

### **Oxidation number of the central atom in coordination compounds**

- The oxidation number of an atom is the charge that would exist on the atom if the bonding were completely ionic.
- In complex ions or molecules, the oxidation numbers of these atoms can be calculated if we assume that the oxidation numbers of the other atoms in the species are fixed.
- The oxidation numbers of metals with more than one oxidation state are represented by Roman numerals.

### **Reactions of coordination compounds**

In coordination compounds following reaction takes place:

1. Substitution reaction.
2. Ligand exchange reaction:
  - a) Dissociative reaction
  - b) Associative reaction.
- 3) Electron transfer (redox) reaction.

### **Thermodynamic and Kinetic stability of complex compounds**

**Thermodynamic stability:** It is a measure of formation of complex under a given sets of equilibrium conditions. It depends on the strength of the bond between metal atom and ligand in the complex. It deals with metal-ligand energies, stability constants and several thermodynamic variables.

**Kinetic stability:** It refers to the speed or rate at which the complex formation takes place. Time plays an important factor in deciding the stability of complex.

## Common name of ligands

**Table 1. Names of Some Common Ligands**

Anionic Ligands	Names	Neutral Ligands	Names
$\text{Br}^-$	bromo	$\text{NH}_3$	ammine
$\text{F}^-$	fluoro	$\text{H}_2\text{O}$	aqua
$\text{O}^{2-}$	oxo	$\text{NO}$	Nitrosyl
$\text{OH}^-$	Hydroxo	$\text{CO}$	Carbonyl
$\text{CN}^-$	cyano	$\text{O}_2$	dioxygen
$\text{C}_2\text{O}_4^{2-}$	oxalato	$\text{N}_2$	dinitrogen
$\text{CO}_3^{2-}$	carbonato	$\text{C}_5\text{H}_5\text{N}$	pyridine
$\text{CH}_3\text{COO}^-$	acetato	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	ethylenediamine

All common names are given in table:

Some common ligands and their name

Anionic Ligand	Ligand Name	Neutral Ligand	Ligand Name
Bromide, $\text{Br}^-$	Bromo	Ammonia, $\text{NH}_3$	Ammine
Carbonate, $\text{CO}_3^{2-}$	Carbonato	Water, $\text{H}_2\text{O}$	Aqua
Chloride, $\text{Cl}^-$	Chloro	Carbon monoxide, $\text{CO}$	Carbonyl
Cyanide, $\text{CN}^-$	Cyano	Ethylenediamine, en	Ethylenediamine
Fluoride, $\text{F}^-$	Fluoro		
Glycinate, $\text{gly}^-$	Glycinato		
Hydroxide, $\text{OH}^-$	Hydroxo		
Oxalate, $\text{C}_2\text{O}_4^{2-}$	Oxalato		
Thiocyanate, $\text{SCN}^-$	Thiocyanato*		
	Is thiocyanato <sup>†</sup>		

\* Ligand donor atom is S. <sup>†</sup>Ligand donor atom is N.

Name of some common ligand with their respective names are given above.

### **Order of naming ligands**

Ligands are listed in the following order: negative ions, neutral molecules, and positive ions. Ligands with the same charge are listed in alphabetical order.

### **Naming of bridging groups in polynuclear coordination compounds**

If the complex contains two or more metal ions, it is termed as polynuclear. The monodentate ligands that link the two metal atoms simultaneously are called bridging ligands and are denoted by prefix -  $\mu$ .

### **Isomers of coordination compounds**

Isomers are those compounds which have the same molecular formula but different structural arrangements of their atoms. Broadly two types of isomerisms are shown by coordination compounds as: Stereo isomerism and Structural isomerism.

#### **Structural isomerism**

This type of isomerism arises due to the difference in structures of coordination compounds. Types are:

- Ionisation isomerism
- Solvate isomerism
- Linkage isomerism
- Coordination isomerism

#### **Space isomerism**

It arises on account of the different positions and arrangements of ligands in space around the nucleus. It is of two types:

1. Geometrical isomerism
2. Optical isomerism

#### **Ionisation isomers**

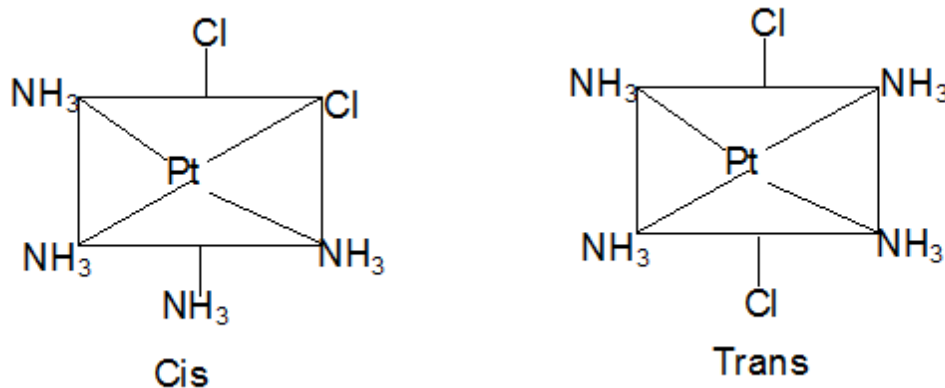
Compounds which give different ions in solution although they have same composition are called ionization isomers.

### Space or stereo isomerism

In coordination compounds, the ligands are arranged in space in specific orientation around a given metal atom or ion. Space isomerism arises on account of the different positions and arrangements of ligands in space around the metal ion. It is of two types :

- 1 ) Geometrical or Cis-trans Isomerism
- 2 ) Optical Isomerism

#### Geometrical isomerism



This type of isomerism is found in heteroleptic complexes due to different possible geometrical arrangements of the ligands. When two identical groups occupy adjacent positions, the isomer is called cis and when arranged opposite to one another, the isomer is called trans.

#### Characteristics of ionisation isomers

This type of isomerism occurs when a counter ion of the complex is also a potential ligand. Hence, it can displace the ligand which can then become a counter ion.

#### Characteristics of linkage isomers

This type occurs in compounds containing ambidentate ligands. In case of  $\text{NO}_2^-$ , either nitrogen or an oxygen may act as a donor.

#### Characteristics of coordination isomerism

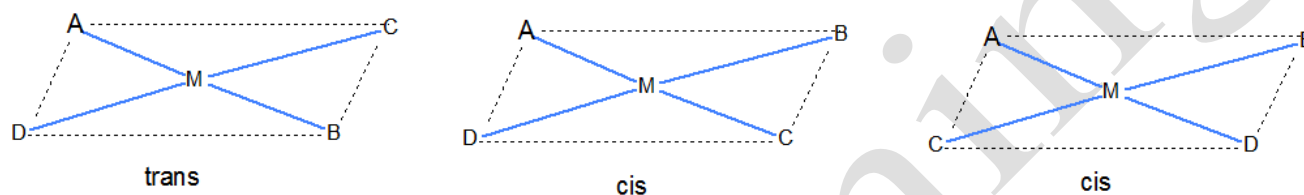
This type of isomerism is possible when both the positive and negative ions of a salt are complex ions and the two isomers differ in the distribution of ligands in the cation and the anion.

### Characteristics of geometrical isomers

This type of isomerism occurs in heteroleptic complexes due to different possible geometric arrangements of the ligands. When two identical groups occupy adjacent positions, the isomer is called cis and when arranged opposite to one another, the isomer is called trans. However, cis-trans isomerism is quite common in square planar and octahedral complexes.

For example : diamminedichloridoplatinum ( II )

### Geometrical isomerism in MABCD



### Chirality and chiral compounds

The molecules which are non super-imposable mirror images of each other are called chiral compounds and this property is called chirality. They do not have a plane of symmetry. Optical isomers do not have a plane of symmetry.

### Werner's theory of coordination compounds

Werner's theory states that-

1. Metals possess two types of valencies called primary / ionizable and secondary / non - ionizable valency.
2. Every metal atom has a tendency to satisfy both its primary and secondary valencies.
3. The ligands satisfying secondary valencies are always directed towards fixed positions in space thereby giving a definite geometry to the complex but primary valencies are non - directional.

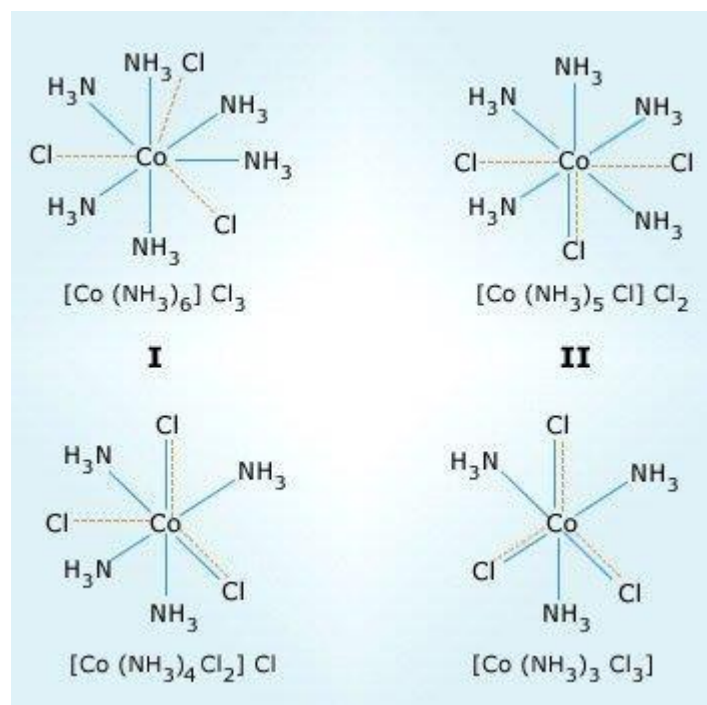
### Main postulates of Werner's theory

- (a) The central metal atom\ ion in a coordination compound exhibits two types of valencies - primary and secondary
- (b) Primary valencies are ionisable and correspond to the number of charges on the complex ion. Primary valencies apply equally well to simple salts and to complexes and are satisfied by negative ions.
- (c) Secondary valencies correspond to the valencies that a metal atom (or) ion exercises towards

neutral molecules (or) negative ions in the formation of its complex ions.

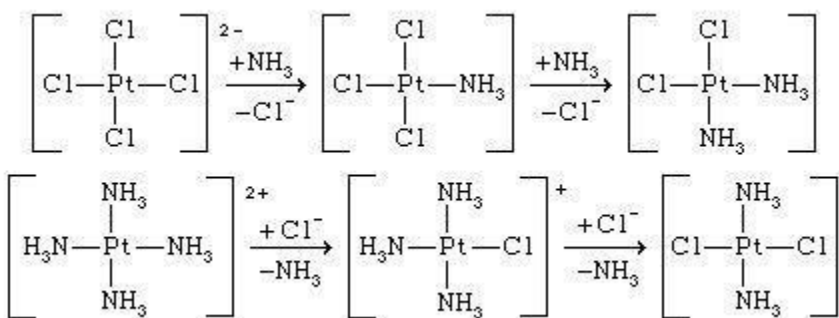
d) Secondary valencies are directional and so a complex has a particular shape. The number and arrangement of ligands in space determines the stereochemistry of a complex.

#### Structure of complex on the basis of Werner's theory



Dotted line represents the primary valency. Normal line represents the secondary valency.

#### Complexes formed between platinum tetrachloride and ammonia



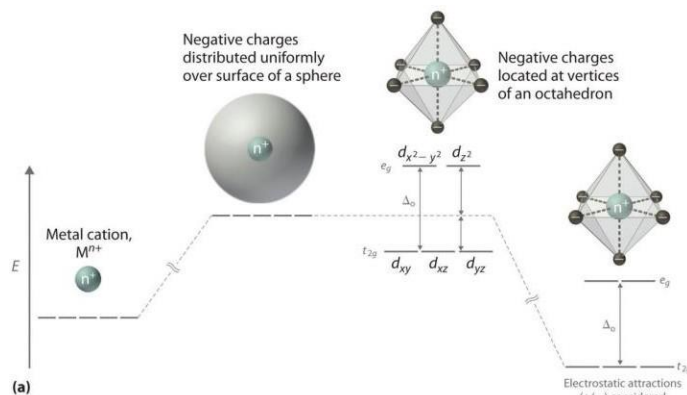
#### Limitations of Werner's theory

It failed to explain why all elements don't form coordination compounds.

It failed to explain the directional properties of bonds in coordination compounds.

It does not explain the colour, and the magnetic and optical properties shown by coordination compounds.

## Crystal field theory

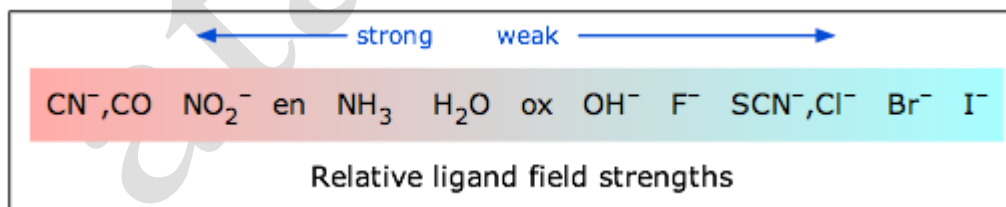


The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules.

## Features of CFT

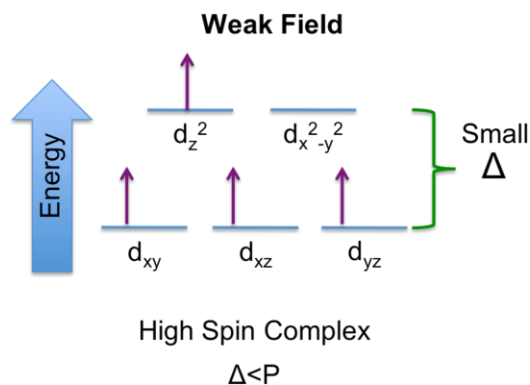
Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color.

## Strong field ligands



Strong field ligands have large  $\Delta$ . They are  $\pi\pi$ -acceptor ligands. They have the tendency of pairing of electrons of the metal ions.

## Weak field ligands



Ligands that produce a small  $\Delta$  are called weak-field ligands and lie at the left end of the spectrochemical series. Weak field ligands cannot make pairing of electrons to the metal atoms. They are  $\pi\pi$  donor ligands, e.g., halide ions are weak field ligands.

### Properties of octahedral

High spin state and low spin state

Magnetism

Colour

### Factors affecting orbital splitting energy

Oxidation state of the metal

Nature of the metal

Geometry of the coordination entity

Nature of the ligand

### Limitation of crystal field theory

As ligands are regarded as point charges, the anionic ligands should exert greater splitting effect. It treats the metal-ligand bond as purely ionic and does not take into the account the covalent character of the bond.

### Properties of tetrahedral and square planar complex

Magnetic property-Strong field ligands cause low spin states to be more stable and the weak field ligands cause high spin states to be more stable, we can determine whether the electrons are paired up or not and hence we can predict the diamagnetism or paramagnetism.



Colour- The CFSE for most of the complexes is of the same order of magnitude as the energy of the photon of visible light. It is possible for transition-metal complex to absorb visible light which thereby excites electron from the lower energy d-orbitals into the higher ones.

#### **Advantages of crystal field theory over valence bond theory**

CFT predicts a gradual change in magnetic properties of complexes rather than the abrupt change predicted by VBT. According to VBT, the bond between the metal and the ligand is covalent, while according to CFT it is purely ionic. The bond is now considered to have both ionic and covalent character. Unlike valence bond theory.

#### **Stability of coordination compounds in solution and stability constant**

When the term stability is applied to coordination compounds (metal complexes) there can be two interpretations, thermodynamic or kinetic stability. Thermodynamic stability refers to the change in energy on going from reactants to products i.e.  $\Delta G$  for the reaction. Kinetic stability refers to reactivity, generally ligand substitution. Substitution occurs extremely rapidly in some cases and extremely slowly in others. Complexes of the former type are referred to as labile and those of the latter type inert. Sometimes these two types of stability parallel one another, but often they do not.

Thermodynamic stability often refers to the energetics and associated equilibrium constant for the reaction of an aquated metal ion with some other ligand (other than water). Stability constant is the reciprocal of the instability constant ( $\beta$ ).

#### **Factors affecting the stability of complex**

Charge on the central metal ion

Nature of the metal ion

Basic nature of the ligand

Presence of chelate rings

Effect of multi-dentate cyclic ligands

#### **Class a receptors**

They are the metals belonging to group 1 and 2, earlier members of the transition series, i.e., groups 3 to 6 and inner transition elements. They form stable complexes when the donor atoms of the ligands are N, O, F.

### Class b receptors

They are the transition metals mostly after group 6 which have relatively filled d orbitals (Rh, Pd, Ag). They form stable complexes when the donor atoms of the ligand are heavier members of N, O, F family.

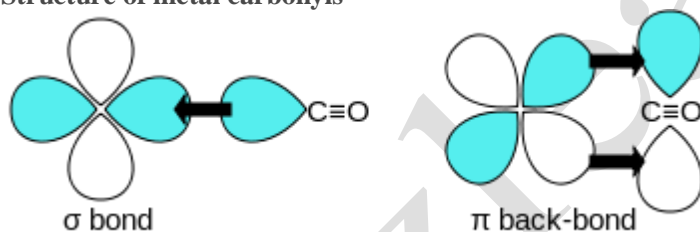
### Macrocyclic effect

If the ligand happens to be multi-dentate and cyclic without any steric effects, the stability of the complex is further increased. The effect is called macrocyclic effect.

### Characteristics of pi-bonded organometallic compounds

Compounds have  $\pi\pi$  electrons i.e electrons in their  $\pi\pi$  molecular orbitals. Overlapping of these  $\pi\pi$  orbitals with the vacant orbitals of the metal atom gives rise to an arrangement in which the metal atom gets bound to all the C atoms over which the  $\pi\pi$  molecular orbital of the organic ligand is spread.

### Structure of metal carbonyls



Carbon monoxide bonds to transition metals using "synergistic  $\pi\pi^*$  back-bonding". The bonding has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of the non-bonding (or weakly anti-bonding) sp-hybridized electron pair on carbon with a blend of d-, s-, and p-orbitals on the metal. A pair of  $\pi\pi$  bonds arises from overlap of filled d-orbitals on the metal with a pair of  $\pi\pi$ -antibonding orbitals projecting from the carbon atom of the CO. The latter kind of binding requires that the metal have d-electrons, and that the metal is in a relatively low oxidation state ( $<+2$ ) which makes the back donation process favorable. As electrons from the metal fill the  $\pi^*$ -antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened.

### Properties of metal carbonyls

Most of the metal carbonyls are solids at room temperature and atmospheric pressure. They are soluble in nonpolar and polar organic solvents. Their reactivity is partly due to the central metal atom and partly due to the CO ligands.

### Uses of metal carbonyls

Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis, such as hydroformylation, In the Mond process, nickel carbonyl is used to produce pure nickel.

### Bonding in metal carbonyls

Carbon monoxide bonds to transition metals using "synergistic pi star back-bonding." The bonding has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of the nonbonding (or weakly anti-bonding) sp-hybridized electron pair on carbon with a blend of d-, s-, and p-orbitals on the metal. A pair of bonds arises from overlap of filled d-orbitals on the metal with a pair of  $\pi$ -antibonding orbitals projecting from the carbon atom of the CO. The latter kind of binding requires that the metal have d-electrons, and that the metal is in a relatively low oxidation state ( $\leq +2$ ) which makes the back donation process favorable. As electrons from the metal fill the  $\pi$ -antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened. Because of the multiple bond character of the M-CO linkage, the distance between the metal and carbon atom is relatively short, often  $< 1.8$  Å, about 0.2 Å shorter than a metal-alkyl bond. Several canonical forms can be drawn to describe the *approximate* metal carbonyl bonding modes.

### Importance and applications of coordination compounds

- In Analytical chemistry
- In qualitative analysis
- In biological systems
- In medical field
- In quantitative analysis
- Purification of metals

## Importance and applications of organometallic compounds

Homogeneous catalysis

Heterogeneous catalysis

Purification of metals

Organic synthesis

Medicine

Agriculture

Future expectations

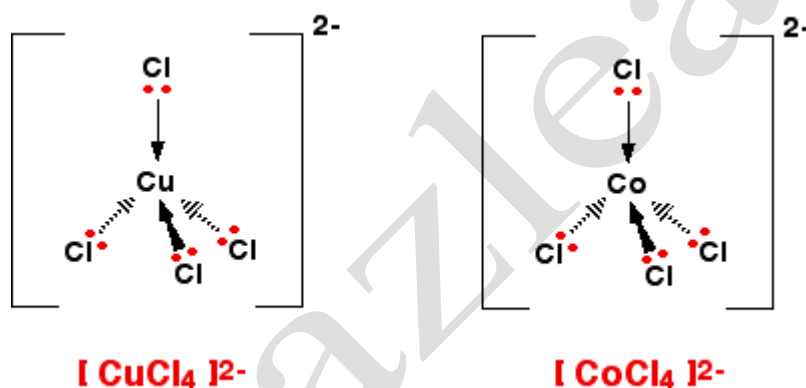
## Synergic bonding

Self strengthening bond in the coordination complexes knows as **Synergic bonding**.

The bond between a Carbonyl group acting as a ligand and a metal.

It is formed by pi-acid ligands like CO. Pi-acid ligands are those which have lone pair of electrons to donate metal atom and an empty antibonding molecular orbital for back bonding with the d-orbital electrons of metal atom.

## Complex ion



A complex ion has a metal ion at its centre with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by co-ordinate (dative covalent) bonds. There is a bit of unique nomenclature to complex ions. The metal is known as the central metal ion. The anions or molecules attached to the metal are called ligands.

## Difference between double salt and complex compounds

### Double salt:

1. These exist only in solid state and dissociate into constituent species in their solution.
2. They lose their identity in dissolved state.

3. In double salt the metal atom/ion exhibit normal valency.

**Complex compound:**

1. They retain their identity in solid as well as in solution state.
2. They do not lose their identity in dissolved state.
3. In co-ordination compounds, the number negative negative ions or molecules surroundings the central metal atom is beyond its normal valency.

**Ligands**

The donor atoms, molecules or anions, which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it, are called ligands. e.g.,  $\text{H}_2\text{O}$ , ethylene diamine.

**Properties of ligands**

Ligands act like Lewis bases because they share their electron pairs (electron donors) with the central metal atom.

Ligands do not form ionic bonds with the central metal atom. Rather, they form covalent bonds with the central metal atom because they share electron pairs.

**Classification of ligands on the basis of charge**

Cationic

Anionic

Neutral

**Ligands on the basis of donor atoms**

Uni-dentate

Bi-dentate

Tri-dentate

Polydentate

**Monodentate ligand**

The ligands which have only one donor atom and are coordinated through one pair of electrons are called monodentate ligand or uni-dentate 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. Example: Water, Ammonia, Halide ion.

### **Bi-dentate ligands**

The ligand which contain two donor atoms positioned in such a way that a five or six membered ring is formed with the metal ion, these ligand are known as bidentate ligands.

Examples: ethylenediamine and oxalate ion.

### **Tri-dentate ligands**

Ligand which contains three donor atoms that are capable of bonding with the central metal or ion.

Examples of tri-dentate ligands are: di-ethylene tri-amine and iminodiacetic acid anion.

### **Tetra-dentate ligands**

Ligand which has four donor atoms having binding capability with the central meta atom or ion known as **Tetradentate ligands**.

Example: triethylenetetramine (abbreviated trien).

Tetradentate ligands bind via three connectivities depending on their topology and the geometry of the metal center.

### **Pentadentate ligands**

Pentadentate ligands bind with five atoms, an example being ethylenediaminetriacetic acid.

### **Hexadentate ligands**

Hexadentate ligands bind with six atoms, e.g., EDTA.

### **Bridging ligands**

A bridging ligand is a ligand that connects two or more atoms, usually metal ions. The ligand may be atomic or polyatomic. Virtually all complex organic compounds can serve as bridging ligands, so the term is usually restricted to small ligands such as pseudo halides or to ligands that are specifically designed to link two metals.

### **Denticity**

The number of ligating groups present in a ligand is called the denticity of that ligand, e.g., ethylenediamine is a didentate ligand.

### **Chelation and chelating ring**

The ligand may contain two donor atoms positioned in such a way that a five or six membered ring is formed with the metal ion, then it is called didentate chelating ligand and the ring is called chelating ring, the resulting complex is called a metal chelate and this property is called chelation.

### **Important characteristics of chelate**

They form more stable complexes than the unidentate analogs.

Greater the denticity of the ligand, more stable is the complex formed.

Ligands with large groups form unstable rings than the ligands with smaller groups due to steric hinderance.

### **Importance of chelates**

It is used in softening of hard water.

It is used in the separation of lanthanoids and actinoids.

It is used in the detection of metal ions in qualitative analysis.