Basic Concepts and Terminology

1.1 BASIC CONCEPTS

When solutions, containing two or more salts are mixed and crystallized, often some new compounds called **molecular addition compounds** are formed. These are classified into following two categories on the basis of their behavior in aqueous solution;

(i) **Double Salts:** These are those compounds, which when dissolved in water, lose their identity and give the tests of all the ions which they contain. Examples are carnellite $KC1$, $MgC1_2$, $6.H_2O$; Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$ and potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

(ii) **Coordination Compounds:** These are those compounds, which retain their identify both in solid as well as in solution state. These dissolve in water to produce a complex ion and a simple ion of opposite charge. For example when aqueous solutions of $Fe(CN)_2$ and KCN are mixed in stoichiometric ratio, a new compound $4KCN.Fe(CN)_2$ is formed, which in aqueous solution breaks as;

$$\underset{\text{Simple}}{4K^+} + \underset{\text{Complex ion}}{Fe(CN)_6^{4-}}$$

and should thus be formulated as $K_4[Fe(CN)_6]$. The complex ions formed by the ionisation of a coordination compound, may be of the types, as shown below;

Complex cation

$$CuSO_4 \cdot 4(NH_3) = \underset{\text{Complex cation}}{[Cu(NH_3)_4]^{2+}} + \underset{\text{Simple ion}}{SO_4^{2-}} = [Cu(NH_3)_4]SO_4$$

Complex anion

$$3KCN.Fe(CN)_6 = \underset{\text{simple ion}}{3K^+} + \underset{\text{complexan ion}}{Fe(CN)_6^{4-}} = K_3[Fe(CN_6)]$$

Neutral complex

$PtCi_2.2(NH_3)$ = No ionisation or formulated as $[Pt(NH_3)_2Cl_2]$

1.2 TERMINOLOGY AND DEFINITIONS

(a) **Complex ion: The cation or the central metal ion, to which one or more neutral groups or charged ions are attached or a charged aggregate formed when metal atom or ion becomes directly, attached to a group of neutral molecules or anions is called a complex ion.** As shown, the complex compounds, may be classified as a cationic complex (if complex ion has a positive charge, an anionic complex (if complex ion has a negative charge) or a neutral complex which has no charge or does not ionise.

(b) **Coordination sphere: The whole entity, in which a certain number of neutral molecules or anions are attached to the metal ion, is called the coordination sphere.** In writing the formulae of complexes, the coordination sphere is indicated as enclosed by two big brackets [ ] and the portion outside the coordination sphere, which contains the simple ion is called **Ionisation sphere.**

(c) **Coordination number:** This is also called **ligacy and is equal to the total number of neutral molecules or anions attached to the metal ion, usually arranged in a definite geometry.** Coordination number is usually a fixed quantity for a particular metal ion in a particular oxidation state, but a large number of metal ions are also known to exhibit more than one coordination number. The most common coordination numbers encountered in complexes are **4 and 6** but in many cases coordination numbers as **2, 3, 5, 7, 8, 9 and 12** have also been well established and recognised.

(d) **Ligands: The neutral molecules or anions attached directly to central metal ion, are called Ligands.** Studies reveal that all such groups possess, at least one atom with a lone pair of electrons. The atom in the ligand, which possesses the lone pair is called a **donor atom** and the ligand as a whole acts as a **Lewis base** (or electron pair donor) and the metal ion acts as a **Lewis acid** (or electron pair acceptor), and the formation of a coordination compound (as shown in following equation), is therefore an acid-base reaction;

$$\underset{\substack{\text{Lewis}\\\text{Acid}}}{M^{n+}} + \underset{\substack{\text{Lewis}\\\text{Acid}}}{xL} \longrightarrow \underset{\substack{\text{Salt or}\\\text{Complex}\\\text{Compound}}}{[ML_x]^{n+}}$$

(e) Dissociation properties and stability: One of the characteristics of complex compounds is that, it tends to retain its identity in solution, although, partial dissociation may occur. In fact, the extent of dissociation and also the time taken for dissociation, may vary from slight to very extensive. For example the compound with molecular formula $2KBr.HgBr_2$, which is a tetrahedral complex of Hg, $K_2[HgBr_4]$ dissolves in solution with very slight dissociation. On the other hand, the compound $2KCl.CoCl_2$ which is also a tetrahedral complex, but of Co of formula $K_2[CoCl_4]$ is found to dissociate extensively in solution into chloride ions, potassium ions and hydrated cobalt (II) ions. These two examples illustrate, the differences in the relative thermodynamic stability of coordinate bonds and it may be inferred that mercury (II) bromide bond is more stable than mercury (II) water bond whereas cobalt (II) chloride bond is less stable than cobalt (II) water bond.

Complexes which exchange ligands rapidly that is, within mixing times are generally referred to as **labile complexes,** while those which exchange ligands at slower rate are called **non-labile or inert** complexes. The thermodynamic stability of complexes, should not be confused with kinetic stability as the two terms are different. For example the average energy per bond in $[Cr(H_2O)_6]^{3+}$ (122kcals/mole) is nearly the same as that in $[Fe(H_2O)_6]^{3+}$ (116Kcals/mole), yet former exchanges water molecules with the labelled solvent water molecules at a slower and measurable rate, whereas latter exchanges them very rapidly.

Much of the chemistry of coordination compounds is determined by the: (i) electronic configuration of central ion, (ii) donor and acceptor properties of ligands and (iii) nature of linkage between the ligands and central ion. All these aspects have been discussed at their proper places in the book, but some aspects such as nomenclature, classification of ligands, types of complex compounds and the isomerism encountered among these are discussed in this chapter.

1.3 NOMENCLATURE OF COORDINATION COMPOUNDS

The following are the basic rules, adopted by the **International Union of Pure and Applied Chemistry (IUPAC)** in 1976 for naming these compounds.

(i) In writing the formula, the central metal atom or ion is written first.

(ii) In the coordination sphere, ligands are named first and then the metal ion, to which these are coordinated. The ligands are named in alphabetical order regardless of their charge. Thus, in complex $[Pt(NH_3)_2Cl_2]$ ammine is named first and then chloride ions. Water, ammonia and carbon monoxide are special ligands which are named aquo, ammine and carbonyl respectively. The names of negative ligands are modified to end in 'o', thus O_2 is oxo, OH^- is hydroxo, CN^- is cyano and Cl^- is chloro etc. Organic ligands are named by their own names e.g. CH_3 as methyl, C_6H_5, as phenyl and C_5H_5 as cyclopentadienyl.

(iii) The number of ligands coordinated to the metal ion, is denoted by prefixes di, tri, tetra, penta, hexa, hepta and so forth. A donor that can attach to the same metal ion, through more than one of its donor atoms is called a **chelate** or a **multidentate ligand,** and these are denoted as bidenate, tridentate, tetradentate pentadentate and sexadentate corresponding to the possession of two, three, four, five and six donor sites respectively. If the name of the ligand itself contains a number, to avoid confusion, it's name is also indicated by prefixes bis, tris, tetrakis, etc.

(iv) When a ligand contains two or more donor atoms and possibility of linkage stands in more than one way, the point of attachment of ligand to the metal ion, is indicated by writing the chemical symbol of atom, which is attached to the metal after the name of ligand. Thus, Thicyanato-S- and Thiocyanato-N- are used to distinguish SCN^- group bonded through sulphur or nitrogen respectively. When nitrite ion $(NO_2)^-$ is the ligand, the terms nitrite-N- and nitrite-O- are used to indicate N or O coordination.

(v) The name of the central metal ion in a cationic and neutral complex, is written as such but in an anionic complex the ending 'ate' is added, either after the full name of metal or after a part of it. For example $CoCl_6^{3-}$ is named as hexachlrocobaltate ion, $Fe(CN)_6^{4-}$ as hexacyanoferrate ion, and $[Pt(NH_3)_2Cl_2]$ as diamminedichloroplatinum, respectively.

(vi) The oxidation number of metal ion is indicated by a roman numeral enclosed in small brackets, immediately after the name of the metal without any gap.

(vii) The prefix -μ- is used for designating, a ligand which is bridging in nature. For two bridging groups of the same type, the prefix di -μ- is used, otherwise the prefix -μ- is repeated before the name of each different bridging ligand.

(viii) Complexes containing two or more metal ions are called **polynuclear complexes** and in these complexes bridging ligands are always present, which are named first, followed by the metal-metal bond, present in parenthesis.

(ix) Geometrical isomers are named by the term **cis for adjacent and trans for opposite** groups. For square planar complexes, positions (1,2) and (3,4) are cis while positions (1,3) and (2,4) are trans. In simple mononuclear octahedral complexes, positions (1,2), (2,3), (3,4) (4,1), (1,5) (6,2), (6,3),(4,5) are **cis,** while (1,6), (2,4) and (3,5) and (1,6) are **trans.**

(x) For optical isomers, the terms dextro and laevo or (+) and (–) are used to designate, those isomers which rotate the plane of polarized light to right and left, respectively.

Some examples are given below to illustrate the application of these rules;

$[CO(NH_3)_6]Cl_3$ – Hexamminecobalt (III) chloride

$[CO(NH_3)_5Cl]Cl_2$ – Pentamminechlorocobalt (III) chloride

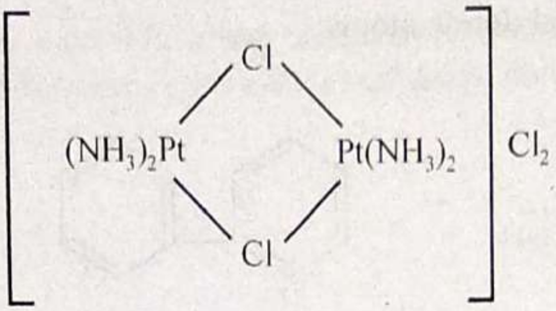
$[Pt(NH_3)_2Cl_2]$ – Diamminedichloroplatinum (II)

$K_2[PtCl_6]$ – Potassium (I) hexachloroplatinate (IV)

Cis-$[Cr(H_2O)_4Cl_2]Cl$ – Cis-tetraquodichlorochromium (III) Chloride

$[CO(NH_3)_6]\,[CrCl_6]$ – hexaminecobalt (III) hexachlorochromate (III)

$[(NH_3)_5CO-NH_2-CO(NH_3)_4H_2O]Cl_5$ – Pentammine cobalt (III)-μ amidotetrammineaquo cobalt (III) chloride



di-μ-chlorobis-diammineplatinum (II) chloride

1.4 CLASSIFICATION OF LIGANDS

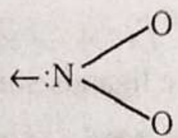
1.4.1 The most commonly used classification of ligands, is based on the number of donor atoms present in them, and the following classes of ligands have been recognised:

(a) Monodentate: Ligands, containing only one donor atom, donating only one lone pair of electron to any metal ion and coordinating through only one site are called **menodentate ligands**. Examples include H_2O, NH_3, halide ions, triphenylphosphine(PPh_3), nitrosonium ion (NO^+) and hydrazinium ion ($NH_2NH_3^+$).

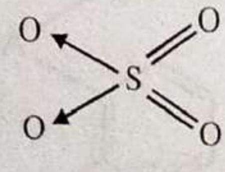
Sometimes, a monodenate ligand may have more than one atom with lone pair of electrons and can simueltaneously coordinate to two or more metal ions, either same or different, structures making a bridge between them. Such ligands are called bridging ligands and these form two coordinate bonds with two metal ions. The examples include;

Dinitrogen (N_2) : $\leftarrow:N \equiv N:\rightarrow$
Hydrazine (N_2H_4) : $H_2\ddot{N}-\ddot{N}H_2$
Thiocyanato (SCN) : $\leftarrow:SCN:\rightarrow$
Perxo (O_2) : $\leftarrow:O-O:\rightarrow$

Nitro (NO_2^-) :



Sulphato (SO_4^{2-}) :

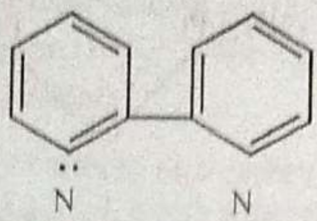


(b) Bidentate ligands: Ligands having two donor atoms, both of which can simultaneously form two coordinate bonds with the same metal ion are called **bidentate ligands**. As a result of coordination, a ring structure incorporating the metal ion, called the chelate ring, is formed. The structures of some of these ligands along with their standard abbreviated names are given below:

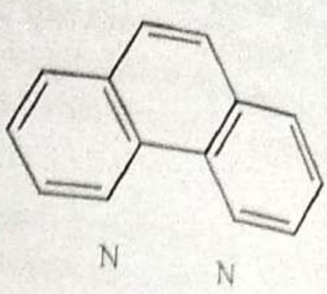
Ligands with two neutral donor atoms

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

ethylenediamine (en)

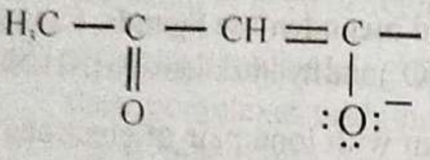


2.2 dipyridyal
(dipy)



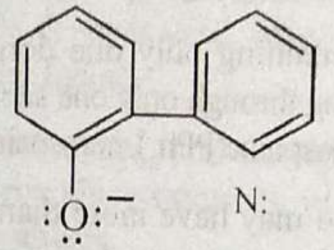
o-phenanthroline
(phen)

Ligands with one neutral and one anionic donor atoms

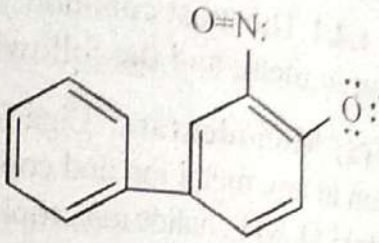


$$H_3C-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{:\ddot{O}:^-}{|}}{C}-CH_3$$

acetylacetanato (acac)

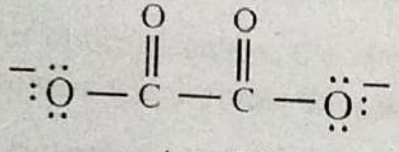


8-hydroxyquinialate



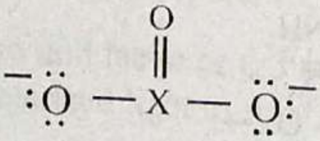
α-nitroso-β-napthal

Ligands with two anionic donors



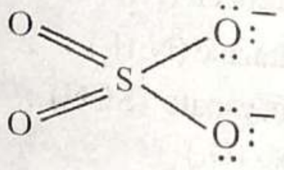
$$^-:\ddot{\underset{..}{O}}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\ddot{\underset{..}{O}}:^-$$

oxalato (OX)



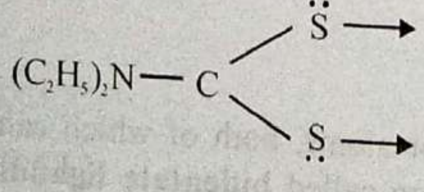
$$^-:\ddot{\underset{..}{O}}-\overset{\overset{O}{\|}}{X}-\ddot{\underset{..}{O}}:^-$$

Carbonato (Carb)

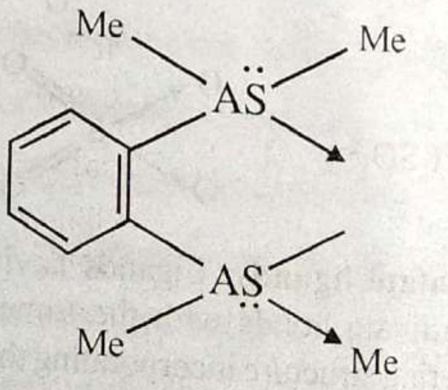


Sulphato (Sulph)

The structures of two other important neutral bidentate ligands studied some what recently is:

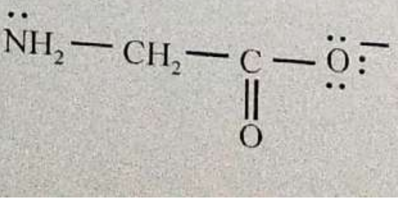


N, N-diethyldithiocarbonate (dtc)



O-phenylesbisdimethylarsine (diars)

The bidentate ligands may be symmetrical if the two donors are the same, or unsymmetrical if these are different. The symmetrical ligand is denoted as A-A, and unsymmetrical as A-B, where A and B are the two donor atoms. An example of later is glycinate ion;



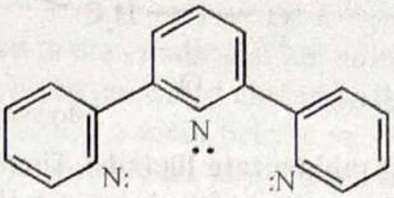
$$\ddot{N}H_2-CH_2-\underset{\underset{O}{\|}}{C}-\ddot{\underset{..}{O}}:^-$$

(c) Polydentate ligands: These include ligands having more than two donor atoms and may be tri, tetra, penta or hexadentate depending upon number of donor atoms. Some examples of such ligands are given below:

(i) Tridentate

$\ddot{N}_2H - (CH)_2 - \ddot{N}H - (CH)_2 - \ddot{N}_2H$

diethyline triamine (dien)

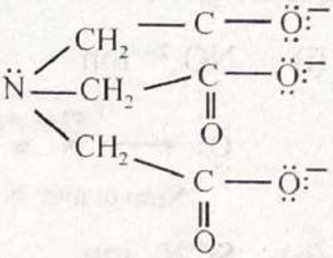


2′, 2′, 2″ - Terpyridine (terpy)

(ii) Tetradentate

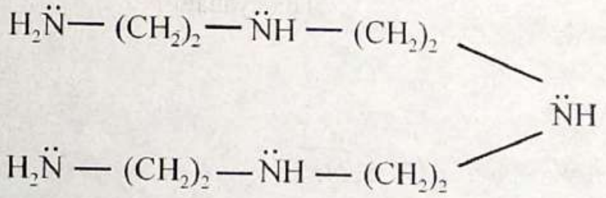
$H_2\ddot{N}-(CH_2)_2-\ddot{N}H-(CH_2)_2-\ddot{N}H-(CH_2)_2-NH_2$

Triethylene-tetramine (trien)

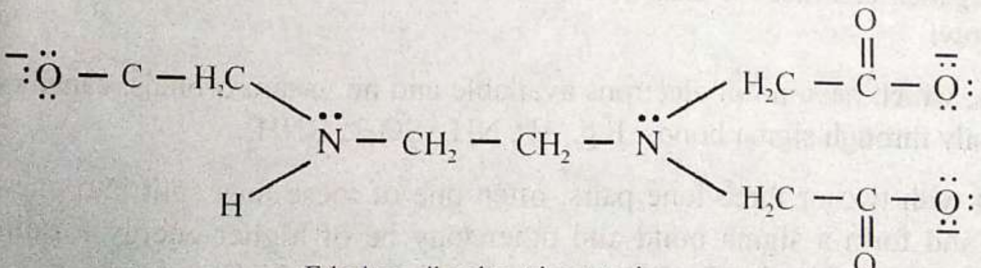


Nitrilotriacetateo (nta)

(iii) Pentadentate



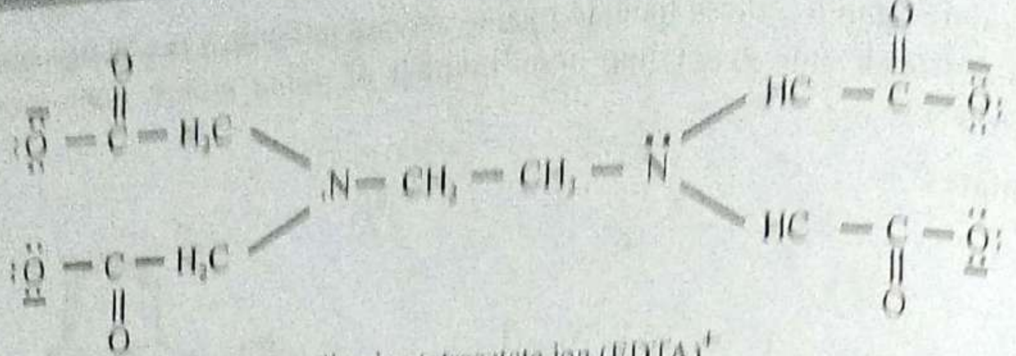
Tetraethylene pentamine (tetraen)



Ethylene diamine triacetate ion

(iv) Hexadentate

It is not necessary that a polydenate ligand may use all its donor atoms for coordination. Thus, number of donor atoms to be used (nitrate or sulphate ions may act as mono or bidentate ligands), depends on the metal concerned as well as the symmetry of the resulting complex formed.



Ethylenediamine tetracetate ion $(EDTA)^{4-}$

(d) Ambidentate ligands: There are certain ligands, which have two or more donor atoms in their structure, but in forming a complex, only any one of the two donor atoms, may be attached to a metal ion at a certain time. These ligands, thus give different compounds which have different structures and are infact isomeric in nature (discussed later). Some common examples, along with their different structures are given below and the donor atom has been marked with an asteric;

(i) NO_2^{2-} ion

$\underset{..}{\ddot{O}}: \longleftarrow \overset{*}{\bar{N}} = \ddot{O}:$ or $\underset{..}{\ddot{O}}: \text{——} \overset{*}{\bar{N}} = \ddot{O}:$

Nitro or nitro-N Nitrilo nitro-O

(ii) SCN^- ion

$^{-}:\underset{..}{\ddot{S}} \text{——} \overset{*}{\bar{C}} \equiv N:$ or $^{-}:\underset{..}{\ddot{S}} = C = \overset{*}{\bar{N}}:$

Thiocyanato-S Thiocyanato-N

(iii) CN^-

$:\overset{*}{\bar{C}} = N:$ or $:C \equiv \overset{*}{\ddot{N}}:^{-}$

Cyano-C Cyano-N

1.4.2. The ligands can also be classified on the basis of the nature of coordinate bond, which form as given below:

(a) Ligands, which have no pi electrons available and no vacant orbitals, can coordinate to the metal only through sigma bonds. E.g., H^-, NH_3, SO_3^{2-}, RNH_2.

(b) Ligands with two or three lone pairs, often one of these may split into one pair of lower energy and form a sigma bond and other may be of higher energy forming a pi bond. E.g., N^3, O^{2-}, F^-, Cl^-, Br^-, I^-, OH^-, S^{2-}, NH^{2-}, H_2O, R_2S, NH^{2-}.

(c) Ligands having a sigma bonding pair of electrons and low energy empty pi antibonding orbitals, suitably oriented so as to accept non-bonding d-orbital electrons from the metal ion may result in back bonding. E.g., CO, R_3P, R_3As, I^-, CN^-, Py. Thus in such complexes both metal and ligands function as donor and acceptor simultaneously.

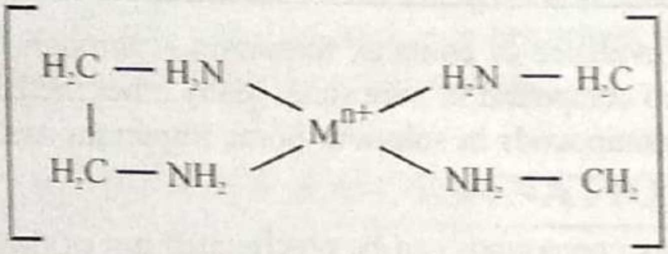
(d) Ligands without unshared lone pair but having pi bonding electrons, which can form only pi bonds. E.g., alkenes, alkynes, benzene, cyclopentadienyl anion.

(e) Ligands that can form two sigma bonds with two separate metal ions, and can thus act as bridging in nature. E.g., OH^-, Cl^-, F^-, NH_2^-, O_2^{2-}, CO etc.

1.5 CHELATION

As mentioned earlier, many polydenate ligands, if attached to the same metal ion through two or more donor atoms, result in a strain-free ring structure. Such ligands are called **chelating ligands** and the phenomenon is called **chelation.** But every multidentate ligand, cannot behave as chelating in nature because its donor atoms have to be so arranged, so as to coordinate to the same metal atom producing a ring structure.

Most important example of such a ligand is ethynediamine which can give a ring structure around the metal ion as shown;



$[M(en)_2]^{n+}$

The chelated complexes, in general are known to be more stable than non-chelated complexes and this effect is known as **chelate effect.** This may be explained by taking the examples of chelated and non-chelated complexes of the same metal ion.

Thus $[Cu(H_2O)_4]^{2+}$ forms four coordinate complexes with methylamine CH_3NH_2, ethylenediamine (en) and triethylenetetramine formulated as $[Cu(CH_3NH_2)_4]^{2+}$; $[Cu(en)_2]^{2+}$. $[Cu(trien)]^{2+}$.

Complex (i) is expected to possess no rings, while (ii) and (iii) will have, two five membered rings around Cu^{2+} ion. The stability of the three complexes follows the order;

$$[Cu(NH_2CH_3)_4]^{2+} < [Cu(en)_2]^{2+} < [Cu(trien)]^{2+}$$

and this is explained by the change in the free energy ΔG° of the three systems. The larger is the negative value of ΔG°, greater is the stability of the system. The value of ΔH° for all the three reactions is negative and same. The three complexes are formed from $Cu(H_2O)_4^{2+}$, according to following reactions,

(i) $[Cu(H_2O)_4]^{2+} + 4CH_3NH_2 \rightarrow [Cu(NH_2CH_3)_4]^{2+} + 4H_2O$

(ii) $[Cu(H_2O)_4]^{2+} + 2en \rightarrow [Cu(en)_2]^{2+} + 4H_2O$

(iii) $[Cu(H_2O)4]^{2+} + trien \rightarrow [Cu(trien)]^{2+} + 4H_2O$

The number of molecules on both the sides is the same in reaction (i) and thus there is no change in the entropy of system, i.e., ΔS° = 0 and hence ΔH° is negative.

In reaction (ii), four molecules of water are replaced by two molecules of ethylenedimaine and as there is a decrease of two molecules in the formation of products, the value of ΔS° increases and is also positive. In reaction (iii), four molecules of water are replaced by one molecule of triethylenetetramine (triene), and there is a decrease of 3 molecules in product and hence there is a greater increase in the positive value of ΔS°. The ΔG°, has a negative value in all the three reactions, but its negativity increases in regular order from reaction (i), to reaction (iii). Thus $[Cu(trien)]^{2+}$ is the stablest of all the three complexes.

It is also known that if a group is present near the donor atom, the stability is lowered. This is called **steric effect, steric hindrance or steric strain** and in accordance, it is seen that though, ethylene diamine and N-tetramethylenediamine both form chelate complexes of octahedral geometry, with nickel (II), but complex of former is more stable than complex of latter. Similarly 8-hydroxyquinoline, forms more stable complexes, than its 2-methylderivative. The lower stability, is due to the steric overcrowding, due to the presence of methyl groups on the donor atom in N-tetramethylenediamine and near the donor atom in 2-methyl-8-hydroxoquinoline.

1.6 DETECTION OF COMPLEXES

Though, the truly conclusive evidence of complex formation is through its isolation, it is not always possible to isolate the desired compound in pure state. Many other methods are thus used, to confirm the formation of complex compounds in solution. Some important methods amongst these, are given below:

(i) **Precipitation** – The complex compounds can be precipitated out of their solutions as,

(a) a neutral covalent complex, in polar medium as a result of reaction of metal ion with anionic ligand, for e.g., formation of bis (dimethylglyoximato) nickel (II) and tris (acctylacetonato) aluminium (III) by the following reactions;

$$Ni^{+2} + 2DmgH \rightarrow [Ni(Dmg)_2] + 2H^+$$

$$A1^{3+} + 3CH_3COCH_2COCH_3 \rightarrow [Al(CH_3COCHCOCH_3)_3] + 3H_2O$$

(b) ion pairs, i.e., a large complex anion, by the addition of a big cation like Hg^+; Cs^+; Ph_4As^+; or $Cr(NH_3)_6^{3+}$ or a large complex cation by the addition of a large anion like $[Cr(SCN)_6]^{3-}$ as shown below;

$$Hg^{2+} + 21 \rightarrow HgI_2 + 21^- \rightarrow HgI_4^{2-} + 2Cu \rightarrow Cu[HgI_4]$$

$$CO^{2+} + 4SCN'' \rightarrow [CO^{2+}(SCN)_4]^{2-} \xrightarrow{Hg^{2+}} Hg[CO^{2+}(SCN)_4]$$

(ii) Change in chemical behaviour – The chemical behaviour of metal ions in the presence and absence of ligands changes considerably, thereby indicating the formation of a complex. Thus, copper (II) ions are not precipitated from their solutions, by the addition of an alkali in presence of amines (am) and also H_2S fails to precipitate it, in presence of CN^- ions, due to the formation of complex $[Cu(am)_4]^{2+}$ and $Cu(CN_4)^{2-}$ ions.

(iii) Dissolution of an insoluble compound – It is seen that many times, an insoluble precipitate dissolves readily in the presence of a ligand due to the formation of complex ions. For e.g., AgCl and HgI_2 dissolve in excess of ammonia and iodide solutions on account of the formation of the complex cations,

$$[Ag(NH_3)_2]^{1+} \text{ and } [HgI_4]^{2-} \text{ respectively.}$$

(iv) Absorption spectra – A change in the colour of solution, on the addition of another reagent indicates the formation of a new complex ion, which gives a distinct absorption peak in the visible region of spectrum (400-1000nm). Some common examples are;

$Co^{2+} + 4Cl^{-} \rightarrow [Co^{2+}Cl_4]^{2-}$
Pink Blue

$Cu^{2+} + 4Cl^{-} \rightarrow [CuCl_4]^{2-}$
Blue Green

$Ni^{2+} + 2en \rightarrow [Ni(en)_2]^{2+}$
Green Pale Yellow

(v) Other properties – Besides the few properties discussed above, almost any other physical property of the system depending upon the nature of species present, can be used as an indication of complex formation. Some of these are ion exchange behaviour, polarography, mass spectrometry, NMR and ESR spectroscopy and finally the x-ray analysis.

1.7 CLASSIFICATION OF COORDINATION COMPOUNDS

Because of the great variety of coordination compounds known, a systematic classification is difficult. Further, no one method has been found suitable. However, some methods devised are outlined below:

(i) If the compounds are classified on the basis of **coordination number**, then almost 98% of all known complexes will fall under coordination numbers 4 and 6, since most of the metal ions exhibit either or both of these. The number of metallic elements with a true odd coordination number, is rare. However, more examples are turningup in recent years, with coordination number 5, 7 and 9. For e.g., the number of complexes of dioxocations as UO_2^{2+} with coordination number 5 may be almost as large as the complexes of coordination numbers 4 and 6. But it is still true that odd coordination numbers, prevail only under unusual conditions, which involve unusual stereochemistry, unusual coordinate bond character and the possession of a particular d^n configuration by the central atom.

(ii) The compounds may be classified, on the basis of kind of **metal atoms or ions** involved. However a total of some 84 elements, may act as a central atom or ion in a complex and most of these display several oxidation states, each of which must be considered as an entirely different ion. In fact, several transition metals, can exist as different oxidation species of type MO_x^{n+1} (in the same oxidation state), where x may be 1, 2 or 3 and n may vary integrially from 0 to 5. For example, Mo^{5+} may be found as central species of complex ions, in any of the three mononuclear forms Mo^{5+}, MoO^{3+}, MoO_2^{1+} as well as dinuclear forms as $Mo_2O_2^{6+}$, $Mo_2O_3^{4+}$ etc.

(iii) A classification of complexes according to the kind of **ligand,** present is a better approach and elements whose atoms in appropriate molecules or ion may be attached directly to metal atoms are shown below;

C	N	O	Cl
(Sn,Sb)	(P,As,Sb)	(S,Se,Te)	(F,Br,I)

Most of the ligand atoms include the true non metals. In general, it is found that there is a ver distinct preference amongst the metals of first short period for ligands, and it is possible to recognis two extreme classes of acceptor metals on this basis:

Class a — Those metals which form their most stable complexes with the first element of eac group (i.e N, O, F) Most of the metals with empty or completely filled (n–l)d-orbitals fall into this clas and are in fact hard acids.

Class b — Those metals which form most stable complexes, with the second or subsequen element of each group and only a small number of metals fall in this category and these are soft acids.

(iv) Finally all complexes may be placed into one of the following four categories depending upon the electronic configuration of the metal atom or ion.

Category I

Such metal ions, possess a valence shell inert gas configuration $1s^2$ or ns^2 np^6. These ions, are spherically symmetrical with the element being in the highest oxidation state. The latter, situation is true for 4f and 5f elements in their +3 oxidation state, where the incomplete 4f energy levels are buried sufficiently deep below the valence shell and can thus exert only relatively minor effect on the nature of metal ligand bond. However, in the actinide series, the 5f orbitals are close to the surface of ions and exert significant role in bonding.

In general, the central atoms of this category are **class a acceptors**. As we proceed from left to right, the bond type goes from highly ionic to higly covalent. Sigma bonds increase in strength regularly from left to right. As we reach the transition elements, an ever increasing contribution to the M-L pi bonding is expected, provided the ligand has such orbitals. It is for this reason, that oxygen is an important ligand, as we go from left to right in the table and is capable of forming double or even triple bonds with the transition elements, by virtue of its capacity to delocalise its pi bonding electrons into the empty d-orbitals of central atom/ion resulting in p_π–d_π bonding. Fluoride may also form stronger bonds via this bonding.

Category II

The metal ions of this category, possess a pseudo inert gas configuration (n–1) d^{10} where n = 4, 5 or 6. These central atoms are also spherically symmetrical and the complexes formed are highly covalent. As we move from right to left in the table, the contribution to metal ligand bond from $M \rightarrow L_\pi$ bonding, becomes increasing important and this mechanism enables the central atom to delocalise the negative charge, which would otherwise accumulate on them (Chapter 3).

Therefore, we have seen that metals of both category are involved in pi bonding, but the difference between the two is that, for species of the first category the d_π acceptor orbitals are of lower principal quantum number than the s bonding s and p orbitals, whereas for metals of second category, the π acceptor orbitals, are the higher d orbitals.

Category III

Under this category, those metal ions are included which in their complexes, have a pseudo inert gas plus two configuration, i.e., (n–l)d^{10} ns^2 where n is 4, 5, and 6. These metal ions are spherical symmetrical in terms of their d electron distribution, but the outer pair of s^- electron, even though non-bonding, are placed at a special position in the molecule. Relatively little data is available to support this, but $SnCl_3^-$ and GeF_2 are distorted sufficiently, to make room for lone pair.

Category IV

In this category, those metal ions are placed which in their complexes have occupied but incompletely filled d orbitals $(n-1)d^{1-9}$ where n is 4, 5, or 6. This group is by far the largest and most diverse, since it includes all the transition metals in all of their many oxidation states. This category for convenience has been further subdivided on the basis of number of d electrons and the nature of bond formed with a particular ligand. Thus in this category are included coordinate bonds, which range from ionic to highly covalent including both (M→L) π and (L→M) π bonding. The complexes may have perfectly regular, slightly distorted as well as grossly distorted structures also.

1.8 ISOMERISM IN COMPLEX COMPOUNDS

The compounds of identical composition, but having divergence in their properties and structures are regarded as isomers and the phenomenon is called **isomerism**. This difference, is due to different structural arrangement of atoms in their molecule. Formerly the phenomenon was shown to be associated with organic compounds only, but with the development of coordination chemistry, a vast number of complexes are also known to exhibit isomerism.

Among complexes of metals of first transition series, it is found that majority of those that exhibit isomerism, are octahedral complexes of chromium (III), low spin complexes of Co (III) but a few cases involving octahedrally coordinated iron (III) or nickel (II) or planar four coordinated nickel (II) are also known. Many examples of platinum metals also exist in isomeric forms, amongst which four coordinated complexes of Pt (II) are of particular importance. The isomers have been classified as:

Isomerism in Complexes

Structural Isomerism

1. Ionization isomerism
2. Hydrate isomerism
3. Coordination isomerism
4. Linkage isomerism
5. Polymerization isomerism

Stereo Isomerism

1. Geometrical
2. Optical

1.8.1 Structural Isomerism

This type of isomerism arises, due to the difference in structures of compounds and may be of following types;

(i) Ionization isomerism – Compounds having similar empirical composition but producin different ions in solution, are called **ionization isomers** and the phenomenon is observed when th **ligands in the coordination sphere are exchanged with the anions present in the ionizatio sphere.** Some examples are:

Empirical formulae	**Isomer and mode of ionization**	**Colour**	**Ion in solution**
$CO(NH_3)_5Br.SO_4$	$[CO(NH_3)_5Br]SO_4 \rightarrow [CO(NH_3)_5Br]^{2+} + SO_4^{2-}$	Red	SO_4^{2-}
	$[CO(NH_3)_5SO_4]Br \rightarrow [CO(NH_3)_5SO_4]^{+1} + Br^-$	Violet	Br^-
$Pt(NH_3)_4Cl_2Br_2$	$Pt(NH_3)_4Cl_2Br_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Br^-$	Pink	Br^-
	$[Pt(NH_3)_4Br_2]Cl_2 \rightarrow [Pt(NH_3)_4Br_2]^{2+} + 2C1^-$	Red	Cl^-
$CO(NH_3)_4Cl_2NO_2$	$[CO(NH_3)_4Cl_2]NO_2 \rightarrow [CO(NH_3)_4Cl_2]^{1+} + NO_2^-$	---	
	$[CO(NH_3)_4ClNO_2]Cl \rightarrow [CO(NH_3)_4ClNO_2]^{1+} + Cl^-$	–	

The fact, that these isomers give different ions is solution, as shown above, may be confirmed by performing the qualitative test of that particular ion.

(ii) Hydrate isomerism – The water molecules in complex compounds, may be present as coordinated water or water of crystallization and a isomerism may arise, by the replacement of coordinated water by anions present outside the coordination sphere. The best known example of this type is the compound $CrCl_3{\cdot}6H_2O$ which is found to exist in following three isomers;

$[Cr(H_2O)_6]Cl_3$ - Violet in colour, ionizes to produce $3C1^-$ ions in solution

$[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ - green, ionizes to produce $2C1^-$ ions in solution.

$[Cr(H_2O))_4Cl_2]Cl{\cdot}2H_2O$ - Green, ionizes to produce only one Cl^- ion in solution.

The behaviour of these isomers over concentrated H_2SO_4 shows the presence of zero, one an two molecules of water of crystallization in the three complexes respectively.

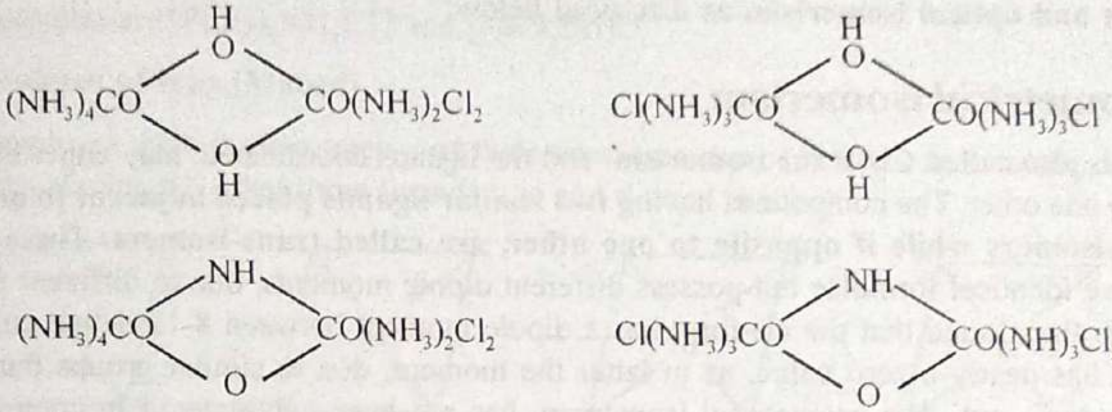
Another example is $[CO(en)_2Cl{\cdot}H_2O]Cl_2$ and $[CO(en)_2Cl_2]Cl{\cdot}H_2O$ which gives two and one Cl^- ions in solution respectively.

(iii) Coordination isomerism – If **both the cation and anion of a complex compound are complex ions**, this type of isomerism may be shown, **by interchange of ligands between the tw metal ions and both the complex compounds of each pair are isomers.** The metal in the comple cation or anion may be same or different. Some typical examples are;

I	II
$[Cr(NH_3)_6]^{3+}[Cr(SCN)_6]^{3-}$	$[Cr(NH_3)_4(SCN)_2]^{1+}$ $[Cr(SCN)_4(NH_3)_2]^{1+}$
$[Pt(NH_3)_4]^{2+}[PtCl_6]^{2-}$	$[Pt(NH_3)_2Cl_2]^{2+}$ $[Pt(Cl_4]^{2-}$
$[Cu(NH_3)_4]^{2+}$ $[PtCl_4]$	$[Pt(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$

(iv) Coordination position isomerism – This type of isomerism is shown by those complex compounds, which contain bridging ligands and arises because of different placement of non-bridging ligands around the central metal ion. The following example, in which I and II are coordination position isomers of one another, is well-known.

I (unsymmetrical) II (symmetrical)

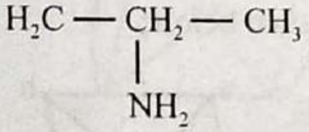


In these compounds NH_3 and Cl are placed in an unsymmetrical and symmetrical manner, around the cobalt (II) ion.

(v) Polymerization isomerism – In this isomerism, the two isomers differ in their formula weight but have the same empirical composition and the formuale appear to be polymers of some simple complex compound. The examples are,

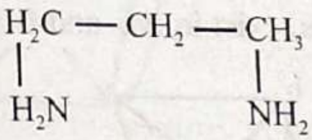
1. $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4][PtCl_4]$
2. $[CO(NH_3)_3(NO_2)_3]$ and $[CO(NH_3)_6] [CO(NO_2)_6]$

(vi) Ligand isomerism – There are certain ligands which themselves exist as isomers, and when these ligands form complexes those are also isomers. One such ligand is diaminopropane which can exist either as 1, 2-diamino or 1, 3-diaminopropane shown below:



$H_2C - \underset{NH_2}{\underset{|}{CH_2}} - CH_3$

1, 2-diaminopropane
(propylenediamine)



$\underset{H_2N}{\underset{|}{H_2C}} - CH_2 - \underset{NH_2}{\underset{|}{CH_3}}$

1, 3-diaminopropane
trimethyene diamine

The isomeric complexes of the ligand of type $[Co(pn)_2Cl_2]^+$ and $[Co(tr)_2 C1_2]^+$ are known, both of which have octahedral geometry.

(vii) Linkage isomerism – Certain ligands, contain two donor atoms and can coordinate to central metal ion through, either of these two donors giving isomers. Example of such ligands are NO_2^-, and SCN^-. The former can coordinate to metal either through nitrogen (M – N bond) or through oxygen (M – O bond) and later through either sulphur (M – S bond) or through Nitrogen (M – N bond). Two different nitro pentammine cobalt (III) chlorides have been prepared, as shown below;

$[CO(NH_3)_5NO_2]Cl_2$ and $[CO(NH_3)_5ONO]Cl_2$

Many other similar complexes have also been prepared.

1.8.2 Stereo Isomerism

Those compounds, which contain the same ligands coordinated to the same metal ion, but the arrangement of these ligands around the metal ion in space is different, give rise to **stereo isomerism** and individual pair of compounds are called **stereo isomers**. This isomerism is of two types, **geometrical isomerism and optical isomerism,** as discussed below:

(A) Geometrical isomerism

This is also called **Cis-trans isomerism** and the ligands coordinated, may either be adjacent or opposite to one other. The compounds having **two similar ligands placed adjacent to one other, are called Cis-isomers while if opposite to one other, are called trans-isomers**. These geometrical isomers have identical formulae but possess different dipole moments, due to different placement of ligands. It is thus found that the cis-form has a dipole moment between 8-12 debye units while the trans- form has nearly a zero value, as in latter the moment, due to similar groups but in opposite positions, cancels out. The geometrical isomerism, has not been encountered in complexes having coordination numbers 2 and 3 but is very common for coordination number 4 and 6.

(i) Four Coordinate complexes: Geometrical isomerism cannot arise in tetrahedral complexes, because in this geometry all the four ligands are in adjacent position, i.e., Cis- to one other and all the four bond angles are also same (109'45°). It is however, very common in square planer complexes of following type, in which M represents a metal ion, abcd monodentate ligands, A-A, a symmetrical bidentate ligand and A-B, an unsymmetrical bidentate ligand.

(a) Complexes of type [Ma_4], [Ma_3b] and [Mab_3]

Such compounds show no isomerism, since all possible spatial arrangements of ligands are exactly equivalent.

(b) Complexes of type [Ma_2b_2]

These complexes, exist in *cis*- and *trans*- isomers as shown below;

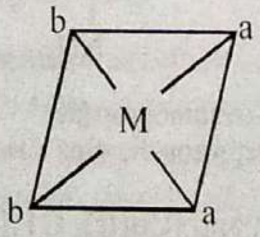


Fig. 1.1 (a) Cis or 1, 2-isomer

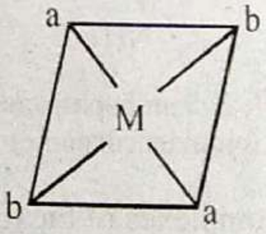


Fig. 1.1 (b) Trans or 1, 3-isomer

Important examples, are [$Pt(NH_3)_2Cl_2$], [$Pt(Py)_2Cl_2$] and [$Pd(NH_3)_2NO_2$] and these can be easily differentiated by their dipole moment measurements.

(c) Complexes of type [Ma_2bc]

Such complexes can also exist in cis- and trans- isomers, depending on whether ligands 'a' are adjacent or opposite to one other and the two isomers, are diagrammatically represented as;

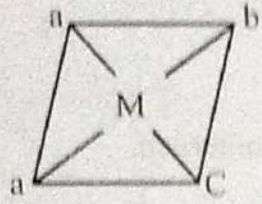


Fig. 1.2 (a) Cis- isomer

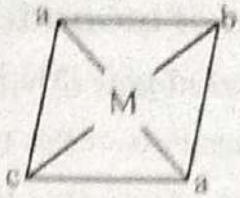


Fig. 1.2 (b) Trans- isomer

Some examples are $[Pt(Py)_2NH_3Cl]^+$ and $[PdCl_2BrI]^{2-}$

(d) Complexes of type [Mabcd]

Such complexes, give three isomers and their structures can be written, by selecting any ligand say (a) and then placing the other three ligands b, c and d trans to it.

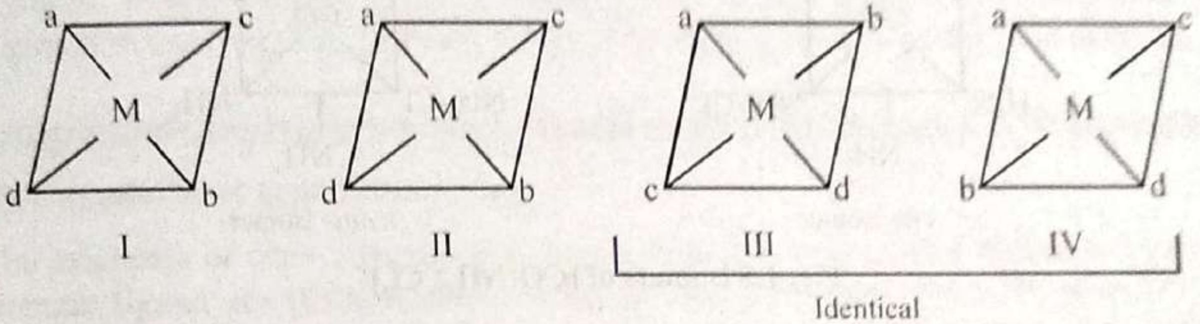


Fig. 1.3 Isomers of complex [Mabcd]

Some examples are, $[Pt(NH_3)(Py)ClBr]$ and $[Pt(NO_2)(Py)ClBr]$

(e) Complexes of type $[M(AB)_2]$

Square planar complexes containing unsymmetrical bidentate ligands, A-B where A and B are the two donor atoms, also show geometrical isomerism as drawn;

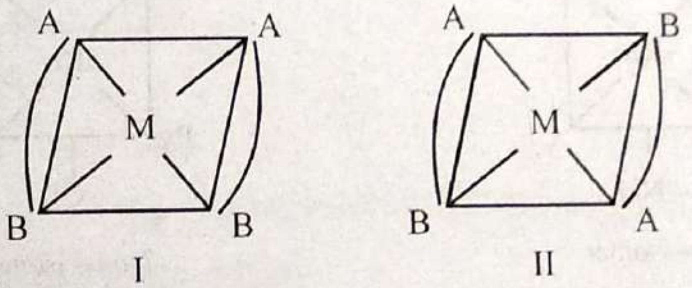


Fig. 1.4 Isomers of complex $[M(A\text{-}B)_2]$

Examples are $[Pt(gly)_2]$ and $[Cu(gly)_2]$ where gly stands for glycinato ion $NH_2\,CH_2COO^-$ which has N and O as the two donor atoms.

(ii) Six coordinate complexes: The metals with coordination number six, generally form octahedral complexes. In this case, if two similar ligands are placed on any of the twelve edges of the octahedron, these are said to be in cis position, while if two similar ligands are lying on a straight line, which passes through the center (where the metal ion is present) these are said to be in trans- position. In terms of numbering, the two ligands at position 1, 2; 2,3; 3,4; 1,4; are Cis and at position 1,3; 2,4 and 5,6 are trans to one other. Some examples are given below, in which M represents the central metal ion; a, b or c monodenate ligands; A-A symmetrical bidentate ligand and A-B unsymmetrical bidentate ligand.

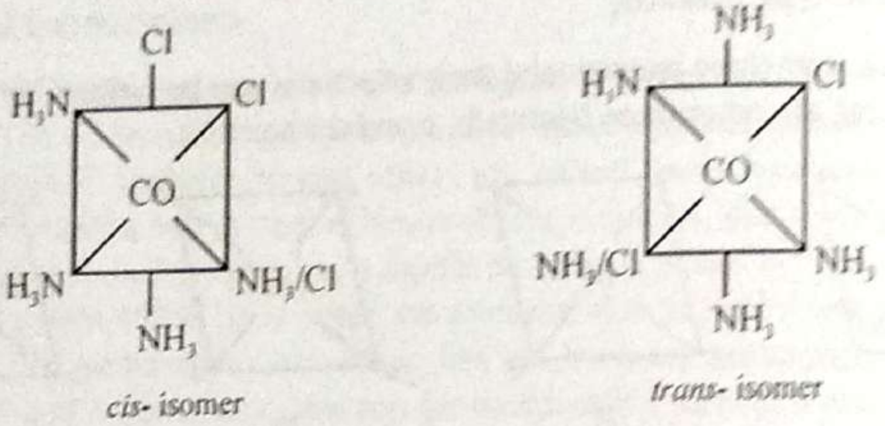
A. Complexes of monodentate ligands

(a) Complexes of type $[Ma_6]$ and $[Ma_5b]$

Octahedral complexs of this type show no geometrical isomerism.

(b) Complexes of type $[Ma_4b_2]$, $[Ma_2b_4]$ and $[Ma_4bc]$

Such complexes show geometrical isomerism and some examples are $[Cr(NH_3)_3Cl_3]$, $[CO(NH_3)_4Cl_2]^+$ and $[CO(NH_3)_4H_2OCl]^{2+}$, drawn in Fig. 1.5.

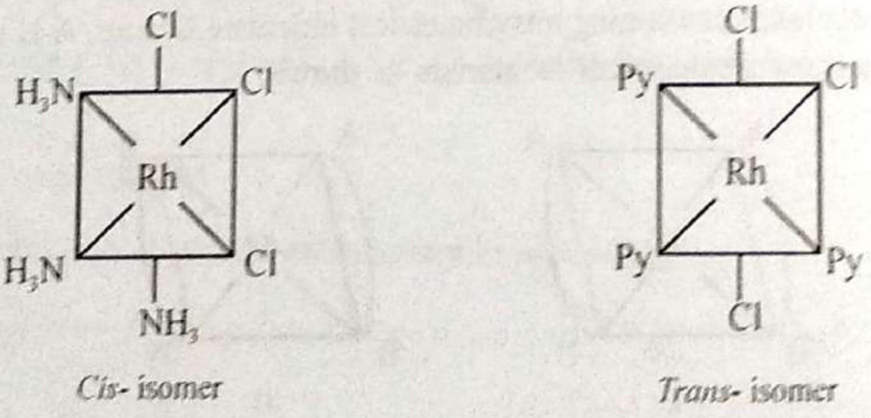


cis- isomer *trans- isomer*

Fig. 1.5 Isomers of $[CO(NH_3)_4Cl_2]^+$

(c) Complexes of type $[Ma_3b_3]$

Several examples of complexes of this type, are known as $[Rh(Py)_3Cl_3]$; $[Cr(H_2O)_3F_3]$; $[Ru(H_2O)_3Cl_3]$; $[Ir(H_2O)_3Cl_3]$; $[Pt(NH_3)_3X_3]$ and $[CO(NH_3)_3(NO_2)_3]$. The two isomers of comple $[Rh(Py)_3Cl_3]$ are drawn in following fig.;



Cis- isomer *Trans- isomer*

Fig. 1.6 Isomers of complex $[Rh(Py)_3Cl_3]$

(d) Complexes of type [Mabcdef]

Such octahedral complexes containing all six different monodentate ligands, are theoreticall known to exist in 15 isomers, while in practice only three isomers have been isolated. The only exampl isolated is $[Pt(Py(NH_3)NO_2(Cl)(Br(I)]$.

(e) Complexes of type $[Ma_2b_2c_2]$

These complexes can exist in five forms, but actually only three isomers have been isolated. On important example of this class is compound $[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$, the three isomers of which a shown in Fig. 1.7.

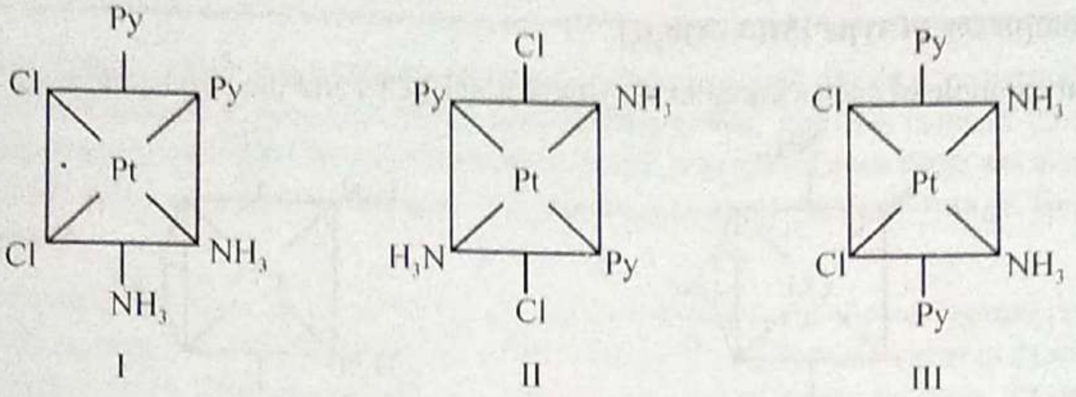


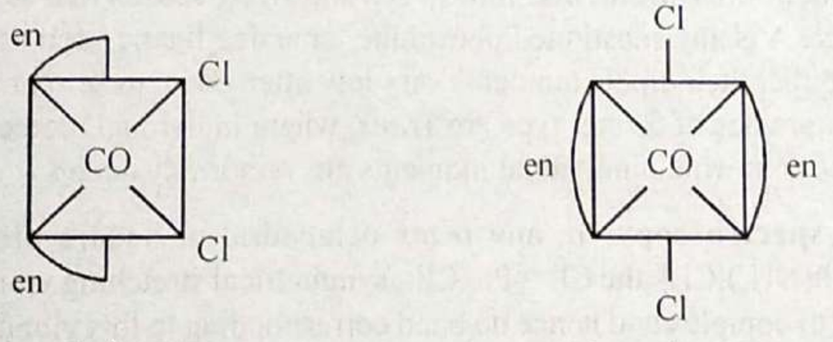
Fig. 1.7 Isomers of $[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$

It can be seen that form I is Cis as similar groups occupy adjacent positions, from II is trans as similar groups occupy opposite position, while form III is a mixture of both the isomers.

(B) Complexes of symmetrical (A-A) and unsymmetrical (A-B) bidenatate ligands

(f) Complexes of type $[M(A\text{-}A)_2a_2]$

The examples of such complexes in which A-A is a symmetrical bidentate ligand and a is a monodentate ligand are $[CO(en)_2Cl_2]^+$, $[CO(en)_2(NH_3)_2]^{3+}$; $[Cr(en)_2Cl_2]^{1+}$; $[Cr(C_2O_4)_2(H_2O)_2]^{1+}$; $[Ir(C_2O_4)_2Cl_2]^{3-}$ and $[Rh(C_2O_4)_2Cl_2]^{2-}$. The arrangement of ligands in the two isomers may be shown as in Fig. 1.8.

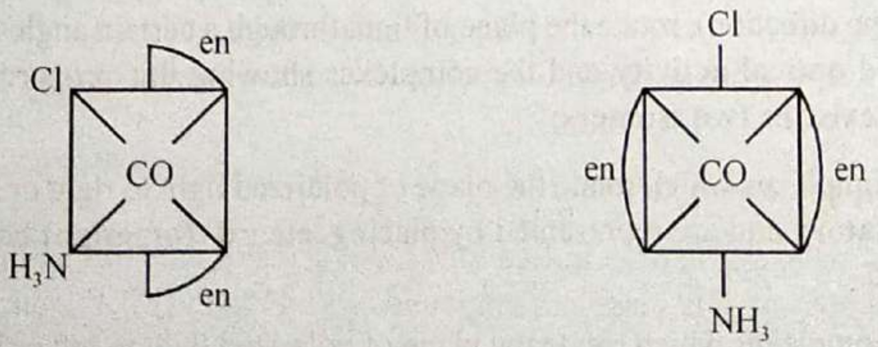


cis- isomer *trans-* isomer

Fig. 1.8 Isomers of complex $[Co(en)_2Cl_2]^{1+}$

(g) Complexes of type $[M(A\text{-}A)_2ab]$

An important example of this class, is the complex $[CO(en)_2Cl(NH_3)]^{2+}$ the cis- and trans- isomers of which are shown in Fig. 1.9.

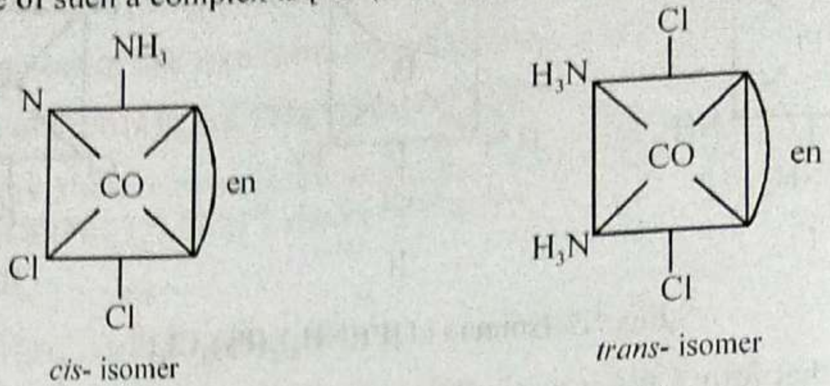


cis- isomer *trans-* isomer

Fig. 1.9 Isomers of $[CO(en)_2Cl(NH_3)]^{2+}$

(h) Complexes of type $[M(A\text{-}A)b_2c_2]$

Typical example of such a complex is $[CO(en)(NH_3)_2Cl_2]$ and the two isomers are drawn below;



cis- isomer

trans- isomer

Fig. 1.10 Isomers of $[CO(en)(NH_3)_2Cl_2]$

(i) Complexes of type $[M(A\text{-}B)_3]$

In the complexes of this type, A-B is the unsymmetrical ligand and an example is $[Cr(gly)_3]$. In the cis- isomer the two N and two O atoms of the two glycine are placed adjacent, while in trans- isomer these occupy opposite positions.

(iii) Distinction between- Cis and trans isomers

The following methods are generally used to make a distinction between cis and trans isomers;-

(a) Dipole moment measurements: It has been shown by Jensen that several Pt(11) complexes of type $[PtA_2X_2]$ where A is any substituted phosphine, or arsine ligand such as $(C_2H_5)_3P(As)$ and X is any halide ion, have either their dipole moments very low often equal to zero or very high equal to 8-12 Debye units. The compounds of former type are *Trans*, where individual moments have cancelled one other, while later are *Cis* in which individual moments are vectorially added.

(b) Infra red spectroscopy: In any *trans* octahedral or square planar complex such as $[CO(NH_3)_4Cl_2]$ and $[Pt(NH_3)_2Cl_2]$,the Cl^{1-}–Pt–Cl^{1-}, symmetrical stretching vibration causes no change in the dipole moment of complex and hence no band corresponding to this vibration is observed in infra red spectrum, while for *cis* isomer, symmetrical as well as unsymmetrical stretching vibrations produce appreciable change in dipole moment and hence C1–M–C1 vibration becomes allowed and a number of bands corresponding to this virbration may be seen in infra red spectrum (Chapter 6).

(B) Optical isomerism

Solutions of certain compounds, when placed in the path of polarized light (light in which waves vibrate in only one direction), rotate the plane of light through a certain angle either to right or left. This property is called **optical activity** and the complexes showing this property are said to be **optically active and can exist in two isomers;**

(i) Those complexes which rotate the plane of polarized light to right or in clockwise direction are called **dextrorotatory** and are represented by placing letter **d- (or +sign)** before the name or formula of the compound.

(ii) Those complexes which rotate the plane of polarized light to left or in anticlockwise direction are called **laevorotatory** and are represented by placing letter **l- (or -sign)** before the name or formula of compound.

These two forms, which have other wise similar chemical and physical properties are called **optical isomers** and the phenomenon is called **optical isomerism**. The two isomers must be mirror image of one other and should also be superimposable on one other and hence these are also refered as **mirror-image isomers or enantiomorphs and phenomenon as mirror-image isomerism or Enantiomorphism.**

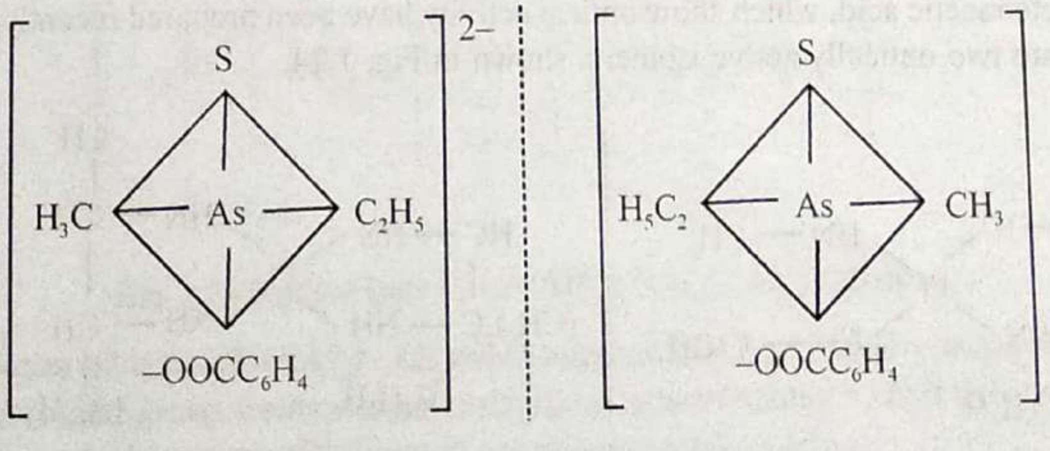
When both these isomers are present in a complex simultaneously, the compound is not capable of rotating the plane of polarized light, because the rotation produced by one isomer is exactly balanced by the rotaton produced by other isomer. Such a compound is called **meso, racemic, dl or (±) isomer** and is optically inactive.

For a complex to show optical activity, the molecule should be asymmetric, i.e., should have no plane of symmetry, which is an imaginary plane, dividing the molecule in such a way that the part on one side of the plane is the mirror image of the part on the other side of the plane. The molecules possessing such plane of symmetries, are always optially inactive, while those having no plane of symmetry are active. Optically active molecules can not be superimposed on mirror image and hence the **two most necessary conditions for showing optical activity is asymmetry and no mirror image relationship between the two forms.**

Optical isomerism, is very frequently shown by both four and six coordination complexes as discussed below;

(i) Four coordinate complexes

(a) Tetrahedral complexes: The tetrahedral complexes are not relatively rich in optical isomers, and the isomerism is not shown by complexes of type $[Ma_4]$ and $[Ma_3b]$, because all possible arrangements of ligands around the metal are equivalent. Complexes of type [Mabcd] show optical isomerism, and one such example is $[As(CH_3)(C_2H_5)(S)(C_6H_4COO^-)]^{2-}$ ion which exists in following two isomers as shown below in Fig. 1.11.

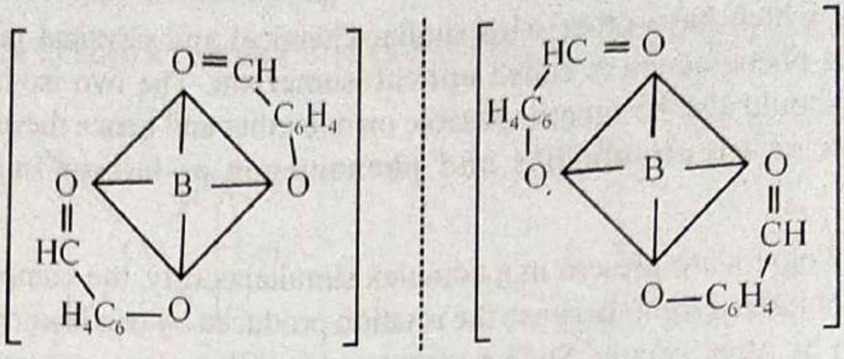


d-from

l-from

Fig. 1.11 Optical isomers of $[As(CH_3)(C_2H_5)(S)(C_6H_4COO^-)]^{2-}$ ion

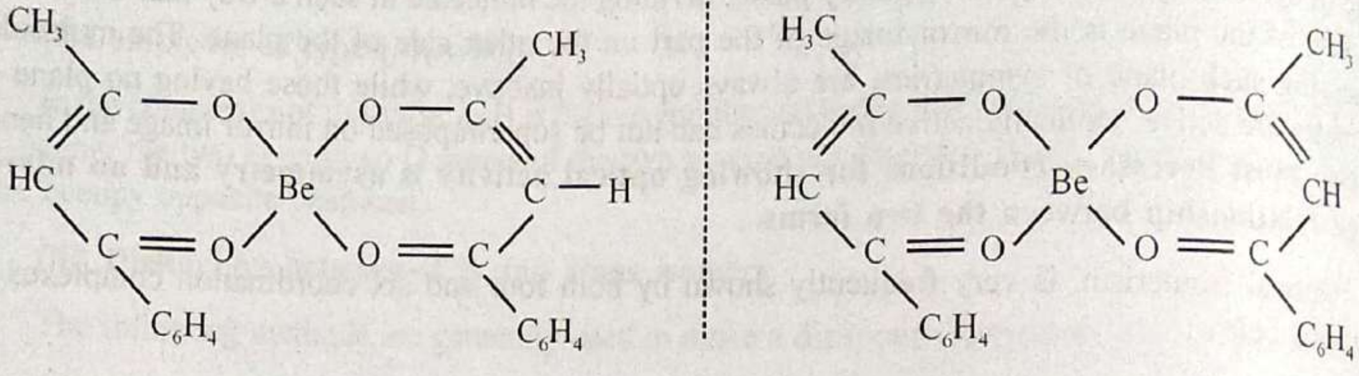
Some tetrahedral complexes of Beryllium, Boron and Zinc with symmetrical bidentate ligands have been resolved into optical isomers. Such examples, include bis (salicylaldehylato) boron (III) ion $[B(C_6H_4O.CHO)_2]^+$ and bis- (benzoylacenato) beryllium (II) $[Be(C_6H_5COCHCH_3CO)_2]$, the isomeric forms of which are shown below in Fig. 1.12 and 1.13.



dextro (object)

laevo (mirror image)

Fig. 1.12 Optical isomers of Boron Complex

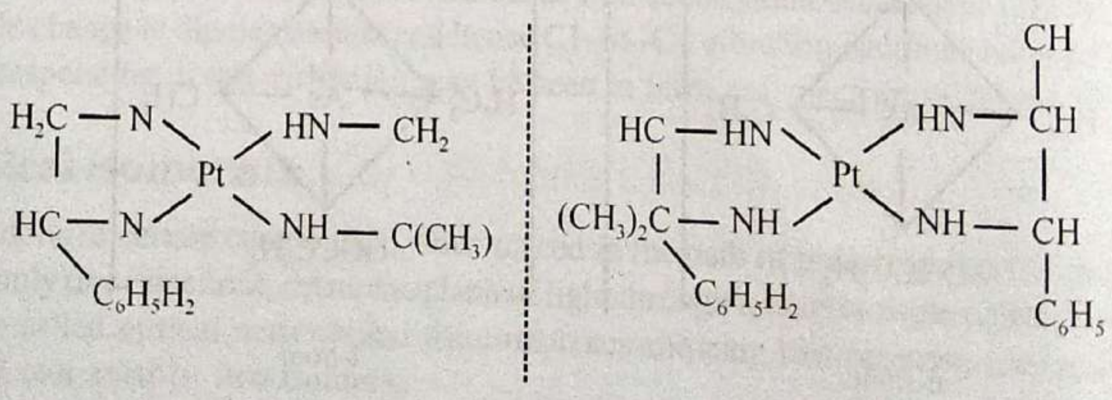


dextro (object form)

laevo (mirror image form)

Fig. 1.13 Optical isomers of Beryllium Complex

In case of square planar complexes, the metal ion as well as all the four ligands, are in the same plane, so that the molecule has a plane of symmetry and such complexes thus rarely show optical isomerism. But complexes of Pd^{2+} and Pt^{2+} with isobutylenediaminemesostilbenediamine and also ethylenediaminetetracetic acid, which show optical activity have been prepared recently, and have also been resolved into two optically active isomers, shown in Fig. 1.14.



isobutylene diamine diamine mesostilbenediamine platinum (II) ion

Fig. 1.14 Optical isomers of isobutylenediaminemesostilbenediame Pt(11)

(ii) Six coordinate complexes

The most well-known cases of optical isomerism, occur among octahedral complexes, containing mostly bidentate ligands, but some isomers containing monodentate ligands have also been prepared as detailed below;

(a) Complexes of type $[Ma_4b_2]$ and $[Ma_3b_3]$: None of these compounds show optical isomerism, though complexes of both types show cis- and trans- isomerism.

(b) Complexes of type $[Ma_2b_2c_2]$: The most important example of such a complex is $[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$, for which the cis-isomer where two identical ligands occupy adjacent positions, exists in two optical isomers. The trans-form is optically inactive, as the molecule has a plane of symmetry. These two optically active forms are shown below:

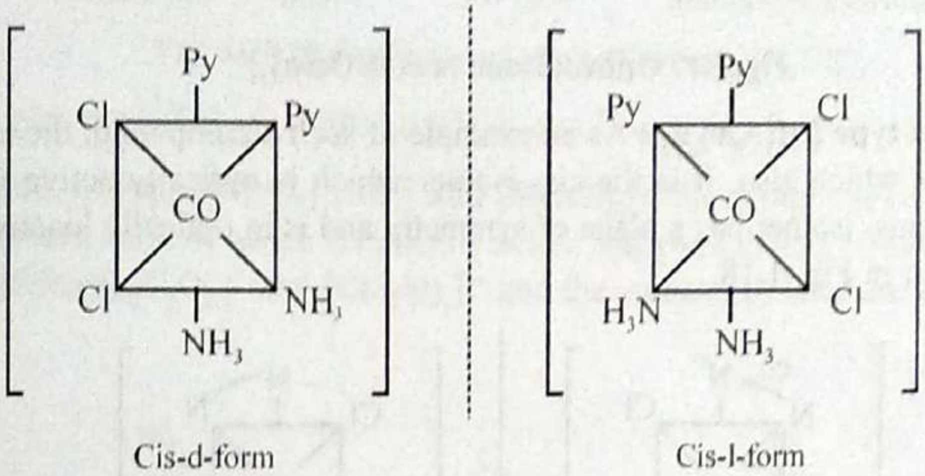


Fig. 1.15 Isomers of $[Pt(NH_3)_2(Py)_2Cl_2]^{2+}$

(c) Complexes of type [Mabcdef]: The only example of an octahedral complex of this type is $[Pt(Py)(NH_3)(NO_2)ClBrI]$, which can theoretically exist in 15 geometrical isomers and each of these forms exists in optical isomers also, giving a total of 30 optically-active d- and l- isomers, two of which are drawn in Fig. 1.16.

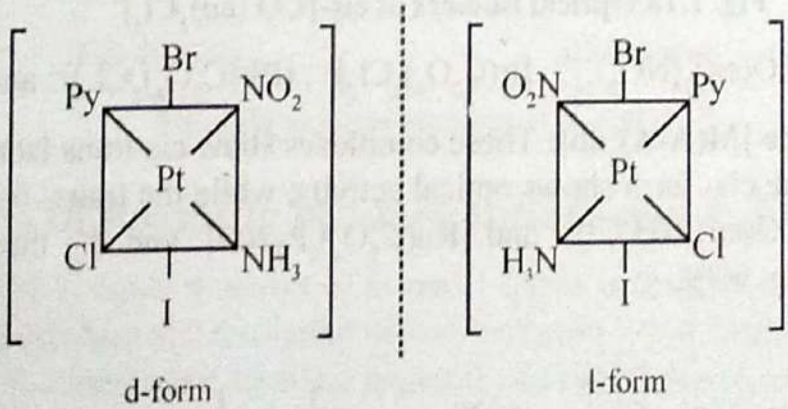
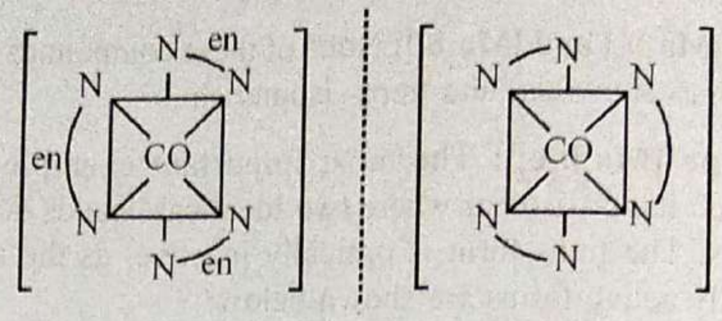


Fig. 1.16 Optical isomers of $[Pt(Py)(NH_3)(NO_2)ClBrI]$

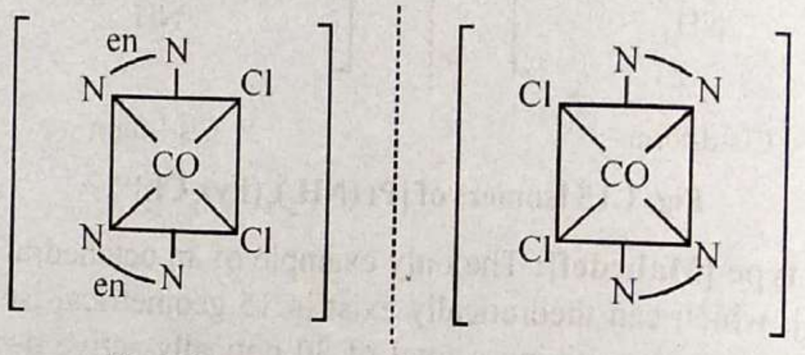
(d) Complexes of type $[M(AA)_3]$: All complexes of this type, show optical activity and are resolvable in dextro and laevo forms. Some example ions are $CO(en)_3^{3+}$; $Cr(OX)_3^{3-}$; $CO(pn)_3^{3+}$ and $Pt(en)_3^{4+}$. The two optical isomers of $CO(en)_3^{3+}$ are shown in Fig. 1.17.



d-form l-form

Fig. 1.17 Optical Isomers of $[CO(en)_3]^{3+}$

(e) Complexes of type $[M(AA)_2a_2]$: As an example of such a compound, the ion $[CO(en)_2Cl_2]^+$ may be considered for which also, it is the cis- isomer which is optically active with no plane of symmetry, while the trans- isomer has a plane of symmetry and is in optically inactive or meso form. These forms are shown in Fig. 1.18.

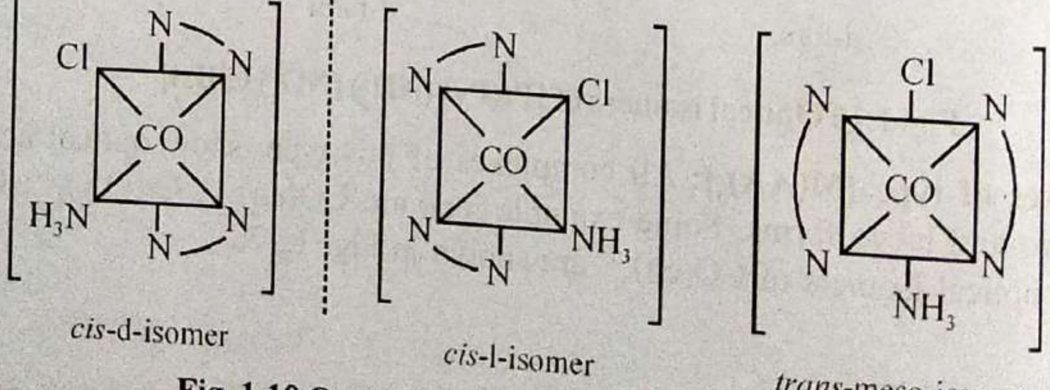


Cis-d-form Cis-l-form

Fig. 1.18 Optical isomers of cis-$[CO (en)_2Cl_2]^+$

Other examples are $[CO(en)_2(NO_2)_2]^{1+}$; $[Ir(C_2O_4)_2Cl_2]^{2-}$; $[Rh(C_2O_4)_2Cl_2]^{2-}$ and $[Cr(C_2O_4)_2(H_2O)_2]^{1}$.

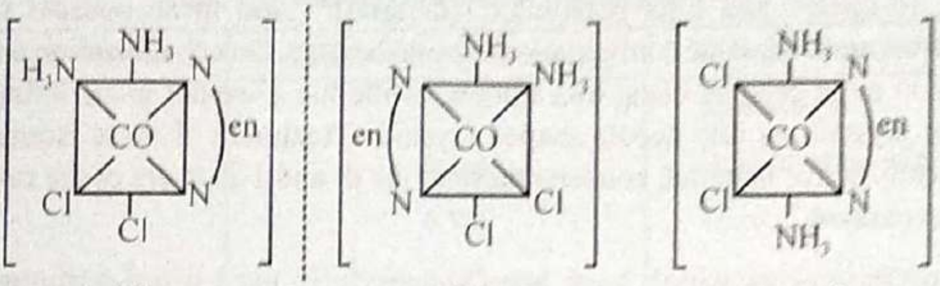
(f) Complexes of type $[M(A\text{-}A)_2ab]$: These complexes show cis-trans isomerism and also exist in three optical isomers. The cis- form shows optical activity, while the trans- form is a **meso isomer.** Important examples are $[CO(en)_2NH_3Cl]^{+2}$ and $[Ru(C_2O_4)_2PyNO]^-$ and the three isomers of former compound are shown in Fig. 1.19.



cis-d-isomer *cis*-l-isomer *trans*-meso-isomer

Fig. 1.19 Optical isomers of cis-$[Co(en)_2NH_3Cl]^{+2}$

(g) Complexes of type $[M(A\text{-}A)a_2b_2]$: Such compounds also exist in cis- and trans- isomers and as expected, the cis- isomer exists in optically active d- and l-forms, while the trans- isomer is an optically inactive meso form. Typical examples are $[Co(en)\ (NH_3)_2Cl_2]$ which exists as shown in Fig. 1.20.

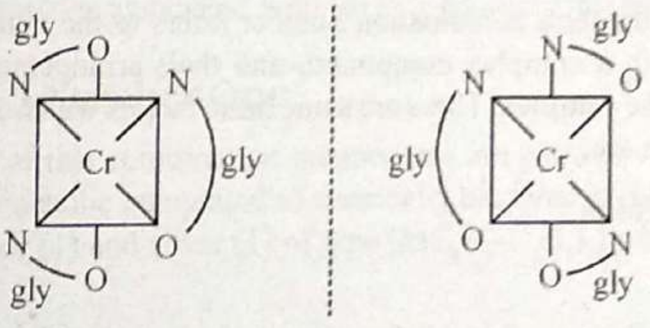


cis-d-form *cis*-l-form *trans*-meso-isomer

Fig. 1.20 Optical isomers of cis-$[CO(en)_2NH_3Cl]^{+2}$

Other examples are $[CO(C_2O_4)(NH_3)_2(NO)_2]^{1-}$ and $[Ru(C_2O_4)_2PyNO]^-$

(h) Complexes of type $[M(AA)_2(BB)]$ and $[M(AB)_3]$: The compounds of this type also exist in cis- and trans- isomers, each of which is optically active and gives d- and 1-isomers. The examples are $[Co(en)_2CO_3]^+$; $[CO(en)_{2(}C_2O_{4)}]^+$ and $[Cr(gly)_3]^{3+}$ and the isomers of later are drawn in Fig. 1.21.



Cis-d-isomer Cis-l-isomer

Fig. 1.21 Optical Isomers of $[Cr(gly)_3]^{3+}$

1.8.3. Resolution of Racemic Mixture into d- and 1- Forms

A mixture containing equal amounts of d- and 1-forms is incapable of showing optical activity and is called a **racemic mixture** and resolution of such a mixture into d- and 1-forms is called **resolution.** Since both the d- and 1- forms have identical physical and chemical properties, the ordinary methods of separation, such as fractional crystallization and distillation cannot be used.

The most widely used method of resolution, is by the formation of diastereo isomers — **which are optically active isomers,** but posses no mirror image relationship. Such isomers possess different solubility in water and can thus be separated by fractional crystallization. The principle underlying, is that, **if an optically active isomer is acidic, it is to be treated with an optically active base and if it is basic, it is to be treated with an optically active acid**. The reaction of each pair, gives two diastereo isomers which are salts. These salts posses different solubilities in a given solvent, and can be separated from one other. The separated salts are then treated with an optically inactive material, to regenerate the d- and l-forms.

In order to illustrate the use of this process, the example of the resolution of complex $[CO(en)_3]Cl_3$ is taken. The solution of the recemic mixture of the compound is a **base** and is therefore treated with **optically active d-tartaric acid**, when two isomers of a new compound are formed. These are d-cis$[CO(en)_2Cl(d\text{-tart})]^{2-}$ and l-cis $[CO(en)_2Cl(d\text{- tart})]^{2-}$- and these possess no mirror image relationship, as d-tartarate has same configuration in both the salts. On crystallization d-cis$[CO(en)_2Cl(d\text{-tart})]^{2-}$ separates in large crystals being less soluble, while the 1-isomer gives initially a gelationous mass which later crystallizes into needle shaped crystals. Treatment of these isomers with dil HCl, which is an optically active material, converts these to the d- and 1-isomers of the original compound, which are thus separated.

Other resolving agents which have been successfully used are d-antimonyltartarate, d-a-bromocomphor and a-sulphonate anions for cationic complexes, while for anionic complexes such as $[M(C_2O_4)_3]^{3-}$ optically active cations Strychnine and Brucine may be used.

1.9 DIFFERENT COORDINATION NUMBER AND THEIR POSSIBLE GEOMETRIES

1.9.1 Introduction

As mentioned earlier, the term coordination number refers to the number of ligands which are attached to a metal cation in a complex compound, and their arrangement in space is called the **coordination geometry of the complex**. There are some basic factors which determine the coordination numbers of metals and these are;

(i) Size and stearic effects

(ii) Nature of ligand,

(iii) The electronic configuration, oxidation state and energetically significant orbitals on metal and

(iv) Electrostatic and ligand field stabilization energies.

The coordination numbers of metals, may take up any value from 1-12 former existing in ion pairs as NaCl in vapour phase and later in some mixed metal oxides. However, the ion pairs are seldom considered as coordination compounds, and the coordination number 12, is also rarely seen in discrete molecules. The typical coordination numbers thus, range from 2 to 9 with 4 and 6 as commonest. Most often, it is not possible to predict a particular geometry in a compound of a particular coordination number, because the difference in energies between various possible structures are very small and in some cases even a small change in environment affects a change in geometry.

As in case of lattices, where coordination number is related to the ratio of radii of ions, in coordination compounds also the same principles apply. Some minimum radius ratios, required for some common geometries for typical coordination numbers are given in following table;

Table 1.1: Radius ratio and common geometries

Coordination number	Minimum radius ratio	Coordination geometry
4	0.225	Tetrahedron
6	0.414	Octahedron/Squre plane.
6	0.528	Trigonal prism
7	0.592	Capped octahedron
8	0.645	Square antiprism
8	0.668	Dodecahedron
8	0.732	Cube
9	0.732	Tri capped trigonal prism
12	0.902	Icosahedran
12	1.000	Cuboctahedron

Some common geometries associated with various coordination numbers are given below;

1.9.2 Coordination Number One

The only examples of this coordination number, are ion pairs in vapour phase, but one typical example is the the organometallic compound of stearically hindered aryl radical derived from 1,3,5-tri phenylbenzene with copper (1) and silver (1) of type [M$C_6H_2(C_2H_5)_3$] which has a structure as shown in Fig. 1.22.

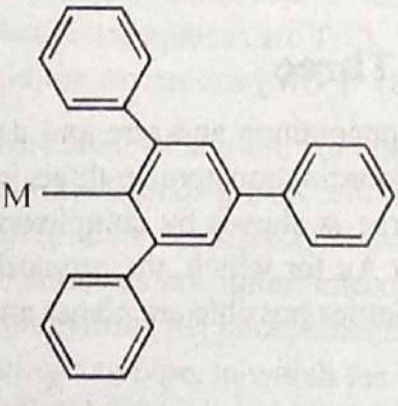


Fig. 1.22 Structure of 1,3,5-triphenylbenzene metal (1) complex

1.9.3 Coordination Number Two

This is also a some what uncommon coordination number and the few examples known, are all of +1 ions of group IB metals and closely related Hg^{2+} species, which possess a d^{10} configuration. There are two geometries possible, linear or bent, of which only linear has been encountered in complexes of type $[Cu(NH_3)_2]^{1+}$, $[Ag(NH_3)_2]^{+}$, $[AgCl_2]^{1-}$, $[CuCl_2]^{1-}$, $[Ag(CN)_2]^{1-}$ and $[Hg(CN)_2]^{1-}$. It is found that, if the ligand is sufficiently stearically hindered such as $[N(SiMe_3)_2]^{-}$ and $[N(PhBMeS_2]$, two coordinate complexes may be formed for d^5, d^6, d^7 and d^8 ions as well. In these complexes, the boryl group draws off one of the lone pairs on nitrogen thorugh N→B dative pi bonding and reduces the tendency of N to bridge, to form dimeric complexes.

This coordination number, however, possesses low stability and in many cases, where stoichiometr implies its presence, a higher coordination is usually favoured, which may be attained by binding o additional ligands as shown;

$$Ag(NH_3)_2^+ + 2NH_3 \rightarrow [Ag(NH_3)_4]^{1+}$$

$$Hg(CN)_2 + 2CN- \rightarrow [Hg(CN)_4]^{2-}-$$

The low stability is also illustrated for Ag(I) and Au(I), which stabilise, by forming a zigzag chai structure, in which the coordination number of metal is three.

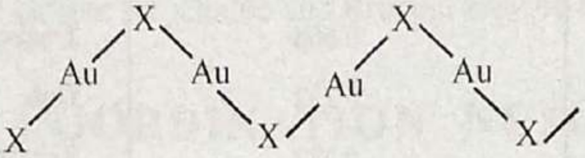


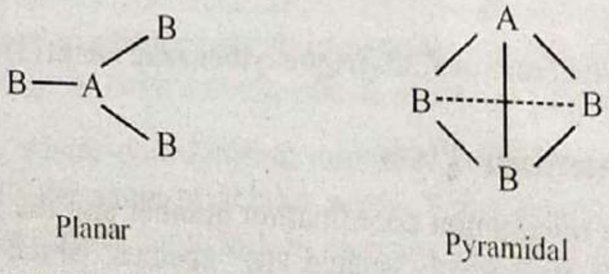
Fig. 1.23 Proposed Structure of gold halides

As mentioned above the geometry of complexes is linear, which is acquired by the use of sp hybrid orbitals on metals. The use of $(n-l)d_{z2}$ orbital of the metal, close in energy to ns and np orbitals helps in removing electron density, from the ligands around z axis towards the xy plane. This i supported by the observation that for these ions the promotional energy for $d^{10} \rightarrow d^9s^1$ is low, as fo Cu^{1+}(2.7ev); Ag^+(4.8ev); Au^{1+}(1.8ev), while for Cd^{2+} and Zn^{2+} it is 10.0 and 9.7 and hence the later tw ions cannot attain stability by this promotion.

The metal atoms in cations such as UO_2^{2+}, VO_2^{1+}; and PuO_2^{2+} are also linear and may be said t possess coordination number two, but these ions also have a strong tendency to interact with additiona ligands and their coordination numbers in actual practice are 4 or even much higher.

1.9.4 Coordination Number Three

This coordination number is also uncommon and rare and usually known for trivalent cations Many compounds which appear to have coordination number three, in reality posses higher coordinatio numbers. True coordination number three is shown by complexes of d^{10} system such as $Zn(OH)_3$, HgI_3; $[M((PH_3P)_3I]$ where M=Cu, Ag or Au for which, the promotional energy for d → S promotio is rather low. The two symmetrical geometries possible are planar and pyramidal as shown in Fig. 1.24



Planar

Pyramidal

Fig. 1.24 Possible geometries for Coordination number

The d→S promotions in these complexes, makes the planar structure more asymmetrical and a example is complex $[Cu(SPMe_3)_3]^+$ which is planar, but has three different bond angles, around th central copper atom which are 119.2°, 118.2° and 122.6°.

Other true examples of three coordination are are $K[Cu(CN)_3]$; tris(trimethylphosphinesulphide copper (I) perchlorate; and tris-(t-butylthiolato) mercurate (II) anion. In all these examples, geometr is approximately an equilateral triangle, with metal atom at centre and hybridization is sp^2. As mentioned above, some d level participation, is also expected due to low d → s promotional energy and a trigonal sd^2 hybridisation may also occur,

A few complexes of planer geometry are also known, in which one angle is either much greater than 120° (T-shaped), or less than 120° (y-shaped) and the bond lengths are also unequal.

1.9.5 Coordination Number Four

This is the first coordination number known, for which isomerism is expected and complexes having this coordination number are tetrahedral or square planar in geometry, although intermediate and distorted structures may also occur.

(A) Tetrahedral Complexes

In terms of valence bond view, tetrahedral structure is formed by sp^3 hybridization. From the molecular orbital viewpoint, tetrahedral structure is not stabilized by large CFSE and is thus formed only with large ligands (like halide ions) and small metal ions which may be classified into three categories;

(i) metal ions with noble gas configuration such as Be^c and Al^{3+}

(ii) metal ions with pseudo inert gas configuration $(n\text{–}l)d^{10}ns^0np^6$ as Zn^{2+}, Ga^{3+}.

(iii) metal ions with low CFSE as CO^{2+} and

(iv) Bulky and weak field ligands as halide ions or oxides.

Tetrahedral complexes are uncommon for d^3 and d^4 ions, because of their large crystal field splittings. Some representative tetrahedral complexes are $TiCl_4^-$; VCl_4^-, MX_4^{2-} (M=Fe, CO, Ni, Cu, Hg, and X = Cl); $Ni(CO)_4$; $Cu(CN)_4^{2-}$ and the oxoanions $[MO_4]^{n-}$ (M=V, Cr, Mn, Fe, Re, Mo, W).

Tetrahedral complexes, which are somewhat more common for neutral or anionic ligands, do not show geometrical isomerism, since all the ligands are cis with respect to one other. Optical isomerism in the complexes of the type [MABCD] i.e., four different substituents, is also seldom observed due to the labile nature of substituents, which makes resolution into optical enantiomorphs difficult. But one such compound, namely cyclopentadienyliron(III) phosphinecarbonyl has been characterized and may be shown to possess a structure of following type, in which the large C_5H_5 ring forces the other ligands back, until the bond angles are essentially 90° instead of 109° as shown in Fig. 1.25.

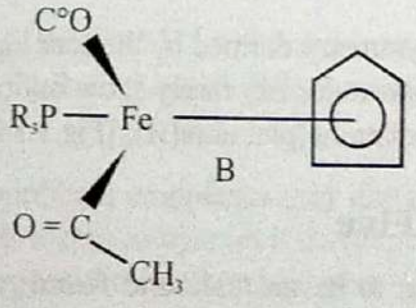


Fig. 1.25 Acetyl (carbonyl) cyclopentadienephospheneiron (III) complex

A second form of optical activity, is also shown by two enantiomers of bis-(benzoylacetanato beryllium (II), which are not superimposable on their mirror images and this activity is analogous to one shown by spirocyclic organic compounds. These two forms are shown in Fig. 1.26.

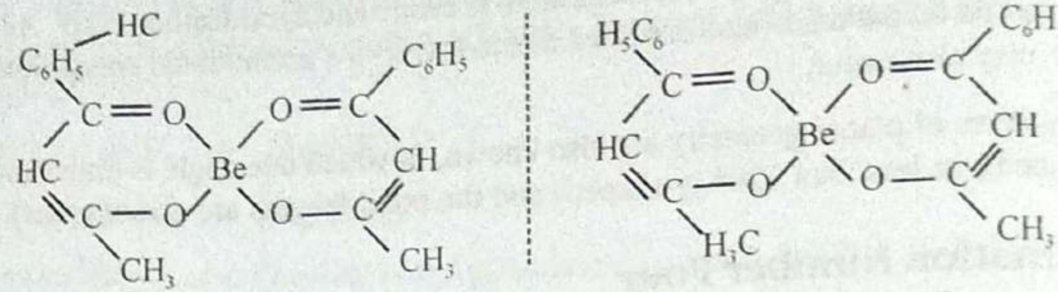


Fig. 1.26 Two forms of bis- (benzoylacetanato) beryllium(II)

(B) Square Planar Complexes

These complexes, are sterically less favoured than tetrahedral complexes and are thus formed b fewer metal ions. The prerequisites, for a planar complex to form are;

(i) No bulky ligands,

(ii) Strong field ligands, and

(iii) Strong bonding capacity to make up for the energy loss through four rather than si coordination.

The best known examples of square planar complexes are of d^8 Ni(II), Au(II) and Pt(II), bu examples of d^9 Cu(II), $d^7(CO^{2+})$ and $d^4(Cr^{2+})$ are not common. In case of Ni(II), cyanide ion forms square planar complex, but ammonia and water form six coordinate octahedral complexes instead. I case of heavier metal ions as Pt(II) and Au(II), the steric requirements are relaxed and the effectiv field strength is increased and hence low spin square planer complex anions $Pt(Cl_4)^{2-}$ and $(AuCl_4)^{1-}$ ar known.

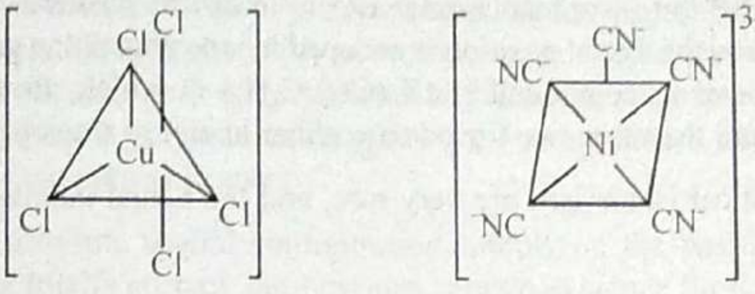
As an example of a d^{10} system, a Cd^{2+} complex has recently been prepared, which is square plana with formula $[Cd(OAr)_2thf_2]$, while the similar zinc complex has a distorted tetrahedral geometr Some macrocyclic ligands as porphyrins and phthalocyanins adopt planar configuration, due to th stereochemistry of coordinating atoms and also due to large resonance energy of the chelated ring which compensates for the tremendous energy lost, in the formation of complex, as required for eve Mg^{2+} ion in chlorophyll.

Square planar complexes of type $[Ma_2b_2]$ show geometrical isomerism and the cis- and trans isomers can be distinguished by dipole moment measurement.

Due to the presence of a plane of symmetry, formed by the four ligating atoms and metal ion bein a mirror plane with no chirality, the planar molecules rarely show optical isomerism. But an interestin case is that of meso-stilbene[isobutylenediamine]platinum(II), [Fig.1.14] which shows optical activity

1.9.6 Coordination Number Five

This has theoretically been shown to be unstable and found to disproportionate to 4- and coordinate complexes. The complexes may be regular or distorted trigonal bipyramidal (TBP) or squa pyramidal (SP) or other highly distorted structures, averaging between the above two. The ener differences between the two structures and the energy barrier tending to prevent interconversion, small and thus one structure is often interconverted into other. These geometries, may be diagrammatica shown in Fig. 1.27.



(i) (ii)

Fig. 1.27 TBP and SP geometries for Coordination number

(i) TBP structure of anion $CuCl_5^{3-}$ in the complex $[Cr(NH_3)_6]\ [CuCl_5]$

(ii) SP Strucure of anion $Ni(CN)_5^{3-}$ in the complex $[Cr(en_3)]\ [Ni(CN)_5]$

As an example of interconversion between the two structures, the anion $Ni(CN)_5^{3-}$ may be cited which is TBP in complex $[Cr(tn)_3]\ [Ni(CN)_5]$ and SP in complex $[Cr(en)_3]\ [Ni(CN)_5]$. It appears that square pyramidal structure is more stable, and on the basis of certain generalizations, it can be stated that d^0-d^4 and d^{10} ions favour TBP structure, while low spin ions favour SP structure. The low spin d^7 complex of Co^{2+}, with 1, 2-bis-[diphenylphosphino)ethane crystallizes in two forms, one red form containing SP ions and other the green form containing TBP ions.

Some polydentate ligands such as tris (2-dimethylaminoethyl)amine, $Me_6tren= [(CH_3)_2NCH_2CH_2)_3N]$, form five coordinate complex, due to the steric requirements of a polydentate ligand of not being able to fit into octahedral coordination.

Though geometrical and optical isomers are expected for five coordinate complexes, none have been isolated so far. This is because, the interconversions are very fast and the axial and equatorial positions are exchanged very rapidly. The ligand repulsion and hydration energies stabilize the TBP configuration, but greater orbital overlap and large CFSE favour square pyramidal configuration. Thus, if a 5-coordinate complex is holding one ligand by a weak bond and other four positions are occupied by strong pi bonding ligands, the structure should be and is square pyramidal. For polydentate ligands, their own steric requirements outweighs all other considerations. For example, as stated above tris- (2-dimethylaminoethyl) amine cannot span a 4-coordinated tetrahedral/planer or six-coordinated octahedral sites. Hence, it forms only 5- coordinate complex, where it occupies one axial position and three equatorial positions to give TBP structure and the fifth position is being occupied by a monodentate ligand.

Many species, other than $[Ni(CN)_5]^{3-}$, which have approximately square pyramidal structures, include d^1-[VO(acac)]; d^6-$[(Ph_3P)_3RuCl_2]$ and d^8- $[Ni(triarsine)Br_2]$, where triarsine is $[(CH_3)_2As(CH_2)_2As(CH_2)_2As(CH_3)_2]$.

d^5, d^6, d^7 and d^8 five- coordinate complexes may either be high spin or low spin. The observed magnetic susceptibility for the low spin complexes is that expected, if one of the d-orbitals is unoccupied. Thus, the value of S or spin quantum number becomes 0, 1/2, 1 and 3/2 for d^8, d^7, d^6 and d^5 ions respectively, and the susceptibility values differ considerably form that of octahedral complexes. The TBP structure results from $d_{z2}sp^3$ and SP structure from $d_{x2-y2}sp^3$ hybridization. Though the examples of isomerisms are few, one example of a TBP-SP isomerism is shown in nickel (II) complex and other example in the Ruthenium complex $[(C_6H_5)_3P)_2Ru.CO.(CF_3)_2C_2S_2]$, which exists in one red and one orange isomer. Both are SP but in orange isomer CO is in apical position, while in red form CO occupies a basal position and the apical position is occuped by one phosphine grouping. An example of Cis-trans isomerism is found in compound $[ReX_2(CO)_2C_6H_5]$ in which, in both the isomers, C_6H_5 occupies apical position and the other two ligands are either at cis- or trans-positions.

The examples of optical isomerisrn are very rare, and the actual compounds, obtained are not enantiomorphic.

1.9.7 Coordination Number Six

This is one of the commonest coordination number and metal ions, such as chromium (II) and cobalt (III), mostly form six-coordinate complexes which are octahedral in shape. This shape is often distorted, and the distortion may be due to elongation or compression along either one of the four fold rotation axes, or along a threefold rotation axis passing through the centre giving, a trigonal antiprism geometry. Another configuration is also possible, as an outcome of reduction of symmetry which may be obtained, by the replacement of six-monodentate ligands in complexes of type $[CO(a)_6]^{3+}$ with bidenate ligands.

Though the greatest number of 6-coordinate complexes are octahedral, some complexes may possess a trigonal prism geometry and the first example of such a complex is tris (cis-1, 2- diphenylethene -1, 2-dithiolato)rhenium, $Re[S_2C_2(C_6H_5)_2]_3$. After wards a number of thiolato complexes of ligand $R_2C_2S_2$ with molybdenum, tungsten, vanadium and zirconium have also been obtained. Reduced species of type $[M(S_2C_2R_2)_6]^{n-}$ are also possible and are obtained by adding one, two or three electrons to the neutral complex. A few trigonal prismatic complexes, have also been obtained with unidentate ligands, but such complexes tend to change over to octahedral geometry.

The geometrical isomerism is possible for octahedral complexs of type $[MA_2B_4]$,in which ligands may be next to one other or on the opposite apexes. Octahedral complexes, in which three ligands may occapy three positions in such a way that two are trans to each other are called **meridional isomer (abbreviated as mer)** or the ligands may form an equilateral triangle on one of the faces, are called **facial isomer (abbreviated of fac)**. It is, however, found that examples of cis- and trans- isomers for octahedral complexes are more numerous, as compared to facial and meridional isomers.

Like geometrical, optical isomerism is also encountered for coordination number six and almost all tris chelate complexes, which lack an improper axis of rotation can exist in two enantiomorphic forms or may also exist as a racemic mixture of both the forms. For finite molecules, absence of an axis of rotatory inversion (possession of n-fold axis of rotatery inversion means that the molecule is brought into coincidence with itself by rotating through 360/n° and inversion through the centre), is sufficient for the molecule to be optically active. The complexes of type $[M(A\text{-}A)_2a_2]$ also show optical activity, because replacement of one chelate with monodentate ligand does not disturb the symmetry. In this case, the trans- isomer is achiral and not aptically active while the cis- form is chiral and optically acitive.

As mentioned before, the separation of dextro and leavo rotatory enantionorphs into individual compounds is termed resolution. One of the most conclusive evidence in favour of octahedral coordination, is the resolution of optical isomers and the first such complex resolved by Werner, was amminochlorobis (ethylenediamine) cobalt (III) cation. After wards a number of complexes of CO (III), Cr (III), Fe (II) and Rh (III), ions containing chelating ligands such as ethylenediamine, oxalate and bipyridine were successfully resolved. A strong objection for this work was the fact, that as all these ligands contain carbon, the optical activity observed was said to be associated with it. In order to show, that optical activity of complex is not associated with carbon, but is due to the lack of symmetry in these complexes themselves, a polynuclear complex tris- [tetrammino-u-dihydroxocobalt (III)] was synthesized and resolved into optical isomers.

The assignment of absolute spatial configuration, simply on the basis of rotation of plane of polarized light, though not totally correct, but provides enough evidence for the phenomenon. But the enantiomorphs have been assigned absolute configurations, by using **anamolous dispersion of x-rays, through object analysis** and the technique has been applied to determine the configuration of $[CO(en)_3]Cl_3$or Br_3.The **optical rotatory dispersion (ORD) methods**, which involve the variation of optical rotation with wavelength, are useful in assignment of absolute configuration. Recently another technique called **Circular Dichroism (CD),** is preferred. The CD effect is possible, only if there is differential absorption of left and right circularly polarized light and it is found that complexes having the same sign of CD, for a given absorption band will have the same absolute configuration.

The configuration of chelate rings is also responsible for stereo selectivity. For e.g., ethylenediamine in gauche form, is dissymmetric and should be resolved theoretically, but in the process the gauche and planer forms can reconvert, making the isolation of the two enantiomorphs of complex $[CO(NH_3)_4en]$ almost impossible. The difference in stability between the two isomers, is related to preferred packing arrangement of chelate rings and the greater stability of one configuration over other, is the source of stereo specific synthesis.

In addition to octahedral geometry for six coordination, trigonal prismatic geometry can also occur. This was recognized for MoS_2. The structure of which may be described, as superimposed layers of sulphur atom with molybdenum atom in the trigonal prismatic holes. This is a layer structure, with the sequence 5Mo:55MoS. The electronic configuration of Mo (IV), is d^2 but $NbS_2(d^1)$ and $ReS_2(d^3)$, also have similar structure.]

Trigonal prismatic coordination of metal atom is also found in $[W(CH_3)_6P]$, and a group of complexes of dianion of diphenylethylenedithiol (HS)PhC = CPh(SH). These include the compounds $[Mo(S_2C_2Ph_2)_3]$ and $[Re\ (S_2C_2Ph_2)_3\ ]$

1.9.8 Coordination Number Seven

This coordination number is not at all common and the complexes are unstable due to:

(i) increased ligand-ligand repulsion,

(ii) weaker bond formation and

(iii) reduced CFSE, as an outcome of non-octahedral geometry.

Such complexes can exist in two idealized geometrical forms, which are all of comparable stability and can be easily reconverted into one other. These known geometries are;

(i) Pentagonal bipyramid eg in ZrF_7^{3-} ion and IF_7

(ii) Capped octahedran, in which seventh ligand occupies a rectangular face and this is sufficient for the molecule to be optically active. In this case the cis-form is chiral and otically active while the trans-form is achiral and optically inactive. The two geometries are shown as;

(i) Pentagonal bipyramid: In many of the complexes, often the requirements of polyde ligands favour 7 coordination. Thus in the iron complex of, 2,3,-dimethyl-3,6,9,12,18- pentaazabicyc [12,4,3,1] octadeca(18),2,12,14,16 pentene and two axial SCN ligands, the five macrocyclic and t coplanar nitrogen atoms in axial positions, result in pentagonal bipyramidal structure. In some ca ligands, even force unfavourable interactions. In a series of complexes of type [M $(Ph_3tren)]^{2+}$, wh M is Mo, Fe, Co or Ni and ph_3tren is $[C_6H_4NCH = NCH_2CH_2]_3N$, the three pyridine nitrogens, are at vertices of one equilateral triangle and three imine nitrogens, at the vertices of another equilat triangle and the seven coordination is forced by the geometry of the other six-coordinating lig atoms. This arrangement, thus appears to be an approximate octahedron, but may better be represent as trigonal antiprism, because the metal ion is closer to imine nitrogen than to the pyridine nitrogen. T structure may be drawn as follows, in which N_1 represents pyridine nitrogen, N_2 imine nitrogen and the seventh unique nitrogen.

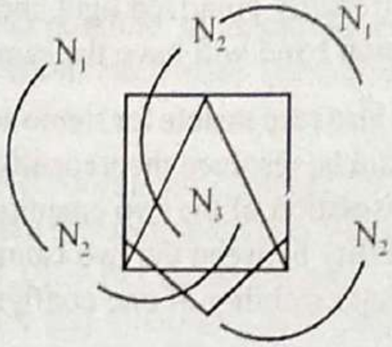


Fig. 1.28 Structure of ligand $[(Ph_3tren)]$

The difference between different geometries are not small, and complexes have structures th deviate significantly from idealized ones.

(ii) Capped trigonal prism:

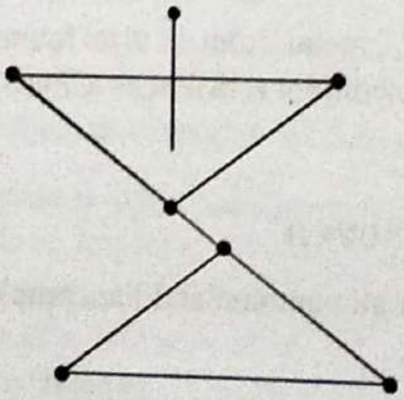


Fig. 1.29 Structure of $[Mn(EDTA/H_2O]^{2-}$ and Nb F_7^{2-}

The seven coordination number is forced on metal due to stereorigidity of ligands and it is establish that it is directed against the 2Eg orbital of metal which may thus be considered as an antibondi orbital and this structure decreases the stability of complex.

It is found that polydentate ligands favour this coordination number. In fact, the possibility mentio above is found to be true in case of complex $[M(py_3tren)]$ M = Mo, Fe, Co, Ni and $py_3tren = [C_5H_4NC$ $= NCH_2CH_2]_3N$, in which the three imine nitrogens are at vertices of one equilateral triangle and thr pyridine nitrogens are at the vertices of one other. There is one very long M-N bond (280-540 p formed by the seventh nitrogen atom directed at the center of a trigonal antiprismatic face while the other M-N bonds are shorter of the order of 190-230 pm.

The M-N bond distances for a series of complexes of Ni, Cu and Zn vary form 323-301 pm and are about 10 pm larger than the sum of Vander waals radii which range between 315-295 pm. The other six M-N bond distances are considerably shorter implying weak bonding. The bond angles at M-N vary from 112°-120° in manganese and iron complexes respectively, as an outcome of minimum and maximum repulsion. Both geometrical and optical isomerisms are possible but no examples are however known.

1.9.9 Coordination Number Eight

After four and six coordination numbers, eight is the third most abundant coordination number. The factors responsible for the formation of 8-coordinate complexes are:

(i) The metal cation should be large enough to accommodate eight ligands without undue strain. Thus 4d and 5d ions like Zr, Hf, Nb, Ta, Mo and W give 8 coordinate complexes while 3d ions do not. A large number of complexes of lanthanides (4f) and actinides (5f) also exhibit this coordination number.

(ii) The ligand atoms should be small and electronegative, commonest amongst these are carbon, nitrogen, oxygen and fluorine.

(iii) The metal should have a high oxidation state i.e., the formal charge on metal should be high, so that the eight coordinate bonds do not transfer excess negative charge density on the central atom. Such metal ion should be d°, d^1 and d^2 ions with +3 or even higher ionic charge.

There are many stereo chemical arrangements for this coordination number. The most regular **cubic** arrangement has been found for PaF_8^{3-} ion and is unstable. The other two common arrangements are **dodecahedron and square antiprism,** both these structures arise from sp^3d^4 hybridization and the use of four d orbitals for hybridization shows why only d^0, d^1 and d^2 metals can form such complexes. The crystal field stabilization energy for both the structures is comparable and no particular choice for one configuration over other can be made.

Extensive possibilities exist for geometrical and optical isomerism but none have been isolated so far. Square antiprism structure is found in TaF_8^{3-}, $[Zr(acac)_4]$, $[Y(acac)_3(H_2O)_2]$, whereas dodecahedral structure is found in $[Ti(NO_3)_4]^{4-}$ and $[Zr(oxalate)_4]^{4"}$. The ion $[Mo(CN)_8]^{2-}$ is square antiprismatic in sodium salt but is dodecahedral in potassium and tetrabutyl ammonium (B_4N^+) salt.

1.9.10 Higher Coordination Number

Discrete 9-coordinate structure exists in $[Lu(H_2O)_9]^{3-}$ and $[Tc/Re\ Hg]^{2-}$ which are formed by adding a ligand to each of the rectangular faces of the trigonal prism giving tricapped prism.

The few 10-coordinate complexes include uranium acetate polymer and $K_4[Th(ox)_4.2H_2O]$ which have a bi capped dodecahedral structure.

The 11-coordinate species are encountered among $[Th(NO_3)_4 3H_2O]$ complex which is suggested to possess a capped trigonal prismatic structure.

The 12-coordinate species known are $[Ce(NO_3)_6]^{2-}$ and $[Th(NO_3)_6]^{2-}$ and these possess icosahedral structures.