 hybridised. In this hybridisation, due to the energy made available by the approach of four CN^- ions (ligands), the two unpaired 3*d*-electrons are paired up, thereby, making one of the 3*d* orbitals empty. This empty 3*d* orbital (which is $3d_{x^2-y^2}$ orbital) is used in dsp^2 hybridisation. This hybridisation makes all the electrons paired ($n = 0$) as shown in Fig. 5.11.

Fig. 5.11. Formation of $[Ni(CN)_4]^{2-}$ ion by dsp^2 hybridisation (Square planar complex ion with $n = 0$)

Conclusion. We have said above that experiments have shown that $[Ni(CN)_4]^{2-}$ ion has no unpaired electron ($n = 0$) and hence is diamagnetic. This magnetic property confirms the fact that $[Ni(CN)_4]^{2-}$ ion has square planar geometry with $n = 0$ and not tetrahedral geometry with $n = 2$.

2. $[Cu(NH_3)_4]^{2+}$ ion

Since the coordination number of Cu^{2+} ion is 4, the given complex ion has either square planar or tetrahedral geometry. Square planar geometry arises due to dsp^2 hybridisation of Cu^{2+} ion as shown in Fig. 5.12 while tetrahedral geometry is due to sp^3 hybridisation of Cu^{2+} ion as shown in Fig. 5.13.

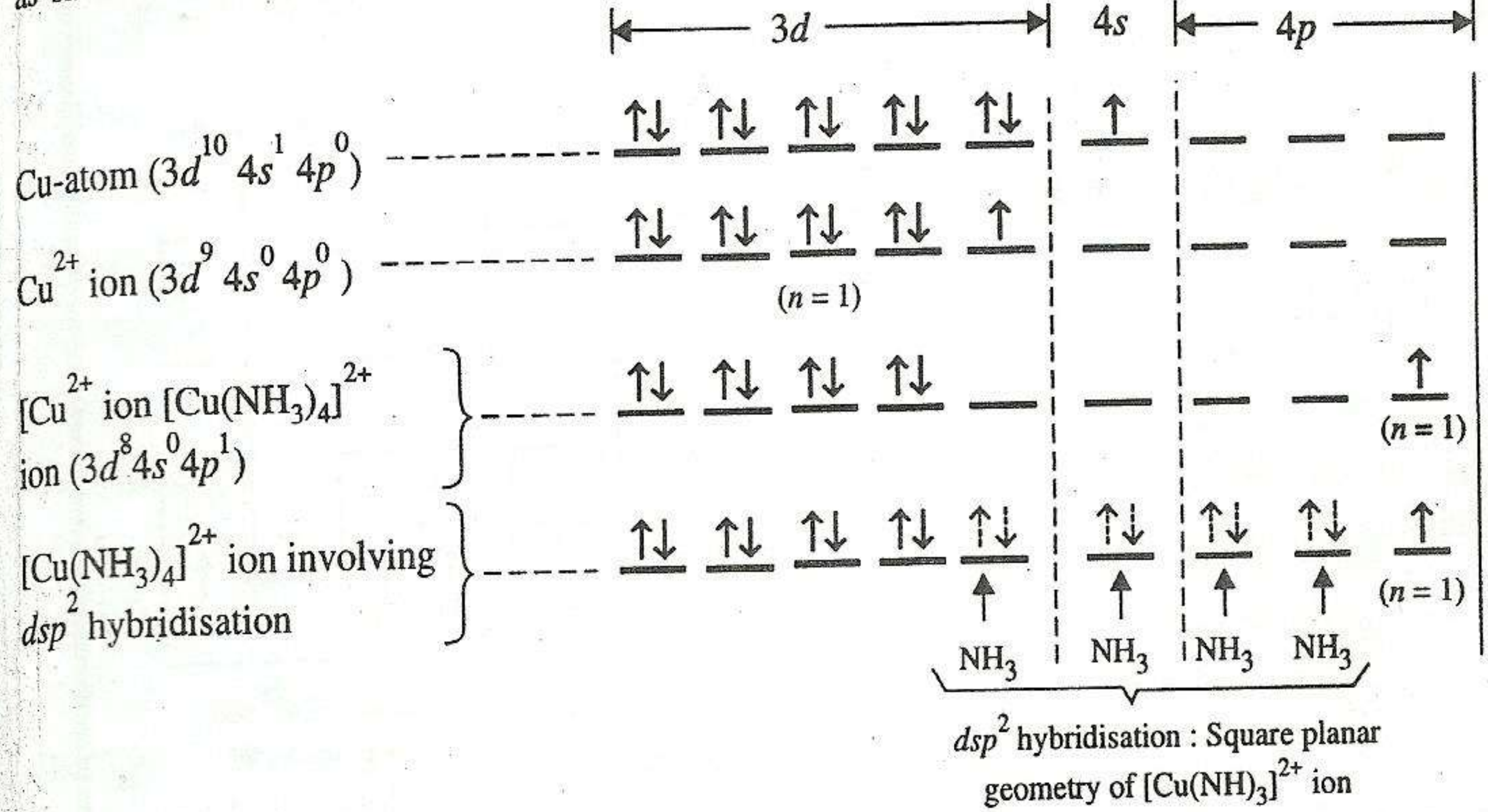


Fig. 5.12. dsp^2 hybridisation of Cu^{2+} ion in $[Cu(NH_3)_4]^{2+}$ ion which has square planar geometry with $n = 1$.

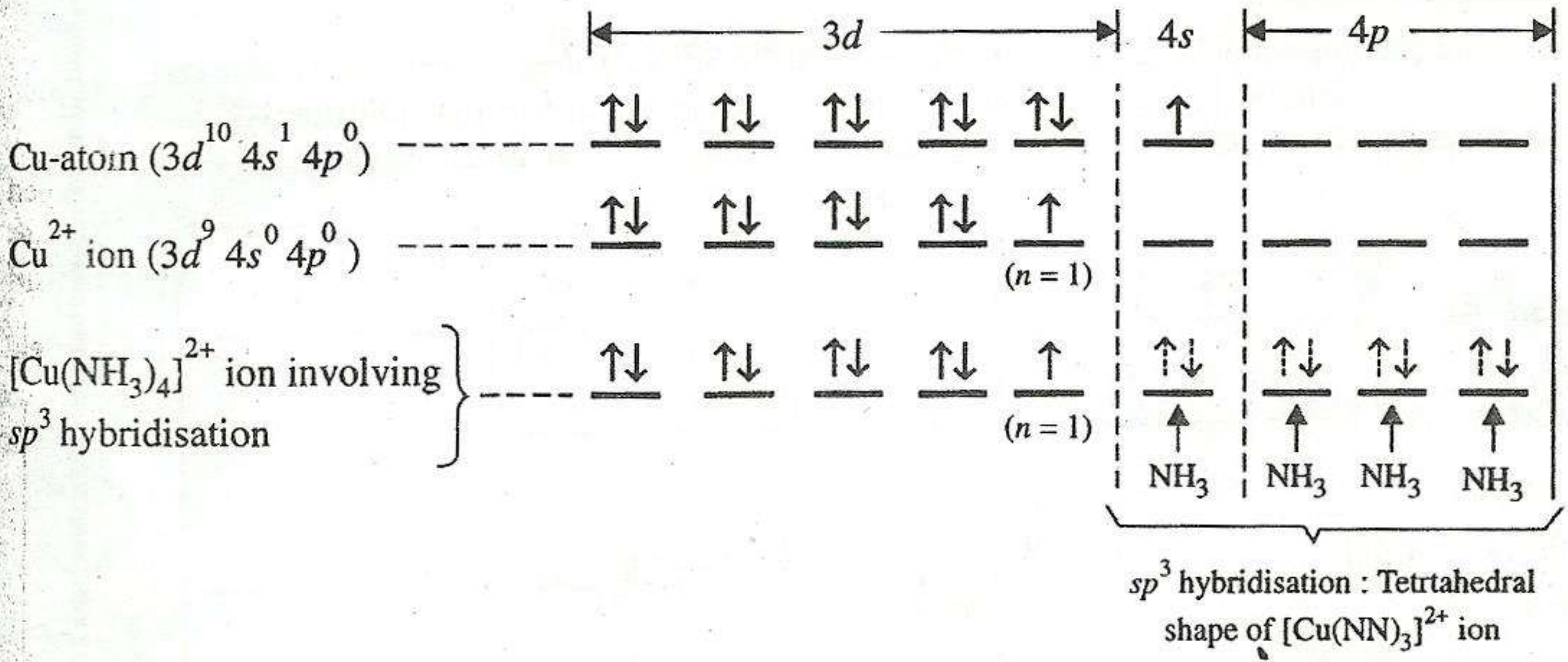
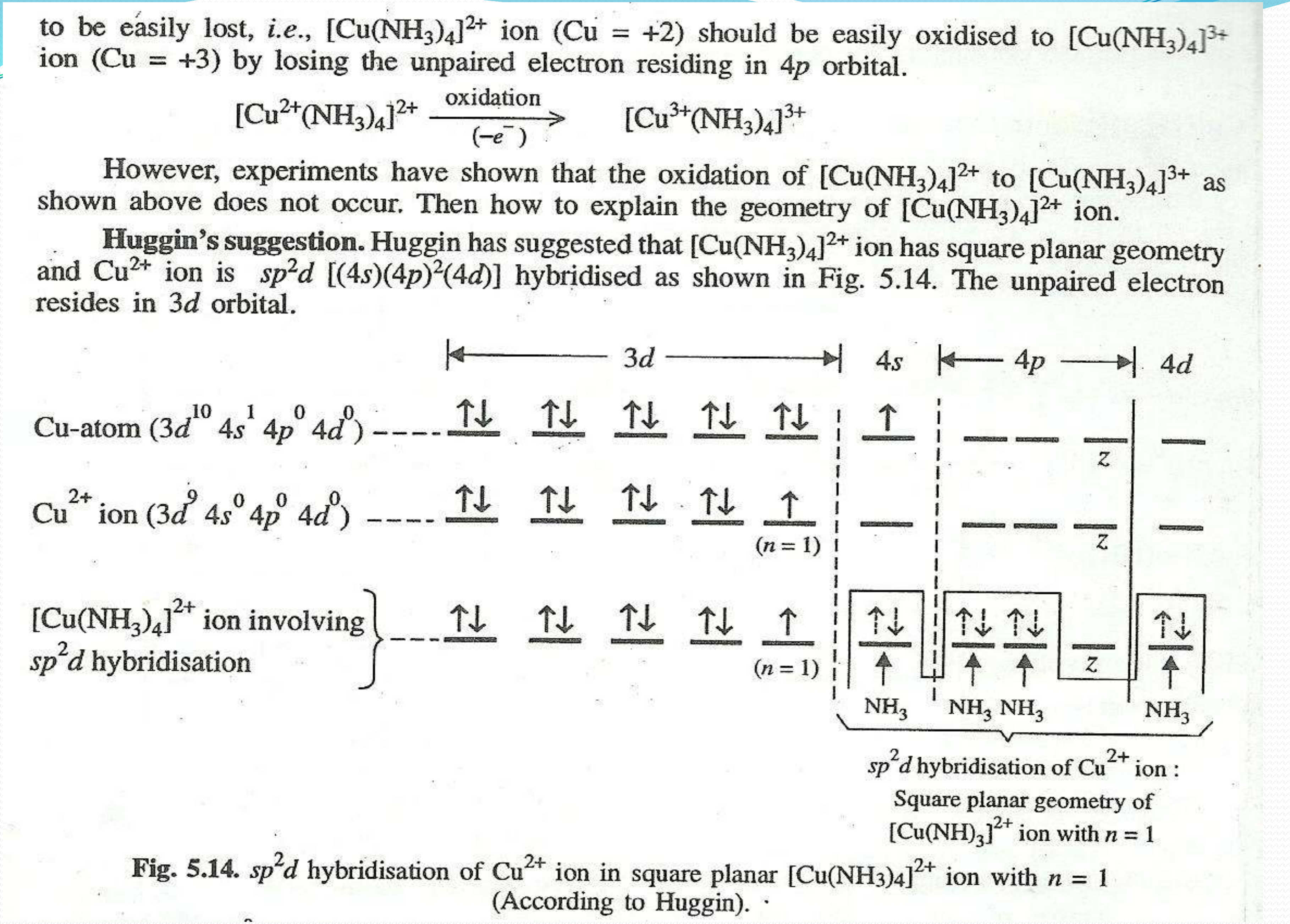


Fig. 5.13. sp^3 hybridisation of Cu^{2+} ion in $[Cu(NH_3)_4]^{2+}$ ion which has tetrahedral geometry with $n = 1$.

As is evident from Figures 5.12 and 5.13 that in both the geometries, $[Cu(NH_3)_4]^{2+}$ ion has one unpaired electron ($n = 1$). In square planar geometry, the unpaired electron resides in 4*p* orbital while in tetrahedral geometry this electron is present in 3*d* orbital.

The above discussion shows that the magnetic property of $[Cu(NH_3)_4]^{2+}$ ion cannot be helpful in deciding as to what is the exact geometry of $[Cu(NH_3)_4]^{2+}$ ion. However, physical measurements have indicated that the tetrahedral geometry for $[Cu(NH_3)_4]^{2+}$ ion is not possible.

Now if the square planar geometry for $[Cu(NH_3)_4]^{2+}$ ion is supposed to be correct, the unpaired electron present in the higher energy 4*p* orbital (*dsp*^{2} hybridisation) should be expected



to be easily lost, *i.e.*, $[Cu(NH_3)_4]^{2+}$ ion (Cu = +2) should be easily oxidised to $[Cu(NH_3)_4]^{3+}$ ion (Cu = +3) by losing the unpaired electron residing in 4*p* orbital.

$$[Cu^{2+}(NH_3)_4]^{2+} \xrightarrow[(-e^-)]{\text{oxidation}} [Cu^{3+}(NH_3)_4]^{3+}$$

However, experiments have shown that the oxidation of $[Cu(NH_3)_4]^{2+}$ to $[Cu(NH_3)_4]^{3+}$ as shown above does not occur. Then how to explain the geometry of $[Cu(NH_3)_4]^{2+}$ ion.

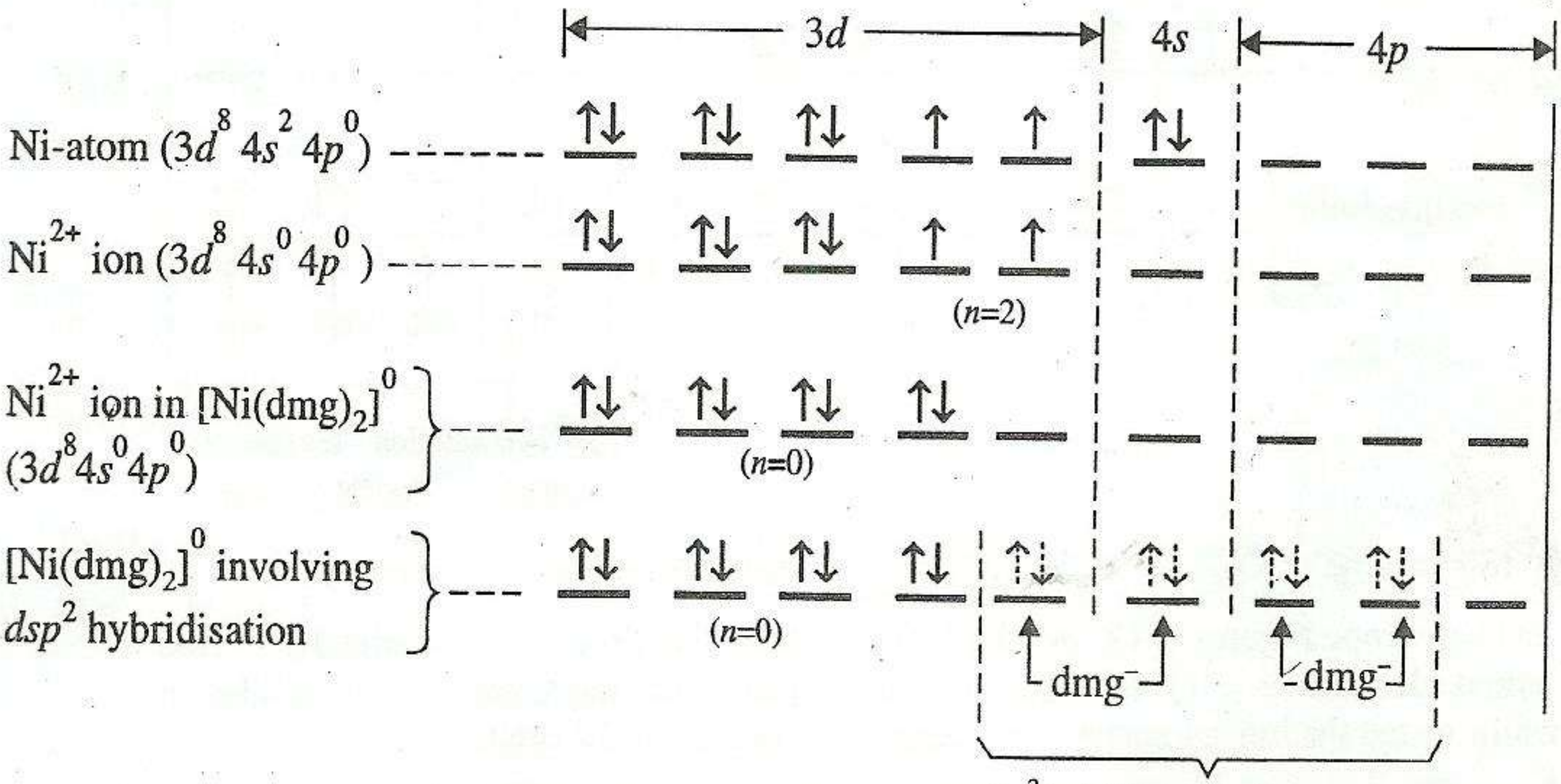
Huggin's suggestion. Huggin has suggested that $[Cu(NH_3)_4]^{2+}$ ion has square planar geometry and Cu^{2+} ion is sp^2d $[(4s)(4p)^2(4d)]$ hybridised as shown in Fig. 5.14. The unpaired electron resides in 3*d* orbital.

sp^2d hybridisation of Cu^{2+} ion :
Square planar geometry of
$[Cu(NH)_3]^{2+}$ ion with *n* = 1

Fig. 5.14. sp^2d hybridisation of Cu^{2+} ion in square planar $[Cu(NH3)4]^{2+}$ ion with *n* = 1 (According to Huggin).

3. $[Ni(dmg)_2]^0$ molecule

In this complex compound, Ni is present as Ni^{2+} ion ($Ni^{2+} = 3d^8 4s^0$). *dmg* is a negatively-charged ion which acts as a bidentate ligand. Magnetic measurements have shown that $[Ni(dmg)_2]^0$ has no unpaired electrons ($n = 0$) and has square planar geometry which arises because of dsp^2



dsp^2 hybridisation : Square planar geometry of $[Ni(dmg)_2]^0$ molecule

Fig. 5.15. dsp^2 hybridisation of Ni^{2+} ion in $[Ni(dmg)_2]^0$ which has square planar geometry. Note that dmg^- ion is a bidentate ligand and hence donates two electron pairs.

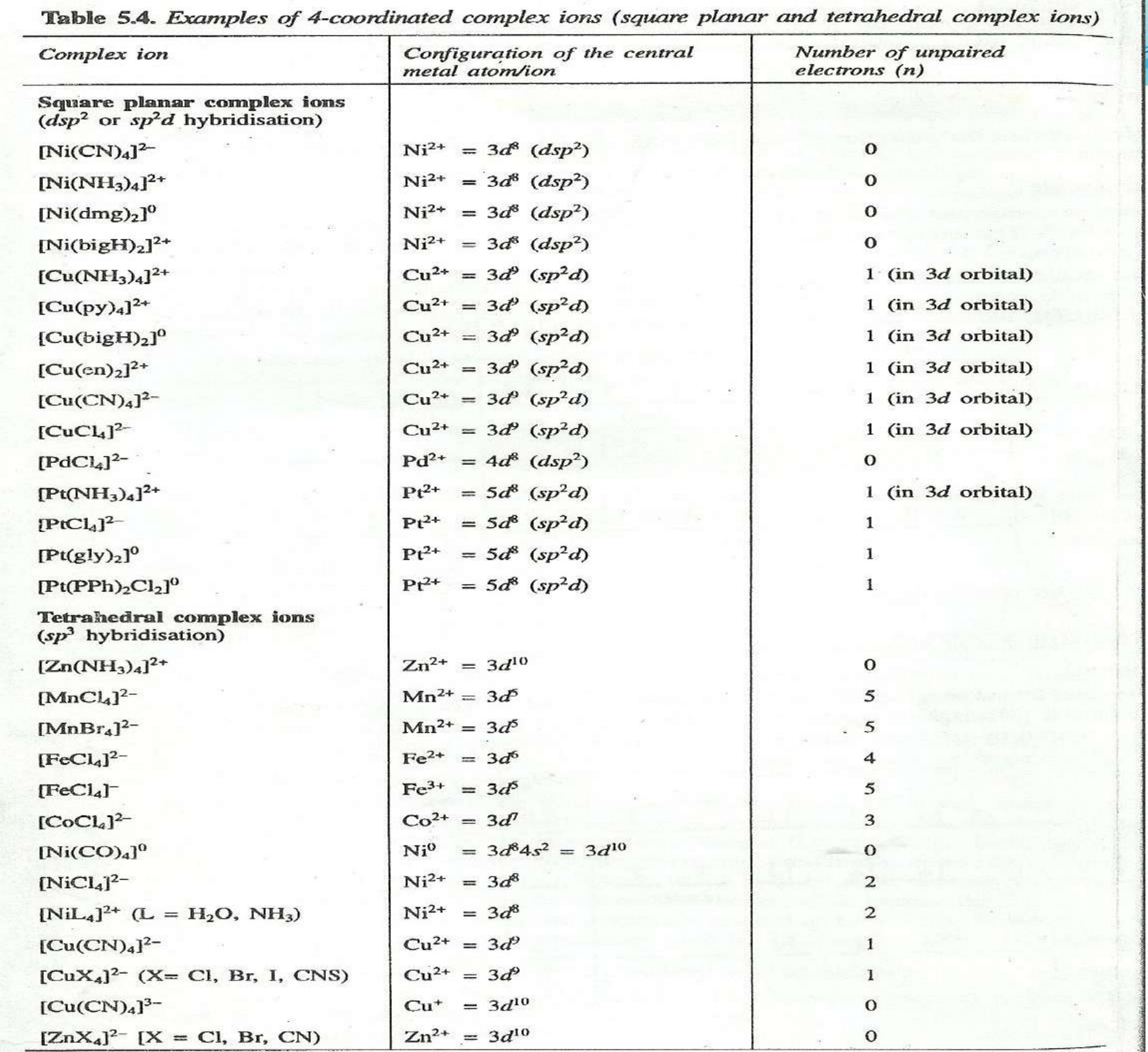


Table 5.4. *Examples of 4-coordinated complex ions (square planar and tetrahedral complex ions)*

Complex ion	*Configuration of the central metal atom/ion*	*Number of unpaired electrons (n)*
Square planar complex ions (dsp^2 or sp^2d hybridisation)		
$[Ni(CN)_4]^{2-}$	$Ni^{2+} = 3d^8\ (dsp^2)$	0
$[Ni(NH_3)_4]^{2+}$	$Ni^{2+} = 3d^8\ (dsp^2)$	0
$[Ni(dmg)_2]^0$	$Ni^{2+} = 3d^8\ (dsp^2)$	0
$[Ni(bigH)_2]^{2+}$	$Ni^{2+} = 3d^8\ (dsp^2)$	0
$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} = 3d^9\ (sp^2d)$	1 (in $3d$ orbital)
$[Cu(py)_4]^{2+}$	$Cu^{2+} = 3d^9\ (sp^2d)$	1 (in $3d$ orbital)
$[Cu(bigH)_2]^0$	$Cu^{2+} = 3d^9\ (sp^2d)$	1 (in $3d$ orbital)
$[Cu(en)_2]^{2+}$	$Cu^{2+} = 3d^9\ (sp^2d)$	1 (in $3d$ orbital)
$[Cu(CN)_4]^{2-}$	$Cu^{2+} = 3d^9\ (sp^2d)$	1 (in $3d$ orbital)
$[CuCl_4]^{2-}$	$Cu^{2+} = 3d^9\ (sp^2d)$	1 (in $3d$ orbital)
$[PdCl_4]^{2-}$	$Pd^{2+} = 4d^8\ (dsp^2)$	0
$[Pt(NH_3)_4]^{2+}$	$Pt^{2+} = 5d^8\ (sp^2d)$	1 (in $3d$ orbital)
$[PtCl_4]^{2-}$	$Pt^{2+} = 5d^8\ (sp^2d)$	1
$[Pt(gly)_2]^0$	$Pt^{2+} = 5d^8\ (sp^2d)$	1
$[Pt(PPh)_2Cl_2]^0$	$Pt^{2+} = 5d^8\ (sp^2d)$	1
Tetrahedral complex ions (sp^3 hybridisation)		
$[Zn(NH_3)_4]^{2+}$	$Zn^{2+} = 3d^{10}$	0
$[MnCl_4]^{2-}$	$Mn^{2+} = 3d^5$	5
$[MnBr_4]^{2-}$	$Mn^{2+} = 3d^5$	5
$[FeCl_4]^{2-}$	$Fe^{2+} = 3d^6$	4
$[FeCl_4]^-$	$Fe^{3+} = 3d^5$	5
$[CoCl_4]^{2-}$	$Co^{2+} = 3d^7$	3
$[Ni(CO)_4]^0$	$Ni^0 = 3d^84s^2 = 3d^{10}$	0
$[NiCl_4]^{2-}$	$Ni^{2+} = 3d^8$	2
$[NiL_4]^{2+}$ ($L = H_2O, NH_3$)	$Ni^{2+} = 3d^8$	2
$[Cu(CN)_4]^{2-}$	$Cu^{2+} = 3d^9$	1
$[CuX_4]^{2-}$ ($X =$ Cl, Br, I, CNS)	$Cu^{2+} = 3d^9$	1
$[Cu(CN)_4]^{3-}$	$Cu^{+} = 3d^{10}$	0
$[ZnX_4]^{2-}$ [$X =$ Cl, Br, CN)	$Zn^{2+} = 3d^{10}$	0

hybridisation of Ni^{2+} ion. For getting dsp^2 hybridisation, one $3d$ orbital should be vacant. In order to make $3d$ orbital vacant, two unpaired electrons present in $3d$ orbitals are forced to get paired (see Fig. 5.15).

b–

Tetrahedral Complex Ions

Here we shall discuss the structure of the following complex compounds which have tetrahedral geometry.

1. $Ni(CO)_4$ molecule

In this complex compound Ni is in zero oxidation state and has its valence-shell configuration as $3d^8 4s^2$. This compound has tetrahedral geometry which arises due to sp^3 hybridisation of Ni atom.

The magnetic studies of $Ni(CO)_4$ have indicated that this molecule is diamagnetic ($n = 0$), showing that the two $4s$ electrons are forced to pair up with $3d$ orbitals. This results in sp^3 hybridisation and $Ni(CO)_4$ molecule has tetrahedral structure. (see Fig. 5.16).

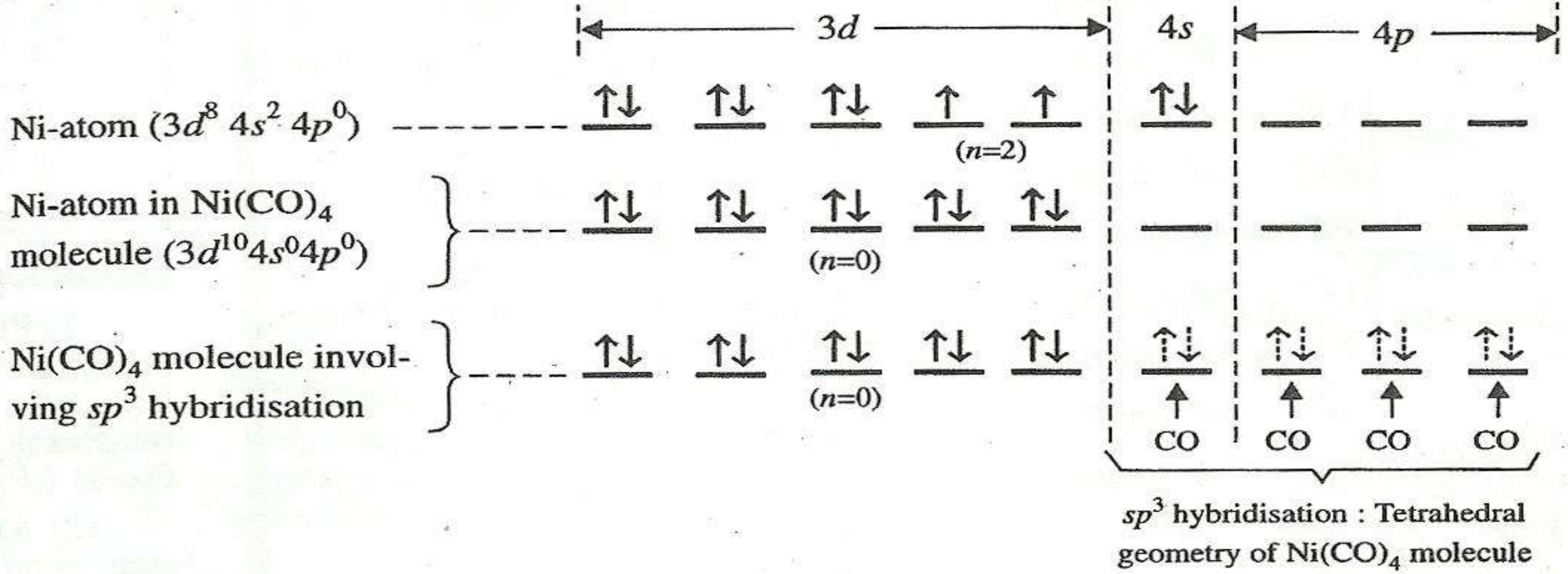
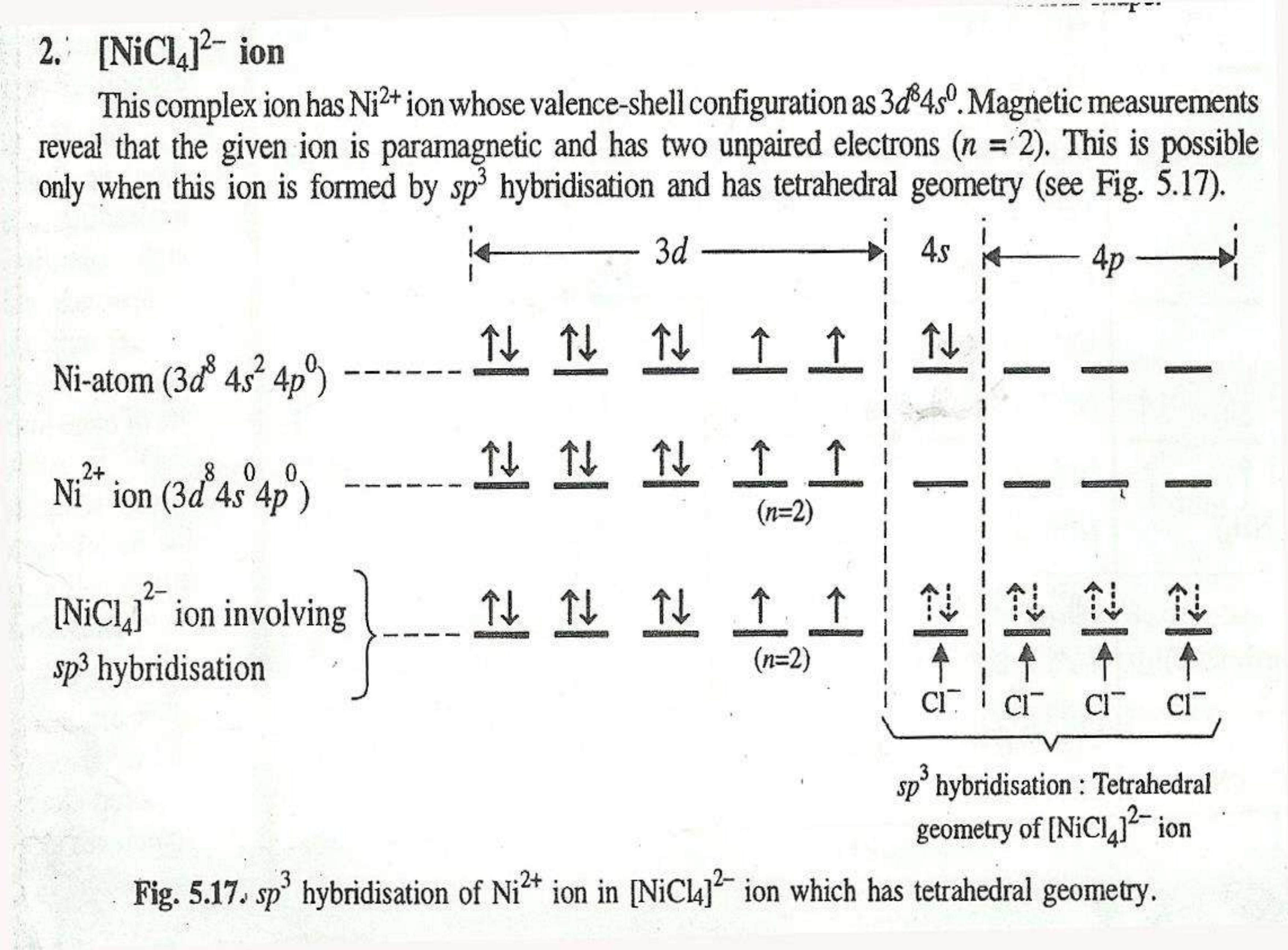


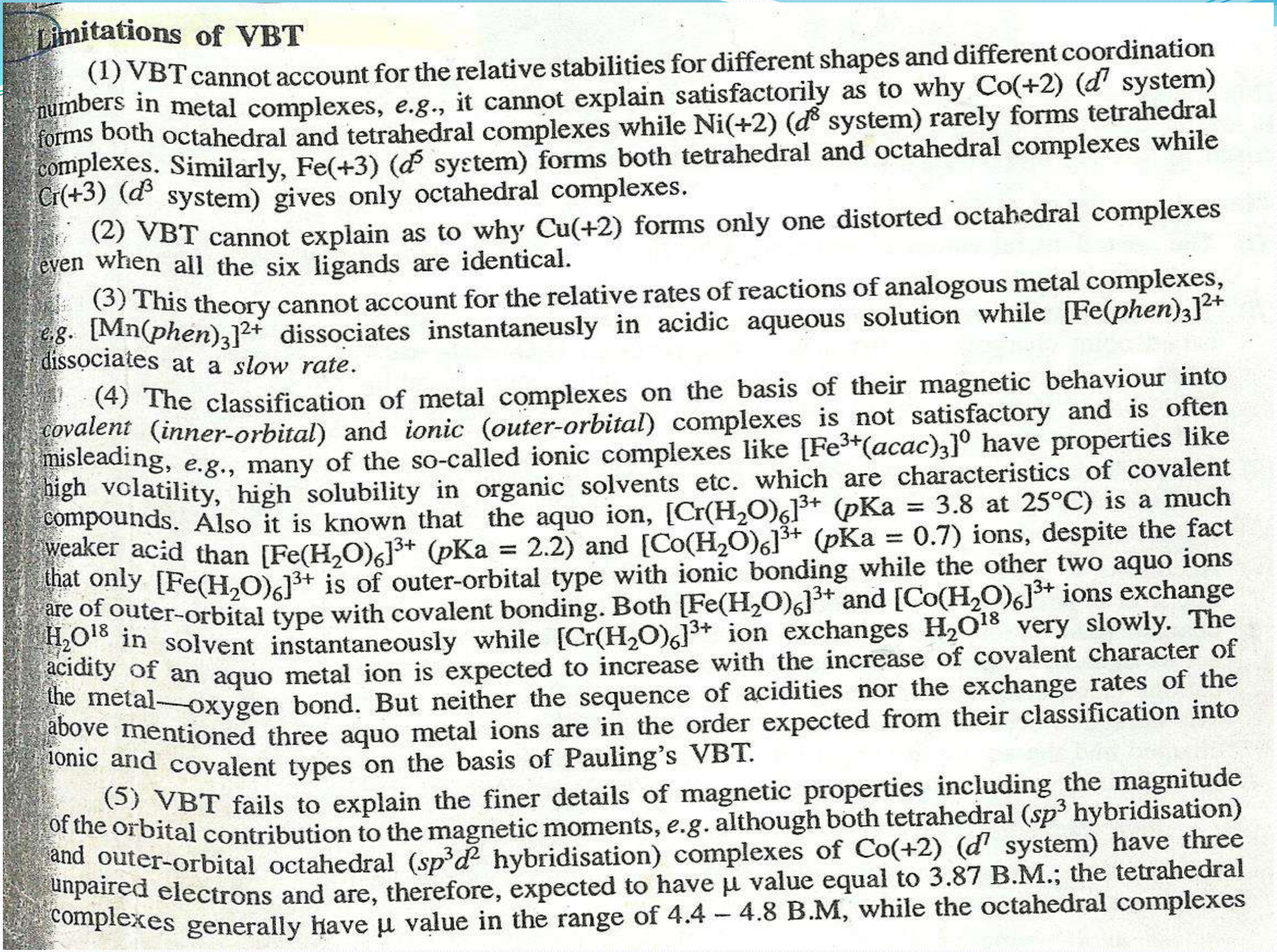
Fig. 5.16. sp^3 hybridisation of Ni-atom in $Ni(CO)_4$ molecule which has tetrahedral shape.



2. $[NiCl_4]^{2-}$ ion

This complex ion has Ni^{2+} ion whose valence-shell configuration as $3d^8 4s^0$. Magnetic measurements reveal that the given ion is paramagnetic and has two unpaired electrons ($n = 2$). This is possible only when this ion is formed by sp^3 hybridisation and has tetrahedral geometry (see Fig. 5.17).

Fig. 5.17. sp^3 hybridisation of Ni^{2+} ion in $[NiCl_4]^{2-}$ ion which has tetrahedral geometry.



Limitations of VBT

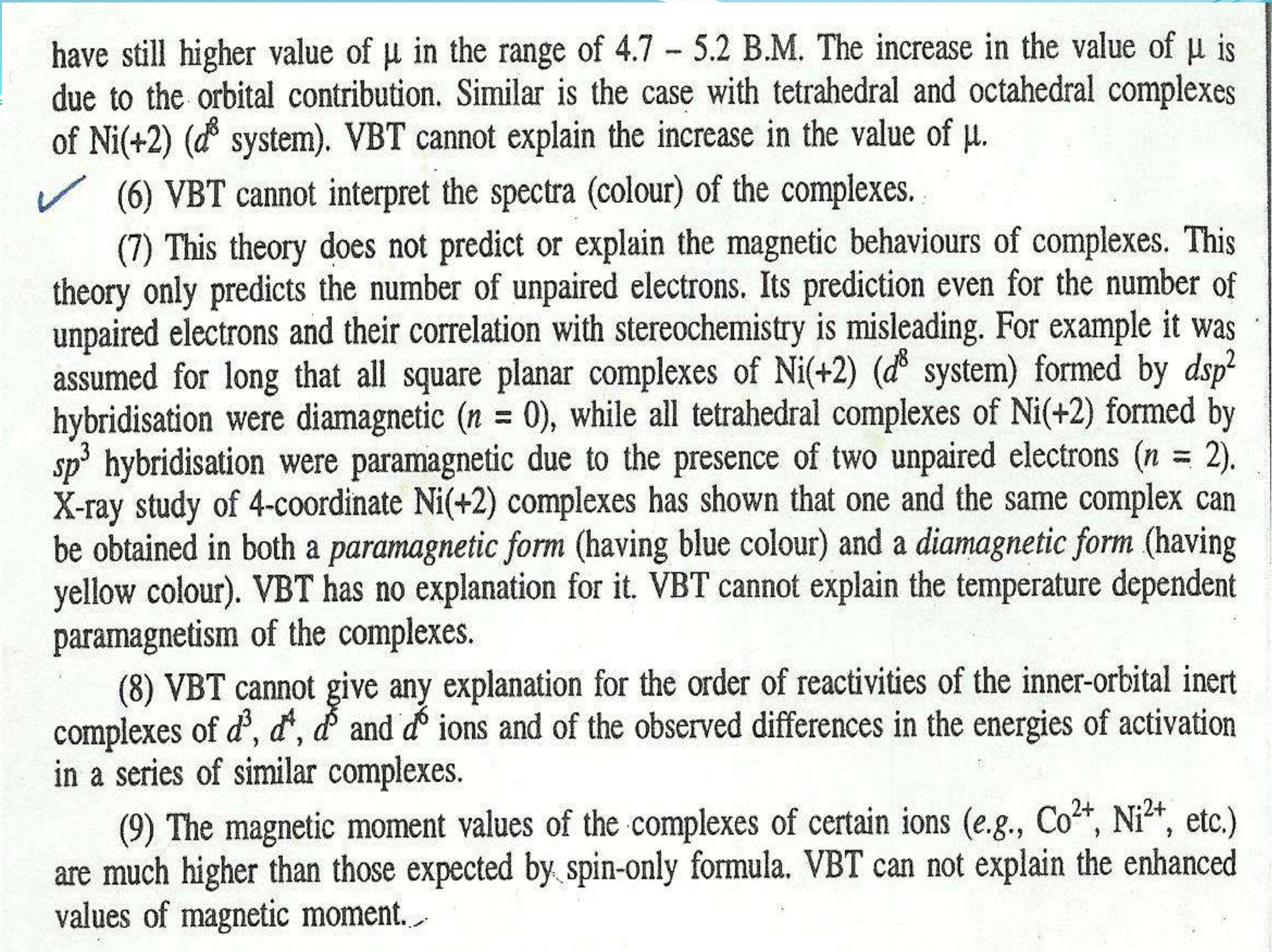
(1) VBT cannot account for the relative stabilities for different shapes and different coordination numbers in metal complexes, *e.g.*, it cannot explain satisfactorily as to why Co(+2) (d^7 system) forms both octahedral and tetrahedral complexes while Ni(+2) (d^8 system) rarely forms tetrahedral complexes. Similarly, Fe(+3) (d^5 system) forms both tetrahedral and octahedral complexes while Cr(+3) (d^3 system) gives only octahedral complexes.

(2) VBT cannot explain as to why Cu(+2) forms only one distorted octahedral complexes even when all the six ligands are identical.

(3) This theory cannot account for the relative rates of reactions of analogous metal complexes, *e.g.* $[Mn(phen)_3]^{2+}$ dissociates instantaneusly in acidic aqueous solution while $[Fe(phen)_3]^{2+}$ dissociates at a *slow rate*.

(4) The classification of metal complexes on the basis of their magnetic behaviour into *covalent* (*inner-orbital*) and *ionic* (*outer-orbital*) complexes is not satisfactory and is often misleading, *e.g.*, many of the so-called ionic complexes like $[Fe^{3+}(acac)_3]^0$ have properties like high volatility, high solubility in organic solvents etc. which are characteristics of covalent compounds. Also it is known that the aquo ion, $[Cr(H_2O)_6]^{3+}$ ($pKa = 3.8$ at 25°C) is a much weaker acid than $[Fe(H_2O)_6]^{3+}$ ($pKa = 2.2$) and $[Co(H_2O)_6]^{3+}$ ($pKa = 0.7$) ions, despite the fact that only $[Fe(H_2O)_6]^{3+}$ is of outer-orbital type with ionic bonding while the other two aquo ions are of outer-orbital type with covalent bonding. Both $[Fe(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$ ions exchange H_2O^{18} in solvent instantaneously while $[Cr(H_2O)_6]^{3+}$ ion exchanges H_2O^{18} very slowly. The acidity of an aquo metal ion is expected to increase with the increase of covalent character of the metal—oxygen bond. But neither the sequence of acidities nor the exchange rates of the above mentioned three aquo metal ions are in the order expected from their classification into ionic and covalent types on the basis of Pauling's VBT.

(5) VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments, *e.g.* although both tetrahedral (sp^3 hybridisation) and outer-orbital octahedral (sp^3d^2 hybridisation) complexes of Co(+2) (d^7 system) have three unpaired electrons and are, therefore, expected to have μ value equal to 3.87 B.M.; the tetrahedral complexes generally have μ value in the range of 4.4 – 4.8 B.M, while the octahedral complexes



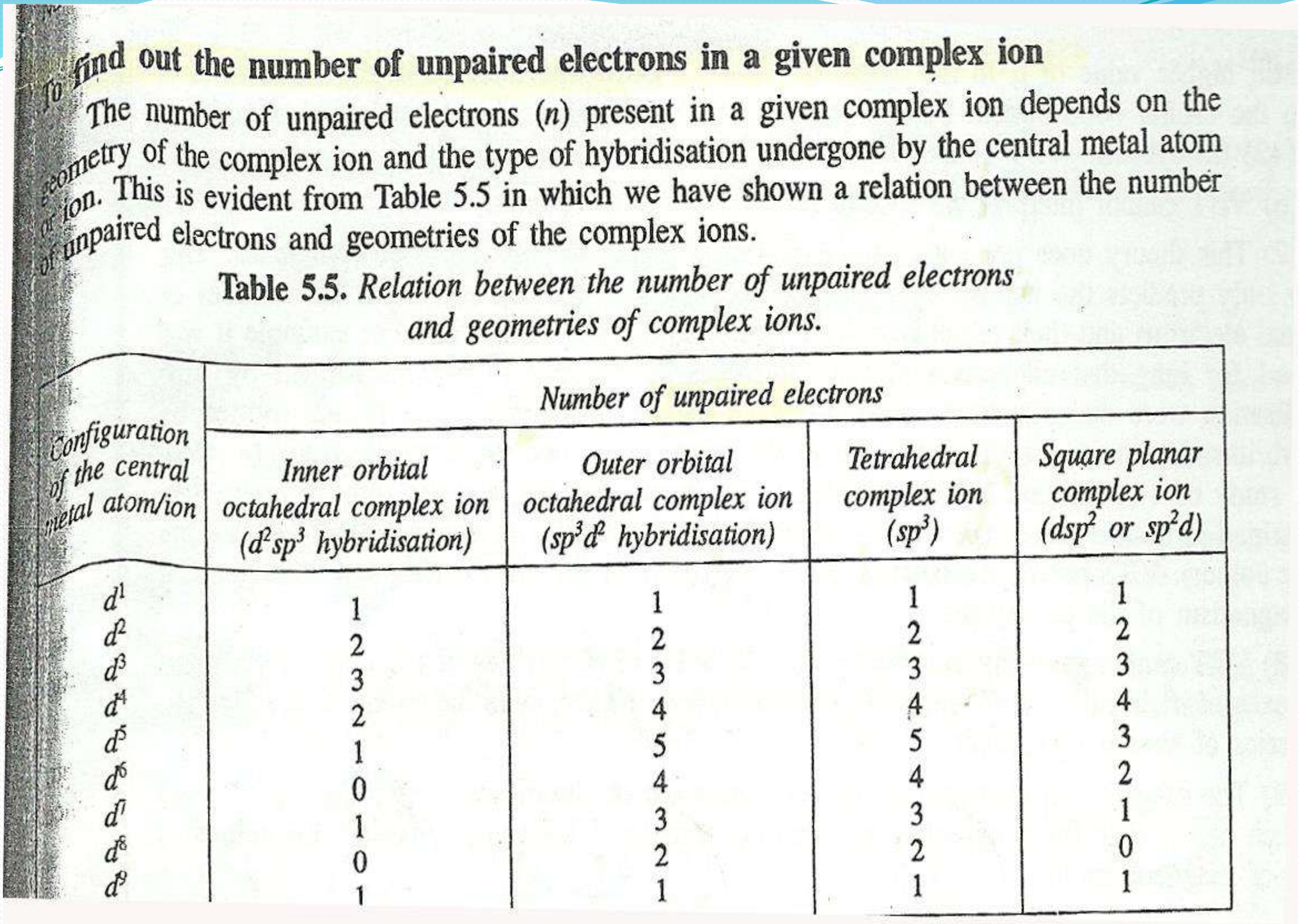
have still higher value of μ in the range of 4.7 – 5.2 B.M. The increase in the value of μ is due to the orbital contribution. Similar is the case with tetrahedral and octahedral complexes of Ni(+2) (d^8 system). VBT cannot explain the increase in the value of μ.

✓ (6) VBT cannot interpret the spectra (colour) of the complexes.

(7) This theory does not predict or explain the magnetic behaviours of complexes. This theory only predicts the number of unpaired electrons. Its prediction even for the number of unpaired electrons and their correlation with stereochemistry is misleading. For example it was assumed for long that all square planar complexes of Ni(+2) (d^8 system) formed by dsp^2 hybridisation were diamagnetic ($n = 0$), while all tetrahedral complexes of Ni(+2) formed by sp^3 hybridisation were paramagnetic due to the presence of two unpaired electrons ($n = 2$). X-ray study of 4-coordinate Ni(+2) complexes has shown that one and the same complex can be obtained in both a *paramagnetic form* (having blue colour) and a *diamagnetic form* (having yellow colour). VBT has no explanation for it. VBT cannot explain the temperature dependent paramagnetism of the complexes.

(8) VBT cannot give any explanation for the order of reactivities of the inner-orbital inert complexes of d^3, d^4, d^5 and d^6 ions and of the observed differences in the energies of activation in a series of similar complexes.

(9) The magnetic moment values of the complexes of certain ions (*e.g.*, Co^{2+}, Ni^{2+}, etc.) are much higher than those expected by spin-only formula. VBT can not explain the enhanced values of magnetic moment.



To find out the number of unpaired electrons in a given complex ion

The number of unpaired electrons (n) present in a given complex ion depends on the geometry of the complex ion and the type of hybridisation undergone by the central metal atom or ion. This is evident from Table 5.5 in which we have shown a relation between the number of unpaired electrons and geometries of the complex ions.

Table 5.5. *Relation between the number of unpaired electrons and geometries of complex ions.*

Configuration of the central metal atom/ion	*Number of unpaired electrons*			
	Inner orbital octahedral complex ion (d^2sp^3 hybridisation)	*Outer orbital octahedral complex ion (sp^3d^2 hybridisation)*	*Tetrahedral complex ion (sp^3)*	*Square planar complex ion (dsp^2 or sp^2d)*
d^1	1	1	1	1
d^2	2	2	2	2
d^3	3	3	3	3
d^4	2	4	4	4
d^5	1	5	5	3
d^6	0	4	4	2
d^7	1	3	3	1
d^8	0	2	2	0
d^9	1	1	1	1

Crystal Field Theory (CFT)

This theory advanced by Brethe and Van Vleck was originally applied mainly to ionic crystals and is, therefore, called **Crystal Field Theory (CFT).** It was not until 1952 that Orgel popularised its use for inorganic chemists.

Important features of CFT

(*i*) The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons.

(*ii*) The ionic ligands (*e.g.*, F^-, Cl^-, CN^- etc.) are regarded as negative point charges (also called point charges) and the neutral ligands (*e.g.*, H_2O, NH_3, etc.) are regarded as point dipoles or simply dipoles, *i.e.*, according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.

(*iii*) The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons, *i.e.*, it does not consider any orbital overlap.

(*iv*) According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic or coulombic attraction between positively-charged (*i.e.*, cation) and negatively-charged (*i.e.*, anions or dipole molecules which act as ligands) species. Complexes are thus presumed to form when centrally situated cations electrically attract ligands which may be either anions or dipole molecules. The attraction between the cations and the ligands is because the cations are positively charged and the anions are negatively charged and the dipole molecules, as well, can offer their negatively incremented ends for such electrostatic attractions.

Grouping of five *d*-orbitals into t_{2g} and e_g sets of orbitals

On the basis of the orientation of the lobes of the five-*d*-orbitals with respect to coordinates these have been grouped into the following two sets.