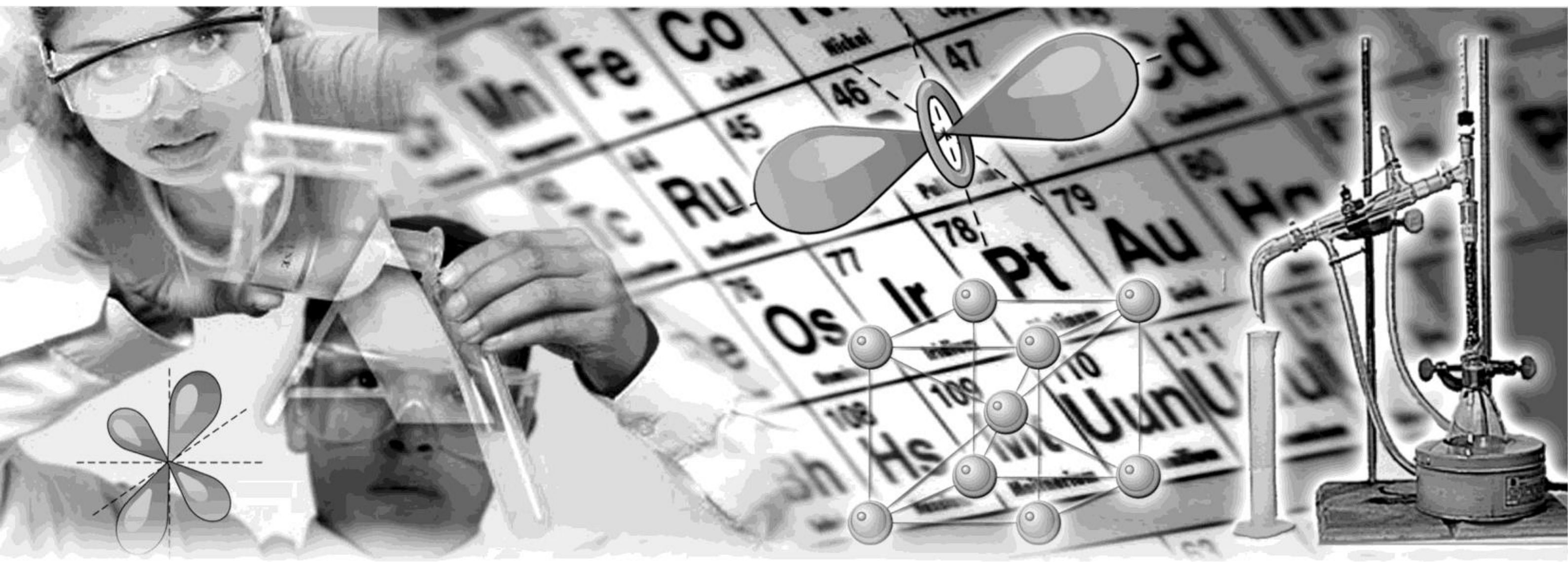


Chapter

20

Co-ordination Chemistry

All transition elements exhibit a characteristic property of complex ion formation. The compounds containing complex ions are called coordination compounds. The branch of chemistry in which coordination compounds are studied that is called co-ordination chemistry.

Double Salts and Co-ordination Compounds

When solutions of two or more stable compounds are mixed in stoichiometric (simple molecular) proportions new crystalline compounds called molecular or addition compounds are formed. These are of two types,

(1) Double salts, (2) Co-ordination or Complex compounds

(1) **Double salts :** Addition compounds, stable in solid state. Dissociate into ions in aqueous solution as such give test for each constituent ion. Examples:

Double Salt	Responds test for the ions
Carnalite : $KCl.\ MgCl_2 6H_2O$	$K^+,\ Mg^{2+}, Cl^-$
Potash alum : $K_2SO_4 . Al_2(SO_4)_3\ 24H_2O$	K^+, Al^{3+}, SO_4^{2-}

(2) **Co-ordination or Complex compounds :** Addition compound, stable in solid state. Retain their identity even in solution. Central metal ion form dative or coordinate bond with the species surrounding it (ligands). Examples :

Complex compound	Cation	Anion
$[Cu(NH_3)_4]SO_4$	$[Cu(NH_3)_4]^{+2}$	SO_4^{2-}
$K_2[PtF_6]$	$2K^+$	$[PtF_6]^{2-}$
$[Co(NH_3)_6][Cr(CN_3)_6]$	$[Co(NH_3)_6]^{2+}$	$[Cr(CN)_6]^{3-}$

Terminology of co-ordination compounds

(1) **Central metal atom or ion :** A complex ion contains a metal atom or ion known as the central metal atom or ion. It is sometimes also called a nuclear atom.

(2) **Complex ion :** It is an electrically charged radical which is formed by the combination of a simple cation with one or more neutral molecules or simple anions or in some cases positive groups also.

(3) **Ligands :** Neutral molecules or ions that attach to central metal ion are called ligands. The donor atom associated with the ligands supplies lone pair of electrons to the central metal atom (forming dative bond) may be one or two more. Monodentate (one donor atom), bidentate (two donor atom), tridentate (three donor atom) etc.

Monodentate Ligands (with one donor site)

Table : 20.1 ***Anionic Ligands*** (Negative legands)

Formula	Name	Formula	Name
X^-	Halo	O_2^{2-}	Peroxo

$:OH^-$	Hydroxo	CH_3COO^-	Acetato
CN^-	Cyano	NO_3^-	Nitrato
O^{2-}	Oxo	$S_2O_3^{2-}$	Thiosulphato
NH_2^-	Amido	NO_2^-	Nitrito
S^{2-}	Sulphido	CO_3^{2-}	Carbonato
CNS^-	Thiocyanato	SO_4^{2-}	Sulphato

Table : 20.2 *Neutral Ligands*

Formula	**Name**	**Formula**	**Name**
CO	Carbonyl	$:NH_3$	Amminato
PH_3	Phosphine	H_2O	Aqua
NO	Nitrosyl	$C_5H_5N:$	Pyridine (py)

Table : 20.3 *Cationic Ligand* (Positive)

Formula	**Name**	**Formula**	**Name**
NO_2^+	Nitronium	NO^+	Nitrosonium
$H_2NNH_3^+$	Hydrazinium		

Polydentate ligands (with two or more donor site)

Table : 20.4 *Bidentate* (Two donor sites)

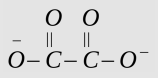
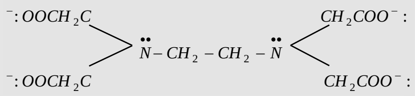
Formula	**Name**	**Formula**	**Name**
$H_2NCH_2CH_2NH_2$	Ethylenediamine (en)	$\begin{array}{c} Me-C=NO^- \\ \vert \\ Me-C=NOH \end{array}$	Dimethylglyoximeto (dmg)
 $\overset{-}{O}-\overset{O}{\overset{\Vert}{C}}-\overset{O}{\overset{\Vert}{C}}-O^-$	Oxalato (ox)	$NH_2-CH_2-COO^-$	Glycinate ion (gly)

Table : 20.5

	Formula	**Name**
Tridentate	$H_2\ddot{N}(CH_2)_2-\ddot{N}H-(CH_2)_2\ddot{N}H_2$	Diethylenetriaminediamine (dien)
Tetradentate	$H_2\ddot{N}(CH_2)_2-\ddot{N}H-(CH_2)_2\ddot{N}H(CH_2)_2\ddot{N}H_2$	Triethylenetetramine (trien)
Hexadentate		Ethylenediamine tetra-acetic acid (EDTA)$^{4-}$

Chelating Ligand : When polydentate ligands bind to the central metal ion they form a ring called chelate and the ligand is referred as chelating ligand.

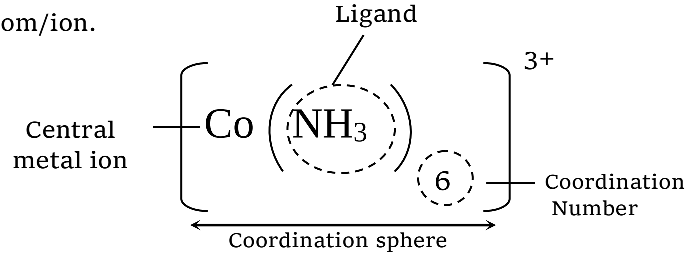
Ambidentate ligands : A ligand which possesses two donor atom but in forming complex it utilizes only one atom depending upon the condition and type of complex.

NO_2 (nitro) , ONO (nitrito), CN (cyano), NC (isocyano), SCN (thiocyanide), NCS (isothiocyanide)

π- acid ligand : Ligands which are capable of accepting an appreciable amount of π- e^- density from the metal atom into emptying π or π^* orbital or their own called $\pi-$ acceptor or $\pi-$ acid ligands eg. CO.

(4) **Co-ordination Sphere :** Ligand with central metal ion is kept in square bracket [ ] retains its identity in the same form is called co-ordination sphere (non-ionisable)

(5) **Co-ordination Number :** Number of monodentate ligands attached to central atom/ion are called coordination number of the central metal atom/ion.



(6) **Ionisation Sphere :** The part present out side of the square bracket is called ionization sphere (ionisable).

IUPAC Nomenclature of complex compounds

In order to name complex compounds certain rules have been framed by IUPAC. These are as follows :

(1) The positive part of a coordination compound is named first and is followed by the name of negative part.

(2) The ligands are named first followed by the central metal. The prefixes *di*-, *tri*-, *tetra*-, etc., are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands), tris (three ligands), etc., are used when the ligands includes a number e.g., dipyridyl, bis (ethylenediamine).

(3) In polynuclear complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens. In polynuclear complexes (a complex with two or more metal atoms), bridging ligand (which links two metal atoms) is denoted by the prefix μ before its name.

(4) **Naming of ligands :** The different types of ligands *i.e.* neutral, negative or positive are named differently in a complex compound.

When a complex species has negative charge, the name of the central metal ends in – ate. For some elements, the ion name is based on the Latin name of the metal (for example, argentate for silver). Some such latin names used (with the suffix – ate) are given below :

Fe	Ferrate	*Cu*	Cuperate
Ag	Argentate	*Au*	Aurate
Sn	Stannate	*Pb*	Plumbate

(5) **Point of attachment in case unidentate ligands with more than co-ordinating atoms** (ambidentate ligands) **:** The point of attachment in case of unidentate ligands with more than one co-ordinating atoms is either indicated by using different names for the ligands (*e.g,* thiocyanato and isothiocyanato) or by placing the symbol of the donor atom attached, the name of the ligand separated by a hypen.

$$\underset{\substack{\text{Ammonium hexathioxyanato -S-chromate (III)}\\ \text{or}\\ \text{Ammonium hexathiocyanatochromate (III)}}}{(NH_4)_3[Cr(SCN)_6]} \qquad \underset{\substack{\text{Ammonium hexathiocyanato - N - platinate (IV)}\\ \text{or}\\ \text{Ammonium hexaisothiocyanatoplatinate (IV)}}}{(NH_4)_2[Pt(NCS)_6]}$$

(6) **Name of the bridging groups :** If a complex contains two or more central metal atoms or ions, it is termed as polynuclear. In certain polynuclear complexes. ligands may link the two metal atoms or ions. Such ligands which link the two metal atoms or ions in polynuclear complexes are termed as bridge ligands. These bridge ligands are separated from the rest of the complex by hyphens and denoted by the **prefix** μ**.** If there are two or more bridging groups of the same kind, this is indicated by *di*- μ–, *tri* –μ–, etc.

$$\underset{\mu\text{-amidobis [pentaamminecobalt (III)]nitrate}}{[(NH_3)]_5Co-NH_2-Co(NH_3)_5](NO_3)_5}$$

$$\underset{\mu\text{- hydroxobis [pentaamminecobalt (III)] chloride}}{[(NH_3)_5Co-OH-Co(NH_3)_5]Cl_5}$$

(7) If any lattice component such as water or solvent of crystallisation are present, these follow the name and are preceded by the number of these groups (molecules of solvent of crystallisation) in Arabic numerals.

For example,

$$\underset{\text{Tetraaquacopper(II)sulphate1 – water}}{[Cu(H_2O)_4]SO_4.H_2O}$$

$$\underset{\text{tetraaquadichlorochromium (III)chloride 2-water}}{[Cr(H_2O)_4Cl_2]Cl.2H_2O}$$

(8) Following punctuation rules should also be followed while writing the name of the complex compounds.

(i) The name of the complete compound should not start a capital letter, *e.g.,* $\underset{\substack{\text{tetraamminecopper (II)sulphate (Correct)}\\ \text{Tetraamminecopper (II)sulphate (Incorrect)}}}{[Cu(NH_3)_4]SO_4}$

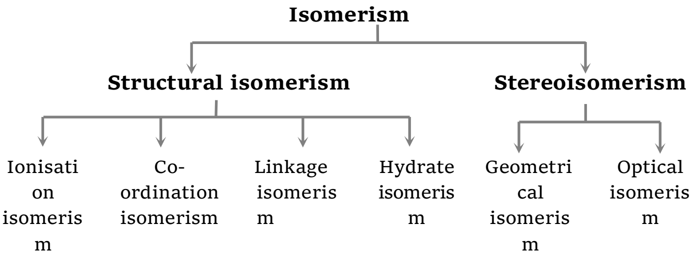
(ii) The full name of the complex ion should be written as one word without any gap.

(iii) There should be a gap between the cation and anion in case of ionic complexes.

(iv) The full name of non-ionic complexes should be written as one word without any gap.

Isomerism in co-ordination compounds

Compounds having the same molecular formula but different structures or spatial arrangements are called isomers and the phenomenon is referred as ***isomerism.***



(1) **Structural isomerism :** Here the isomers have different arrangement of ligands around the central metal atom. It is of the following types :

(i) ***Ionisation isomerism*** : The co-ordination compound having the same composition or molecular formula but gives different ions in solution are called ionization isomers.

There is exchange of anions between the co-ordination sphere and ionization sphere.

Example :

$[Co\,Br\,(NH_3)_5]SO_4$	$[Co\,SO_4(NH_3)_5]\,Br$
Pentaaminebromo cobalt (III) Sulphate	Pentaaminesulphato cobalt (III) bromide
SO_4^{2-} present in ionisation sphere	Br^- present in ionization sphere
Gives white precipitate with $BaCl_2$	Gives light yellow **precipitate** with $AgNO_3$

(ii) ***Co-ordination isomerism*** : In this case compound is made up of cation and anion and the isomerism arises due to interchange of ligands between complex cation and complex anion.

Example : $[Co(NH_3)_6]\,[Cr\,(CN)_6]$

$[Cr\,(NH_3)_6][Co(CN)_6]$

hexaamine cobalt (III) hexacyano chromate (III) hexaamine chromium (III) hexacyanocobalt (III)

complex cation contains $\rightarrow NH_3$ ligand (with cobalt) complex anion contains $\rightarrow NH_3$ ligand (with chromium) complex anion contains $\rightarrow CN^-$ligand (with chromium) complex anion contains $\rightarrow CN^-$ ligand (with cobalt)

(iii) ***Linkage isomerism*** : In this case isomers differ in the mode of attachment of ligand to central metal ion and the phenomenon is called linkage isomerism.

Example : $[Co\,ONO\,(NH_3)_5]Cl_2$; $[Co\,NO_2\,(NH_3)_5]Cl_2$

Pentaamminenitritocobalt (III)

Pentaaminenitrocobalt (III) chloride

$:O-NO^-$ oxygen atom donates lone pair of electrons (nitrito) NO_2^- nitrogen atom donates lone pair of electrons (nitro)

(iv) ***Hydrate isomerism*** : Hydrate isomers have the same composition but differ in the number of water molecules present as ligands and the phenomenon is called hydrate isomerism.

Examples :(a) $[Cr(H_2O)_6]Cl_3$ hexaaquachromium (III) chloride (violet)

(b) $[Cr(H_2O)_5\,Cl\,]Cl_2.H_2O$

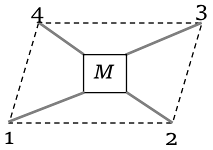
pentaaquachlorochromium (III) chloride monohydrate (blue green)

(c) $[Cr(H_2O)_4\,Cl]Cl_2.2H_2O$ tetraaquadichloro chromium (III) chloride dihydrate (green)

(2) **Stereo isomerism or space isomerism** : Here the isomers differ only in the spatial arrangement of atoms of groups about the central metal atom. It is of two types :

(i) ***Geometrical or Cis-trans isomerism*** : This isomerism arises due to the difference in geometrical arrangement of the ligands around the central atom. When identical ligands occupy positions near to each other called **cis-isomer**. When identical ligands occupy positions opposite to each other called **trans –isomer**. It is very common in disubstituted complexes with co-ordination number of 4 and 6.

- Complexes of co-ordination number 4

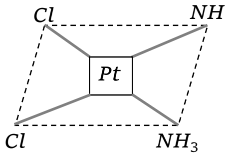


Tetrahedral geometry : In this case all the four ligands are symmetrically arranged with respect to one another as such geometrical isomerism is not possible.

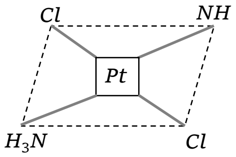
Square planar geometry : The four ligands occupy position at the four corners and the metal atom or ion is at the center and lie in the same plane.

Type : I $[Ma_2b_2]$, $M=Pt, a=Cl, b=NH_3$

Example : $[Pt\,Cl\,(NH_3)(Py)_2]$



cis –isomer (pale



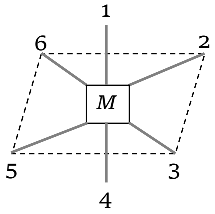
trans –isomer (dark-yellow)

Complexes of co-ordination number 6

Octahedral geometry : Here the metal atom or ion lies at the center and 1 to 6 position are occupied by the ligands.

Cis–Positions : 1–2, 2–3, 3–4, 4–5

Trans – position : 1–4, 2–5, 3–6



Type –I Ma_4b_2 , $M=Co, a=NH_3$, and $b=Cl$

Example : $[CoCl_2(\,NH_3)_4]^+$ ion

Type –II $[Ma_3b_3]$ **,** $M=Rh, a=Cl,$ and $b=Py$

Example : $[Rh\,Cl_3\,(Py)_3$

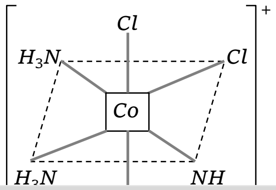
Type –III $[M(aa)_2(en)_2]^{++}$, $M=Co, a-a=$ CH_2NH_2

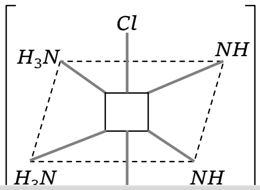
|

CH_2NH_2

(bidentate)

$b=Cl$ (monodentate)





(ii) ***Optical isomerism***

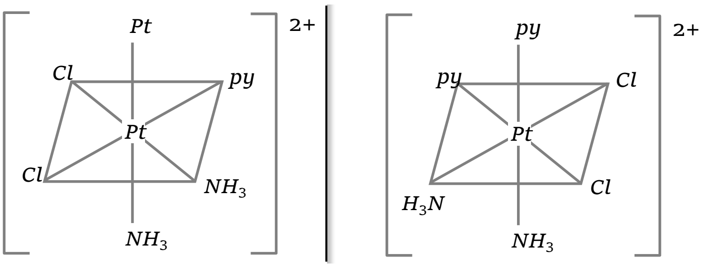
(a) Optical isomers are mirror images of each other and have chiral centers.

(b) Mirror images are not super imposable and do and have the plane of symmetry.

(c) Optical isomers have similar physical and chemical properties but differ in rotating the plane of plane polarized light.

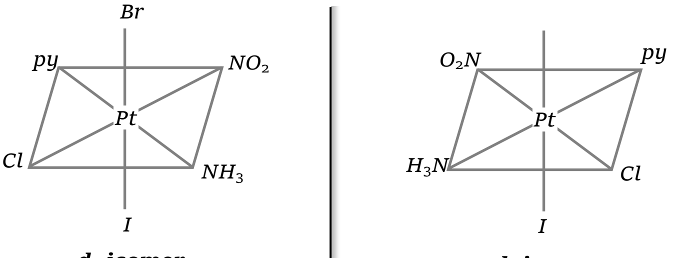
(d) Isomer which rotates the plane polarized light to the right is called dextro rotatory (*d*-form) and the isomer which rotates the plane polarized light to the left is called laevorotatory (*l*–form)

Example : $[Ma_2b_2c_2]^{n\pm}$; $[Pt(Py)_2(NH_3)_2Cl_2]^{2+}$



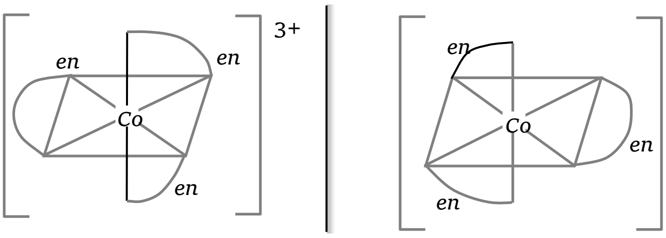
***Cis*-d- isomer** Mirror ***Cis*-l- isomer**

$[M\,a\,b\,c\,d\,e\,f]; Pt\,(py)\,NH_3\,NO_2Cl\,Br]$

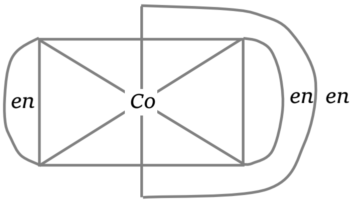


***d*- isomer** Mirror ***l*- isomer**

$[M(AA)_3]^{n\pm}; [CO(en)_3]^{3+}$

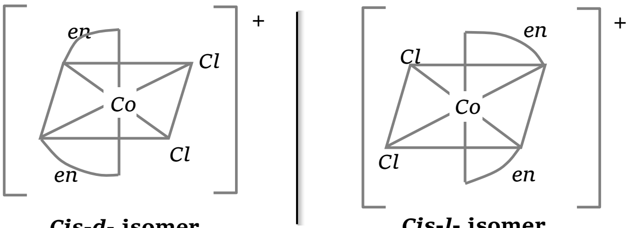


***d*- form** Mirror ***l*- isomer**



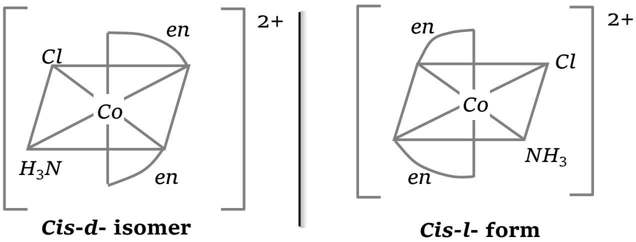
'Meso' or optically inactive form

$[M(AA)_2a_2]^{n\pm}; [Co(en)_2Cl_2]^+$



***Cis-d-* isomer** Mirror ***Cis-l-* isomer**

$[M(AA)_2ab]^{n\pm}; [Co(en)_2\,NH_3Cl]^{2+}$



***Cis-d-* isomer** Mirror ***Cis-l-* form**

Bonding in co-ordination compounds (Werner's Coordination theory)

Werner was able to explain the bonding in complex.

Primary valency (Pv) : This is non- directional and ionizable. In fact it is the positive charge on the metal ion.

Secondary valency (Sv) : This is directional and non- ionizable. It is equal to the number of ligand atoms co-ordinated to the metal (co-ordination number). Example :

$[Co\,(NH_3)_6]Cl_3$	or	$Co(NH_3)_6]^{3+}\,3Cl^-$
$Pv \rightarrow 3Cl^-\,[3]$	Sv	$\rightarrow 6\,NH_3(6)$
$[Co(NH_3)_5\,Cl]Cl_2$	or	$[Co(NH_3)_5\,Cl]^{2+}2Cl^-$
$Pv \rightarrow 2Cl^-(2)$	Sv	$\rightarrow 5\,NH_3 + 1Cl^-(6)$
$[Co(NH_3)_4\,Cl_2]\,Cl$	or	$[Co(NH_3)_4\,Cl_2]^+\;Cl^-$

$Pv \rightarrow Cl^-(1)$ Sv $\rightarrow 4NH_3 + 2Cl^-(6)$

Nature of the complex can be understood by treating the above complexes with excess of $AgNO_3$.

$CoCl_3.6NH_3 \rightarrow 3AgCl, [Co(NH_3)_6Cl_3$ (three chloride ion)

$CoCl_3.5NH_3 \rightarrow 2AgCl, [Co(NH_3)_5Cl_2$ (two chloride ion)

$CoCl_3.4NH_3 \rightarrow 1AgCl, [Co(NH_3)_4Cl_2$ (one chloride ion)

$CoCl_3.3NH_3 \rightarrow no\ AgCl, [Co(NH_3)_3Cl_3$ (no chloride ion)

The nature of bonding between central metal atom and ligands in the coordination sphere has been explained by the three well-known theories. These are :

(1) **Valence Bond theory of coordination compounds**

(i) The suitable number of atomic orbitals of central metal ion (*s, p, d*) hybridise to provide empty hybrid orbitals.

(ii) These hybrid orbitals accept lone pair of electrons from the ligands and are directed towards the ligand positions according to the geometry of the complex.

(iii) When inner *d*-orbitals *i.e.* (*n*-1) *d* orbitals are used in hybridization, the complex is called – ***inner orbital*** or ***spin or hyperligated*** complex.

(iv) A substance which do not contain any unpaired electron is not attracted by 2 magnet. It is said to be diamagnetic. On the other hand, a substance which contains one or more unpaired electrons in the electrons in the *d*-orbitals, is attracted by a magnetic field [exception O_2 and *NO*]. It is said to be paramagnetic.

Paramagnetism can be calculated by the expression, $\mu_s = \sqrt{n(n+2)},$ where $\mu =$ magnetic moment.

s= spin only value and *n*= number of unpaired electrons.

Hence, if $n = 1, \mu_s = \sqrt{1(1+2)} = 1.73\ B.M.$, if $n = 3, \mu_s$ $= \sqrt{3(3+2)} = 3.87\ B.M.$ and so on

On the basis of value of magnetic moment, we can predict the number of unpaired electrons present in the complex. If we know the number of unpaired electrons in the metal complex, then it is possible to predict the geometry of the complex species.

(v) There are two types of ligands namely strong field and weak field ligands. A strong field ligand is capable of forcing the electrons of the metal atom/ion to pair up (if required). Pairing is done only to the extent which is required to cause the hybridization possible for that co-ordination number. A weak field ligand is incapable of making the electrons of the metal atom/ ion to pair up.

Strong field ligands : $CN^-, CO, en, NH_3, H_2O, NO^-, Py$.

Weak field ligands :

$I^-, Br^-, Cl^-, F^-, NO_3^-, OH^-, C_2O_4^{2-}, NH_3, H_2O$.

Limitations of valence bond theory

The valence bond theory was fairly successful in explaining qualitatively the geometry and magnetic behaviour of the complexes. But, it could not explain the following :

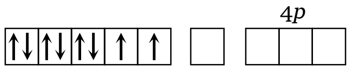
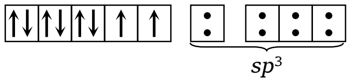
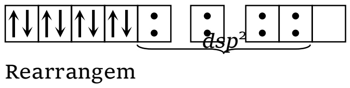
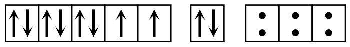
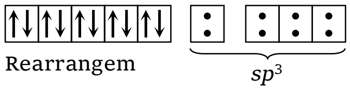
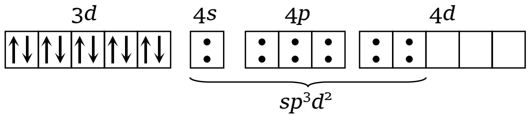
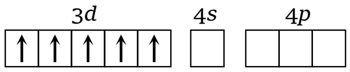
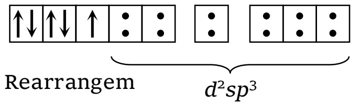
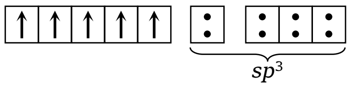
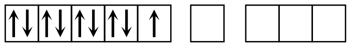
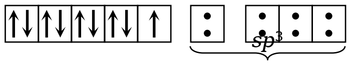
(i) The origin of their absorption spectra could not be explained.

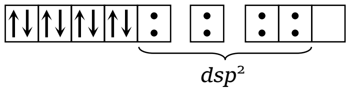
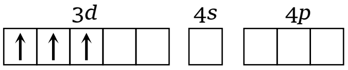
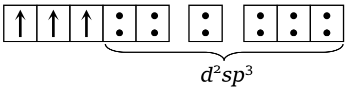
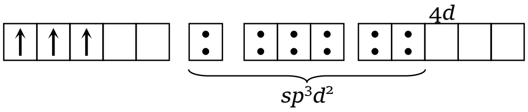
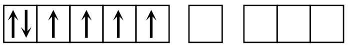
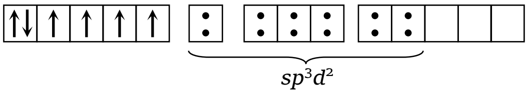
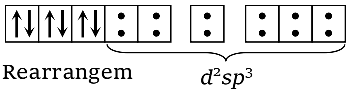
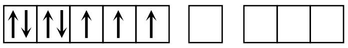
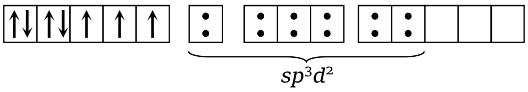
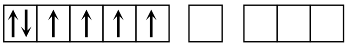
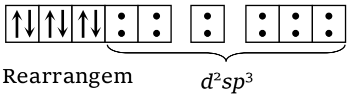
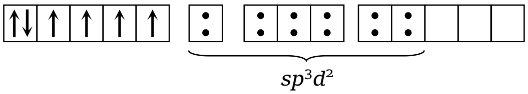
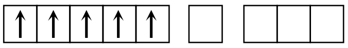
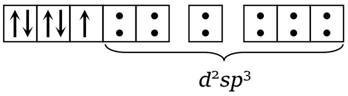
(ii) Why did different complexes of the same metal show different colours.

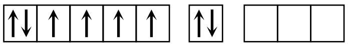
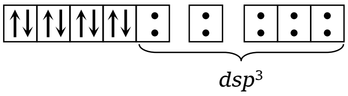
(iii) Relative stabilities of different complexes could not be explained.

(iv) Why should certain ligands form high spin, while others low spin complexes.

Table : 20.6 Geometry and magnetic nature of some complexes

Atom/ion/ complex (1)	**Configuration (2)**	**Oxidation state of metal (3)**	**Type of hybridization (4)**	**Geometry shape (5)**	**No. of unpaired electrons (6)**	**Magnetic nature (7)**
$Ni^{2+}(d^8)$		+2			2	Paramagnetic
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2+}$		+2	dsp^2	Square planar	0	Diamagnetic
Ni		0			2	Paramagnetic
$Ni(CO)_4$		0	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(NH_3)_6]^{2+}$		+2	sp^3d^2 (outer)	Octahedral	2	Paramagnetic
$Mn^{2+}(d^5)$		+2			5	Paramagnetic
$[Mn(CN)_6]^{4-}$		+2	d^2sp^3 (Inner)	Octahedral	1	Paramagnetic
$[MnCl_4]^2$		+2	sp^3	Tetrahedral	5	Paramagnetic
$Cu^{2+}(d^9)$		+2			1	Paramagnetic
$[CuCl_4]^{2-}$		+2	sp^3	Tetrahedral	1	Paramagnetic

$[Cu(NH_3)_4]^{2+}$	 One electron is shifted from $3d$-to $4p$-orbital	+2	dsp^2	Square planar	1	Paramagnetic
(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**
$Cr^{3+}(d^3)$		+3			3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$		+3	d^2sp^3 (Inner)	Octahedral	3	Paramagnetic
$[Cr(H_2O)_6]^{3+}$		+3	sp^3d^2 (Outer)	Octahedral	3	Paramagnetic
$CO^{3+}(d^6)$		+3			4	Paramagnetic
$[CoF_6]^{3-}$		+3	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$		+3	d^2sp^3 (Inner)	Octahedral	0	Diamagnetic
$CO^{2+}(d^7)$		+2			3	Paramagnetic
$[Co(H_2O)_6]^{2+}$		+2	sp^3d^2 (Outer)	Octahedral	3	Paramagnetic
$Fe^{2+}(d^6)$		+2			4	Paramagnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3 (Inner)	Octahedral	0	Diamagnetic
$[Fe(H_2O)_6]^{2+}$		+2	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
$[Fe(NH_3)_6]^{2+}$	Same	+2	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
$Fe^{3+}(d^5)$		+3		Octahedral	5	Paramagnetic
$[Fe(CN)_6^{3-}$		+3	d^2sp^3 (Inner)		1	Paramagnetic

Fe		0			4	Paramagnetic
$Fe(CO)_5$		0	dsp^3 (Inner)	Trigonal bipyramidal	0	Diamagnetic

(2) **Ligand field theory :** According to this theory when the ligands come closer to metal atom or ion, a field is created. This field tends to **split** the **degenerate *d*-orbitals** of the metal atom into **different energy levels**. The nature and number of ligands determine the extent of splitting. Energy gap between the splitted energy levels determine the magnetic (paramagnetic or diamagnetic) and spectral properties (colour etc) of the complexes .

Stability of co-ordination in solution and Spectrochemical series

Stronger is the metal-ligand bond, less is the dissociation in the solution and hence greater is the stability of a coordination compounds.

Instability constant for the complex ion $[Cu(NH_3)_4]^{2+}$ i.e.

$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$, is given by the expression; $K_i = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4]^{2+}}$.

Stability constant of the above complex i.e.

$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)]^{2+}$ is given as under ;

$$K = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{1}{K,}$$

Greater is the stability constant, stronger is the metal – ligand bond

Factors affecting the stability of complex ion

(1) **Nature of central metal ion :** The higher the charge density on the central metal ion the greater is the stability of the complex

For example, the stability constant of $[Fe(CN)_6]^{3-}$ is much greater than the stability constant of $[Fe(CN)_6]^{4-}$.

$$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}; K = 1.8\times10^6$$

$$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}; K = 1.2\times10^{31}$$

Effective atomic number (EAN) or Sidgwick theory : In order to the stability of the complexes sidgwick proposed effective atomic number. EAN generally coincides with the atomic number of next noble gas in some cases. EAN is calculated by the following relation :

EAN = Atomic no. of the metal $-e^-$ lost in ion formation +No. of e^- gained from the donor atom of the ligands.

EAN = Atomic number – Oxidation number + co-ordination no. × 2

Table : 20.7

Complex	**Metal oxidation state**	**At. No. of metal**	**Coordination number**	**Effective atomic number**
$K_4[Fe(CN)_6]$	+ 2	26	6	(26 – 2) + (6 × 2) = 36 [Kr]
$[Cu(NH_3)_4]SO_4$	+ 2	29	4	(29 – 2) + (4 × 2) = 35
$[Co(CH_3)_6]Cl_3$	+ 3	27	6	(27 – 3) + (6 × 2) = 36 [Kr]
$Ni(CO)_4$	0	28	4	(28 – 0) + (4 × 2) = 36 [Kr]
$K_2[Ni(CN)_4]$	+ 2	28	4	(28 – 2) + (4 × 2) = 34
$K_3[Cr(C_2O_4)_3]$	+ 3	24	6	(24 – 3) + (6 × 2) = 33
$K_3[Fe(CN)_6]$	+ 3	26	6	(26 – 3) + (6 × 2) = 35
$[Ag(NH_3)_2]Cl$	+ 1	47	2	(47 – 1) + (2 × 2) = 50

(2) **Nature of ligand :** Greater the base strength is the ease with which it can donate its lone pair of electrons and therefore, greater is the stability of the complex formed by it.

For example : $[Cu(NH_3)_4]^{2+}; K = 4.5\times10^{11}$; $[Cu(CN)_4]^{2-}; K = 2.0\times10^{27}$

(3) **Presence of chelate ring :** Chelating ligands form more stable complex as compared to monodentate ligands. For example : $Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}; K = 6 \times 10^8$; $Ni^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+}; K = 4 \times 10^8$

Spectro chemical series : Ligands can be arranged in increasing order of their strength (ability to cause crystal field splitting) and the series so obtained is called as spectro chemical series.

$$I^- < Br^- < Cl^- < F^- < OH^- < OX^{2-} < H_2O$$

$$< Py < NH_3 < en < NO_2^- < CN^- < CO$$

Ligands arranged left to NH_3 are generally regarded as *weaker ligands which can not cause forcible pairing of electrons within 3d level and thus form outer orbital octahedral complexes.*

On the other hand NH_3 and all ligands lying right to it are *stronger ligands which form inner orbital octahedral complexes after forcible pairing of electrons within 3d level.*

Preparation and Application of coordination compounds

(1) **Preparation :** Coordination compounds are generally prepared by the application of the following methods,

(i) ***Ligand substitution reaction :*** A reaction involving the replacement of the ligands attached to the central metal ion in the complex by other ligands is called a ligand substitution reaction.

$$\underset{\text{Light blue}}{[Cu(H_2O)_4]^{2+}{}_{(aq)}} + 3NH_{3(aq))} \rightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}{}_{(aq)}} + 4H_2O(l)$$

(ii) ***Direct mixing of reagent :***

$$PtCl_2 + 2\underset{(en)}{H_2N - CH_2 - CH_2 - NH_2} \rightarrow \underset{\text{(Dichloro bis ethylene diammine platinum (II)}}{[Pt(en)_2Cl_2]}$$

(iii) ***Redox reactions :*** In these reactions, either oxidation or reduction is involved

$$2CO(NO_3)_2 + 8NH_3 + 2NH_4NO_3 + H_2O_2$$

$$\underset{\text{Penta ammine nitrocobalt (II)nitrate.}}{2[CO(NH_3)NO_2](NO_3)_2} + 2H_2O$$

Application

(1) Estimation of hardness in water, as Ca^{++} and Mg^{2+} ions form complexes with EDTA.

(2) Animal and plant world *e.g.* chlorophyll is a complex of Mg^{2+} and haemoglobin is a complex of Fe^{2+} vitamin B_{12} is a complex of Co^{2+}.

(3) Electroplating of metals involves the use of complex salt as electrolytes *e.g.* $K[Ag(CN)_2]$ in silver plating.

(4) Extraction of metals *e.g.* *Ag* and *Au* are extracted from ores by dissolving in *NaCN* to form complexes.

(5) Estimation and detection of metal ions *e.g.* Ni^{2+} ion is estimated using dimethyl glyoxime.

(6) Medicines e.g. cis-platin *i.e.* cis $[PtCl_2(NH_3)_2]$ is used in treatment of cancer.

Organometallic compounds

These are the compounds in which a metal atom or a metalloid (*Ge*, *Sb*) or a non-metal atom like *B*, *Si*, *P*, etc, (less electronegative than *C*) is directly linked to a carbon atom of a hydrocarbon radical or molecule. Organometallic compounds contain at least one.

(1) Metal – Carbon bond, (2) Metalloid – Carbon bond, (3) Non metal – Carbon bond.

Example :

Compounds : C_2H_5MgBr, $(C_2H_5)_2Zn$, $C_6H_5Ti(OC_3H_7)_3$, $(CH_3)_4Si$

Organometallic bond: $Mg - C$, $Zn - C$, $Ti - C$, $Si - C$

Classification of organometallic compounds : Organometallics have been classified as :

(1) **σ–bonded organometallic compounds :** Compounds such as $RMgX, R_2Zn, R_3Pb, R_3Al, R_4Sn$ etc, contains $M - C\ \sigma -$ bond and are called **σ- bonded** organometallic compound.

(2) **π-bonded organometallic compounds :** The transition metals binds to unsaturated hydrocarbons and their derivatives using their d-orbitals. Here metal atom is bonded to ligands in such a way that donations of electrons and back acceptance by the ligand is feassible. These are called **π–orbitals** of the ligand. These are called **π–complexes**.

Examples : (i) ***$\pi -$ cyclopentadienyl – iron complex***

Ferrocene $[Fe(\eta^5 - CH_5)_2]$, Bis (cyclopentadienyl) iron (II)

It is a π bonded sandwich compound. The number of carbon atoms bonded to the metal ion is indicated by superscript on eta (η^x) i.e. η^5 in this complex.

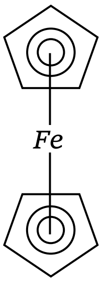
(ii) ***Dibenzene chromium ($\pi -$ complex)***

It is also a $\pi-$bonded sandwich compound. Its formula is $[Cr(\eta^6-C_6H_6)_2]$

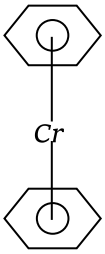
(iii) ***Alkene complex ($\pi-$complex)***

Zeise's salt K $Pt\,Cl_3(\eta^2-C_2H_4)]$; Potassium trichloroethylene platinate (IV).

It is a π bonded complex. μ^2 indicates that two carbons of ethylene are bonded to metals.



Ferrocene
$Fe(\eta^5-C_5H_5)_2$



Dibenzene chromium
$Cr(\eta^6-C_6H_6)$

(3) **Complexes containing both $\sigma-$ and $\pi-$ bonding characteristics :** Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. Metal carbonyls have been included in organometallics.

(i) ***Mononuclear carbonyls*** **:** Contain one metallic atom per molecule. *e.g* $Ni(CO)_4, Fe(CO)_5, Cr(CO)_6$

(ii) ***Polynuclear carbonyls*** **:** Contain two or more metallic atoms per molecule. *e.g.,*

$$Mn_2(CO)_{10}, Fe(CO)_9, Fe(CO)_{12}$$

Applications of organometallics

(1) Grignard reagent $(RMgX)$ has been extensively used for synthesis of various organic compounds.

(2) Wilkinson's catalyst $[(PH_3P)_3RhCl]$ *i.e.* tris (triphenylphosphine) chlororhodium (I) is used as a homogeneous catalyst for the hydrogenation of alkenes.

(3) Zeigler Natta catalyst (composed of a transition metal salt, generally $TiCl_4$ and trialkyl aluminium) are used as heterogeneous catalysts in the polymerisation of alkenes.