CO-ORDINATION CHEMISTRY

INTRODUCTION

(a) The concept of co-ordination compounds arises from the complex formation tendency of transition elements.

(b) These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B_{12} and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively.

(c) The co-ordination compounds play important role in analytical chemistry , polymerisation reactions, metallurgy and refining of metals, photography, water purification etc.

(d) Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

ADDITION COMPOUNDS

They are formed by the combination of two or more stable compounds in stoichiometric ratio.

Addition Compounds

Double salts

Coordination compounds (Complexes)

Molecular / Addition Compound :

Molecular / Addition compounds are formed when stoichiometric amounts of two or more simple compounds join together. Molecular / Addition compounds are of two types.

Double salts : Those which retain their identity in solutions are called double salts. For example.

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underset{\text{carnallite}}{KCl.MgCl_2.\,6H_2O}$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O \longrightarrow \underset{\text{potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

Complex compounds : Those which loose their identity in solution (complexes). For example.

$$CuSO_4 + 4\,NH_3 \longrightarrow \underset{\text{tetrammine copper (II) sulphate}}{CuSO_4.4\,NH_3 \text{ or } [\,Cu(NH_3)_4]SO_4}$$

$$Fe(CN_2) + 4\,KCN \longrightarrow \underset{\text{potassium ferrocyanide}}{Fe\,(CN_2).\,4KCN \text{ or } K_4[Fe(CN)_6]}$$

When crystals of carnallite are dissolved in water, the solution shows properties of K^+, Mg^{2+} and Cl^- ions. In a similar way, a solution of potassium alum shows the properties of K^+, Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state. When the other two examples of coordination compounds are dissolved they do not form simple ions, Cu^{2+} / Fe^{2+} and CN^-, but instead their complex ions are formed.

Representation of Complex Ion :

$$[ML_x]^{n\pm}$$

where M = Central Metal atom /ion (usually of d-block)
L = Ligand
x = No. of ligands
n± = charge on coordination

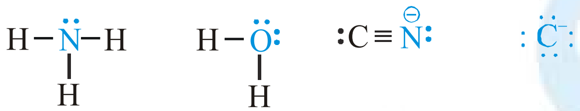
Outside region apart from coordination sphere is called ionisation sphere.

CENTRAL METAL ATOM / ION

Central ion acts as an acceptor (Lewis acid) and has to accommodate electron pairs donated by the donor atom of the ligand, it must have empty orbitals. This explains why the transition metals having empty d-orbitals form co-ordination compounds readily. Thus, in complexes $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$, Ni^{2+} and Fe^{3+} respectively are the central metal ions.

LIGANDS

Species which are directly linked with the central metal atom/ ion in a complex ion are called ligands. The ligands are attached to the central metal atom /ion through co-ordinate or dative bond free ligands have at least one lone pair.

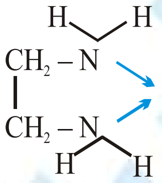


The ligands are thus Lewis bases and the central metal ions / atoms are Lewis acids.

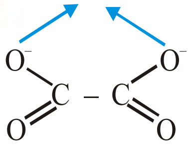
Ligands can be of **following types depending on the number of donor atoms** present in them :

(i) **Mono / Unidentate Ligands** They have one donor atom, i.e., they can donate only one electron pair to the central metal atom /ion eg., F^-, Cl^-, Br^-, H_2O, NH_3, CN^-,NO_2^-, OH^-, CO etc.

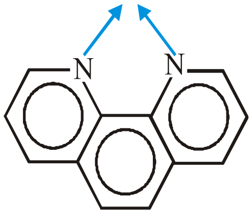
(ii) **Bidentate Ligands** Ligands which have two donor atoms and have the ability to link with the central metal atom /ion at two position are called bidentate ligands e.g.



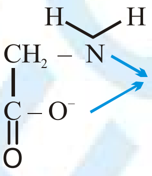
ethylenediamine (en)



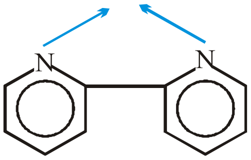
oxalate (ox)



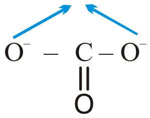
1,10-phenanthroline (phen)



glycinate (Gly)

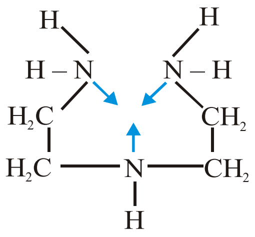


2,2-dipyridine (dipy)

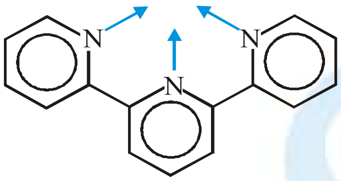


carbonate

(iii) **Tridentate Ligands** Ligands having three donor atoms are called tridentate ligands. Examples are

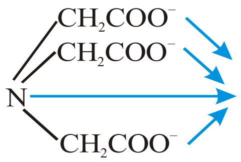


diethylene triamine (dien)

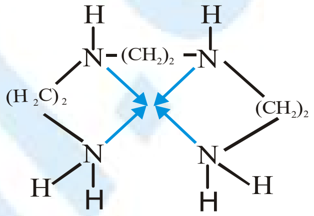


2,2'2"-terpyridine (terpy)

(iv) **Tetradentate Ligands** These ligands possess four donor atoms. Examples are

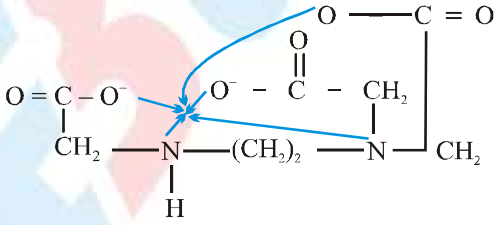


Nitriloacetate



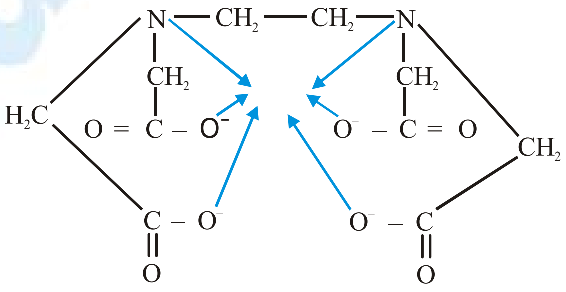
Triethylene tetramine (trien)

(v) **Pentadentate Ligands** They have five donor atoms. For example, ethylenediamine triacetate ion.



ethylendiamine triacetate ion

(vi) **Hexadentate Ligands** They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



ethylenediamine tetraacetate (EDTA)

(vii) **Ambidentate ligands :** There are certain ligands which have two or more donor atoms but in forming complexes, only one donor atom is attached to the metal / ion. Such ligands are called ambidentate ligands. Some examples of such ligands are

$M \longleftarrow NO_2^-$ $\quad$ $M \longleftarrow ONO^-$

nitrite – N $\quad$ nitrite –O

$M \longleftarrow CN^-$ $\quad$ $M \longleftarrow NC^-$

cyanide $\quad$ isocyanide

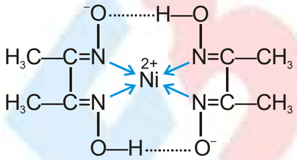
$M \longleftarrow SCN^-$ $\quad$ $M \longleftarrow NCS^-$

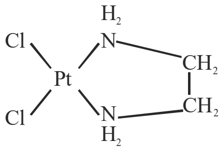
thiocyanide $\quad$ isothiocyanide

(viii) Ligands having more than two donor atoms are called polydentate or multidentate ligands. Multidentate ligands are known as a chelating ligands, it results in the formation of a stable cyclic ring thus, the complexes formed are also called chelates. Chelating ligands are usually organic compounds.

(ix) **Chelate ligand :**

Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring. The complex formed is referred to as a chelate complex and the process of chelate formation is called chelation. The number of such ligating groups is called the denticity of the ligand. Chelate rings may have any number of atoms; the most common contain five or six atoms, including the metal ion. Smaller rings have smaller angles and distances that lead to strain; larger rings frequently result in crowding both within the ring and between adjoining ligands. Some ligands can form more than one ring; ethylene diamine tetraacetate (EDTA) can form five by using the four carboxylate groups and the two amine nitrogens as given in the structures.





The chelate complexes are more stable than similar complexes containing unidentate ligands. The greater stability of the chelate complex in comparison to normal complex is called chelate effect. For example,

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) \qquad K_{formation} = 10^8$$

$$Ni^{2+}(aq) + 3\,NH_2CH_2CH_2NH_2(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) \qquad K_{formation} = 10^{18}$$

The five and six membered rings are more stable.

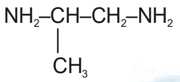
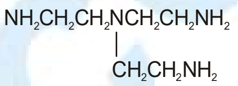
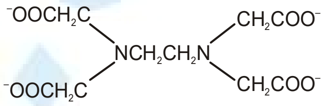
Denticity and Chelation :

Common Monodentate Ligands

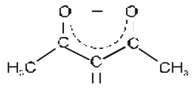
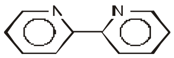
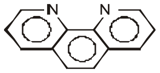
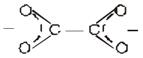
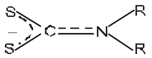
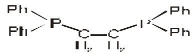
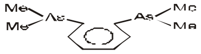
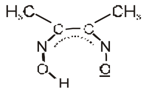
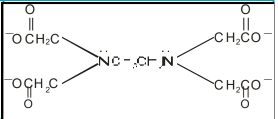
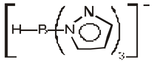
Common Name	IUPAC Name	Formula
methyl isocyanide	methylisocyanide	CH_3NC
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh_3
pyridine	pyridine	C_5H_5N (py)
ammonia	ammine	NH_3
methyl amine	methylamine	$MeNH_2$
water	aqua or aquo	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO
fluoro	fluoro or fluorido*	F^-
chloro	chloro or chlorido*	Cl^-
bromo	bromo or bromido*	Br^-
iodo	iodo or iodido*	I^-
cyano	cyanido or cyanido-C* (C-bonded)	CN^-
isocyano	isocyanido or cyanido-N* (N-bonded)	NC^-
thiocyano	thiocyanato-S(S-bonded)	SCN^-
isothiocyano	thiocyanato-N(N-bonded)	NCS^-
cyanato (cyanate)	cyanato-O (O-bonded)	OCN^-
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO^-
hydroxo	hydroxo or hydroxido*	OH^-
nitro	nitrito–N (N–bonded)	NO_2^-
nitrito	nitrito–O (O–bonded)	ONO^-
nitrate	nitrato	NO_3^-
amido	amido	NH_2^-
imido	imido	NH^{2-}
nitride	nitrido	N^{3-}
azido	azido	N_3^-
hydride	hydrido	H^-
oxide	oxido	O^{2-}
peroxide	peroxido	O_2^{2-}
superoxide	superoxido	O_2^-
acetate	acetato	CH_3COO^-
sulphate	sulphato	SO_4^{2-}
thiosulphate	thiosulphato	$S_2O_3^{2-}$
sulphite	sulphito	SO_3^{2-}
hydrogen sulphite	hydrogensulphito	HSO_3^-
sulphide	sulphido or thio	S^{2-}
hydrogen sulphide	hydrogensulphido or mercapto	HS^-
thionitrito	thionitrito	$(NOS)^-$
nitrosylium	nitrosylium or nitrosonium	NO^+
nitronium	nitronium	NO_2^+

* The 2004 IUPAC draft recommends that anionic ligands will end with-ido.

Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
bidentate	propanediamine	1,2-propanediamine	pn	 $NH_2\text{–}CH(CH_3)\text{–}CH_2\text{–}NH_2$
tridentate	diethylenetriamine	[N-(2-aminoethyl)-1 2-ethanediamine or diethylenetriamine	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
tetradenate	triethylenetetraamine	[N, N'-bis-(2-aminoethyl)-1, 2-ethanediamine or triethylenetetraamine	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	triaminotriethylamine	, , -tris(2-aminoethyl) amine.	tren	 $NH_2CH_2CH_2N(CH_2CH_2NH_2)CH_2CH_2NH_2$
pentadentate	tetraethylenepentaamine	1,4,7,10 pentaazatridecane or tetraethylenepentaamine		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
hexadentate	ethylenediaminetetraacetate	1,2–ethanediyl (dinitrilo) tetraacetate or ethylenediaminetetraacetate	EDTA	

Common Multidentate (Chelating) Ligands

Common Name	IUPAC Name	Abbreviation	Formula	Structure
acetylacetonato	2,4-pentanediono or acetylacetonato	acac	$CH_3COCHCOCH_3^-$	
2,2'-bipyridine	2,2'-bipyridyl	bipy	$C_{10}H_8N_2$	
1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen,o-phen	$C_{12}H_8N_2$	
oxalato	oxalato	ox	$C_2O_4^{2-}$	
dialkyldithiocarbamato	dialkylcarbamodithioato	dtc	$S_2CNR_2^-$	
1,2-bis(diphenylphophine)ethane	1,2-ethanediylbis (dipheylphosphene)	dppe	$Ph_2PC_2H_4PPh_2$	
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethylarsene)	diars	$C_6H_4(As(CH_3)_2)_2$	
dimethylglyoximato	butanedienedioxime or dimethylglyoximato	DMG	$HONC(CH_3)C(CH_3)NO^-$	
ethylenediaminetetraacetato	1,2-ethanediyl (dinitrilo)tetraacetato or ethylenediaminetetraacetato	EDTA	$(^-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$	
pyrazolylborato	hydrotris-(pyrazo-1-yl)borato			

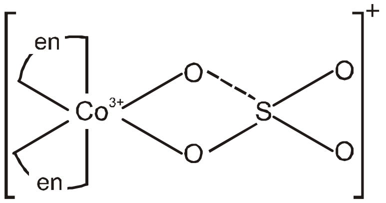
(x) Flexidentate Ligand :

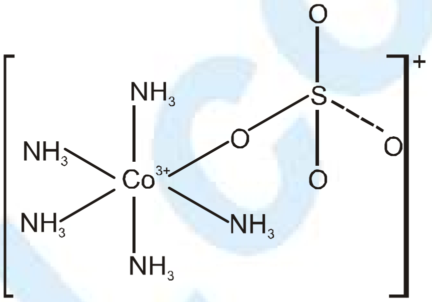
It is not necessary that all the donor items present in the polydentate ligands should form coordinate bonds with the central metal atom or ion i.e. a polydentate ligand which is found to have different denticity in different coordination compounds is called a flexidentate ligand. Note that in a particular complex denticity of a particular ligand is fixed, it can not be flexible in the same compound.

EDTA can act as **hexa, penta** as well as **tetra** dentate ligand. For example ;

EDTA usually acts as hexadentate ligand but in $[Cr(III)(OH)(EDTA)]^{2-}$ and $[Co(III)Br(EDTA)]^{2-}$ as pentadentate and in $[Pd(II)H_2(EDTA)]^0$ as a tetradentate ligand.

Sulphate ion, **SO_4^{2-}** can also be **mono** or **bi** dentate ligand. For example ;





Effective atomic number -EAN (Sidgwick Theory and EAN Rule) : Total no. of electrons present on central metal atom /ion. after accepting electron pairs from donar atom of ligands through coordinate bond is called E.A.N. of central metal atom /ion.

$$\boxed{\text{E.A.N} = Z - \text{O.S.} + 2 \times \text{C.N.}}$$

Sidgwick also suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of nearest noble gas. This total number of electrons is called effective atomic number (EAN) of the metal /ion. This will become clear by taking the example of hexamminecobalt (III) ion $[Co(NH_3)_6]^{3+}$

Atomic number of cobalt = 27

In the present complex, cobalt is present in the oxidation state of +3.

$$\therefore \quad \text{E.A.N. of } Co^{3+} = Z - \text{O.S.} + 2 \times \text{C.N.}$$
$$= 27 - 3 + 2 \times 6 = 36$$

In the above example since the number 36 corresponds to the atomic number of krypton, according to Sidgwick, the complex will be stable. Though EAN rule (which states that those complexes are stable whose EAN is the same as the atomic number of the next noble gas) is applicable in many metal carbonyl complexes, however there are several examples in which EAN rule is not obeyed.

IUPAC NOMENCLATURE OF COMPLEXES

The rules for the systematic naming of co-ordination compounds are as follows.

- The positive part is named first followed by the negative part, whether it is simple or complex.
- In naming of a complex ion, the ligands are named first in alphabetical order, followed by naming of central metal atom /ion.
- When there are several monodentate ligands of the same kind, then we normally use the prefixes di, tri tetra, penta and hexa to show the number of ligands of that type. If ligand's name already contain any of these prefix , then to avoid confusion in such cases, bis, tris and tetrakis are used instead of di, tri and tetra and name of the ligand is placed in parenthesis. For example, bis(ethylene diamine) for two en-ligands.

- Negative ligands have suffix-o, positive ligands have suffix -ium, where as neutral ligands have no specific suffix. The names of negative ligands ending with -ide are changed to ‘o’. For example,

F^-	fluoro /fluorido	H^-	hydrido	HS^-	mercapto
Cl^-	chloro /chlorido	OH^-	hydroxo/hydroxido	S^{2-}	sulphido
Br^-	bromo / bromido	O^{2-}	oxo / oxido	CN^-	cyano / Cyanido
I^-	iodo / iodido	O_2^{2-}	peroxo / Peroxido		

Ligands ending with -ate/-ite are changed to -ato/-ito. For example, SO_4^{2-} (sulphato), SO_3^{2-} (sulphito) etc. Positive groups end with -ium. For example, $NH_2 - NH_3^+$ (hydrazinium) NO^+ (nitrosonium)

- Neutral ligands have No special ending and usually common ligands are provided to neutral ligands except NH_3 (ammine) H_2O (aqua) CO (carbonyl), NO(Nitrosyl).
- The oxidation state of the central metal ion is shown by Roman numeral in brackets immediately following its name.
- Complex positive ions and neutral molecules have no special ending but complex negative ions end with ate. suffix.

Complex ions

Example	Negative complex	Positive /neutral complex
Ni	nickelate	nickel
Pb	plumbate	lead
Sn	stannate	tin
Fe	ferrate	iron

- If the complex compound contains two or more metal atoms, then it is termed as polynuclear Complex compound. The bridging ligand which link the two metal atoms together are indicated by the prefix μ–. If there are two or more bridging groups of the same kind, this is indicated by di– μ–, tri – μ– and so on. If a bridging group bridges more than two metal atoms, it is shown as μ_3, μ_4, μ_5 or μ_6 to indicate how many atoms it is bonded.
- Ambidentate ligands may be attached through different atoms. Thus, M–NO_2 is called nitro and M–ONO is called nitrito. Similarly M–SCN (thiocyanato) or M–NCS (Isothiocyanato). These may be named systematically, thiocyanato–S and thiocyanate –N respectively to indicate which atom is bonded to the metal. This convention may be extended to other cases where the mode of linkage is ambiguous.
- If any lattice component such as water or solvent of crystallisation are present, these follow their name, and are preceded by the number of these groups in Arabic numericals. These rules are illustrated by the following examples.

(a)

Complex cations	IUPAC name
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechloridocobalt(III) ion
$[CoSO_4(NH_3)_4]NO_3$	Tetraamminesulphatocobalt(III) nitrate
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrito-N-cobalt(III)
$[CoCl.CN.NO_2.(NH_3)_3]$	Triammine-chloro-cyano-nitro-N-cobalt(III)
$[Zn(NCS)_4]^{2+}$	Tetrathiocyannato-N-zinc(II) ion.
$[Cd(SCN)_4]^{2+}$	Tetrathiocyanato-S-cadmium(II) ion.

(b) Complex anions

$Li[AlH_4]$	Lithium tetrahydridoaluminate(III)
$Na[ZnCl_4]$	Sodium tetrachloridozincate(II)
$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate(II)
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanidonitrosyliumferrate(II)
$K_2[OsCl_5N]$	Potassium pentachloridonitridoosmate(VI)
$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphato)argentate(I)
$K_2[Cr(CN)_2O_2(O_2)NH_3]$	Potassium amminedicyanidodioxidoperoxidochromate(VI)

(c) Organic groups

$[Pt(py)_4]\,[PtCl_4]$	tetrapyridineplatinum(II) tetrachloridoplatinate(II)
$[Cr(en)_3]Cl_3$	d or ● Tris(ethylenediamine) chromium(III)chloride
$[CuCl_2(CH_3NH_2)_2]$	Dichloridodimethylaminecopper(II)
$Fe(C_5H_5)_2$	Bis(η^5–cyclopentadienyl)iron(II)
$[Cr(C_6H_6)_2]$	Bis(η^6-benzene)chromium(0)

(d) Bridging groups

$[(NH_3)_5Co.NH_2.Co(NH_3)_5](NO_3)_5$	μ-amidobis[pentaamminecobalt(III) nitrate
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri-μ-carbonyl-bis [tricarbonyliron(0)]
$[Be_4O(CH_3COO)_6]$	Hexa-μ- acetato(O,O')-μ_4-oxidotetraberyllium(II) (basic baryllium acetate)

(e) Hydrates

$AlK(SO_4)_2.\ 12H_2O$	Aluminium potassium sulphate 12-water

Writing the formula of a coordination compound :

When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is named first, then the coordinated groups are listed in the order : negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group).

$\boxed{\text{[M negativeligands, Neutral ligands, positive ligands]}^{n\pm}}$

ISOMERISM IN COMPLEXES

Complex compounds that have the same molecular formula but have different structural /spacial arrangements of ligands are called isomers. These are of two types, namely structural and stereo isomers.

Type of isomerism

Structural isomerism
- –Ionisation isomerism
- –Hydrate isomerism
- –Linkage isomerism
- –Coordination isomerism
- –Coordination position isomerism

Space / stereo isomerism
- –Geometrical isomerism
- –Optical isomerism

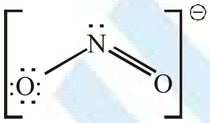
STRUCTURAL ISOMERISM

(i) **Ionisation Isomerism** This type of isomerism is due to the exchange of groups between the complex ion and ions outside it. $[Co(NH_3)_5Br]SO_4$ is red -violet. An aqueous solution of it gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[Co(NH_3)_5SO_4]Br$ is red. A solution of this complex does not give a positive sulphate test with $BaCl_2$. It does give a cream coloured precipitate of AgBr with $AgNO_3$, thus confirming the presence of free Br^- ions. Other examples of ionisation isomerism are $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ and $[Co(en)_2NO_2.Cl]SCN$, $[Co(en)_2NO_2.SCN]Cl$ and $[Co(en)_2Cl.SCN]NO_2$.

(ii) **Hydrate isomerism** These isomers arise by the exchange of groups in the complex ion with water. Three isomers of $CrCl_3.6\,H_2O$ are known. From conductivity measurements and quantitative precipitation of the ionised Cl^-, they have been given the following

$$[Cr(H_2O)_6]Cl_3$$
$$[Cr(H_2O)_5Cl]Cl_2.H_2O$$
$$[Cr(H_2O)_4Cl_2]Cl.2H_2O$$

(iii) **Linkage Isomerism** This type of isomerism arises when the ligand attached to the central metal ion of a complex in different ways. Such ligands are called ambident ligands. Nitrite ion has electron pairs available for co-ordination both on N and O atoms.

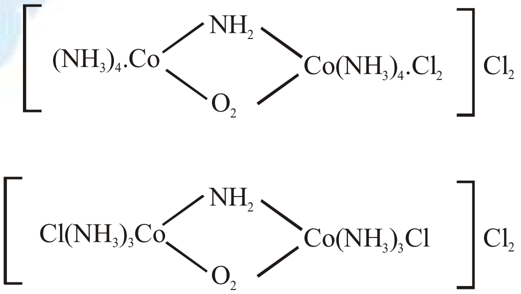


Ex.

(a)	$[Co(NH_3)_5\,ONO]Cl_2$ pentaamminenitrito-o-cobalt(III) chloride **(red)**	and	$[Co(NH_3)_5\,NO_2]\,Cl_2$ pentaamminenitrito-N-cobalt-(III)-chloride **(yellow)**
(b)	$[Mn(CO_5).SCN]^+$ pentacarbonylthiocyanto –S-manganese (II) ion	and	$[Mn(CO_5)\,(NCS]^+$ pentacarbonylthiocyanato –N-manganese (II) ion

(iv) **Co-ordination Isomerism** When both the cation and anion are complex ions, then isomerism may be caused by the interchange of ligands between the anion and cation. For example $[Pt(NH_3)_4]\,[PtCl_4]$ and $[PtCl(NH_3)_3]\,[PtCl_3(NH_3)]$. These isomers are called co-ordination isomers.

(v) **Co-ordination Position Isomerism** In polynuclear complexes, an interchange of ligands between the metal nuclei gives rise to co-ordinaton position isomerism, for example.



Co-ordination position isomers

Polymerisation Isomerism

This is not true type of isomerism because it occurs among compounds having the same empirical formula, but different molecular formula. Thus, $[Pt(NH_3)_2Cl_2]$,$[Pt(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$ all have the same empirical formula.

STEREOISOMERISM

The isomers in which atoms are bonded to each other in the same order but that differ in the arrangement of these atoms in the space are called as stereoisomers and the phenomenon as stereoisomerism.

GEOMETRICAL ISOMERISM

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

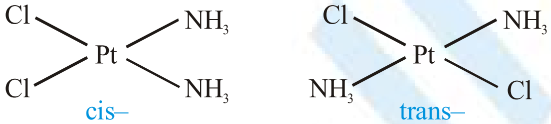
Coordination Number Four :

Tetrahedral Complex :

The tetrahedral compounds can not show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.

Square Planar Complex :

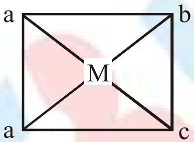
In a square planar complex of formula $[Ma_2b_2]$ [a and b are unidentate], the two ligands 'a' may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted.



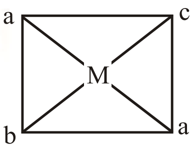
cis– trans–

Geometrical isomers (cis and trans) of $Pt(NH_3)_2Cl_2$.

Square planar complex of the type Ma_2bc (where a,b,c are unidentates) shows two geometrical isomers.

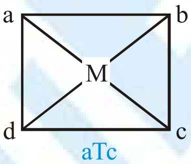


cis–

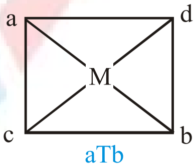


trans–

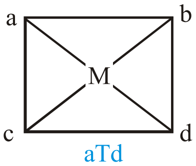
Square planar complex of the type Mabcd (where a,b,c,d are unidentates) shows three geometrical isomers.



aTc



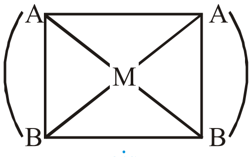
aTb



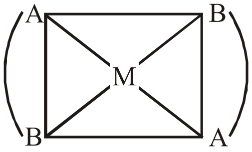
aTd

Example is $[Pt(NH_3)BrCl(py)]$. Three isomers of the complex $[Pt(NH_3)(NH_2OH)(py)(NO_2)]^+$ have been isolated and identified.

Square planar complex of the type $M(AB)_2$ (where AB are unsymmetrical bidentates) shows two geometrical isomers. Example is $[Pt(gly)_2]$ in which gly is unsymmetrical ligand.



cis–



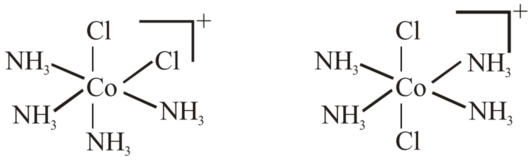
trans–

Similarly, M(AB)(CD) also shows two geometrical isomers.

Note : M(AA)$_2$, (where AA are symmetrical bidentates) does not show geometrical isomerism. e.g., $[Cu(en)_2]^{2+}$ $[Pt(ox)_2]^{2-}$, etc.

Coordination Number Six :

Geometrical isomerism is also possible in octahedral complexes.



cis– trans–

Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

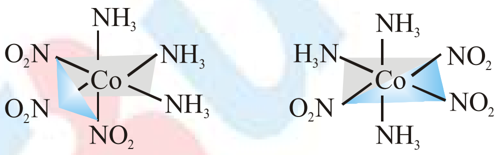
Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(I) Complexes containing only unidentate ligands

(i) Ma_2b_4	**–**	**2**	(aa)(bb)(bb) (ab)(ab)(bb)
(ii) Ma_4bc	**–**	**2**	(aa)(aa)(bc) (aa)(ab)(ac)

(iii) Ma_3b_3

Complexes of the formula Ma_3b_3, where a and b are monodentate ligands, may show two isomeric forms called fac– and mer–. Facial isomers have three identical ligands on one triangular face where as meridional isomers have three identical ligands in a plane bisecting the molecule. Similar isomers are possible with some chelating ligands.



fac– mer–

The facial(fac) and meridional(mer) isomers of $[Co(NH_3)_3(NO_2)_3]$.

Unsymmetrical bidentate ligands also show fac-mer isomerism.

(iv) Ma_3b_2c	–	3	(aa)(ab)(bc) (aa)(bb)(ac) (ab)(ab)(ac)
(v) Ma_3bcd	–	4	(aa)(ab)(cd) (aa)(ac)(bd) (aa)(ad)(bc) (ab)(ac)(ad)
(vi) $Ma_2b_2c_2$	–	5	(aa)(bb)(cc) (aa)(bc)(bc) (bb)(ac)(ac) (cc)(ab)(ab) (ab)(ac)(bc)

(vii) Ma_2b_2cd – 6

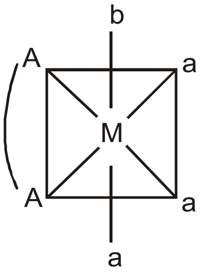
(viii) Ma_2bcde – 9

(ix) Mabcdef, $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$ – 15

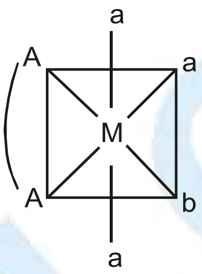
Note : **Ma_6 and Ma_5b have only one form.**

(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)a_3b$ – Two geometrical isomers are possible.

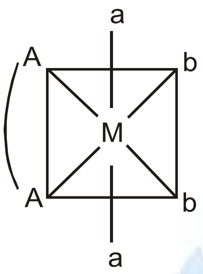


bTa

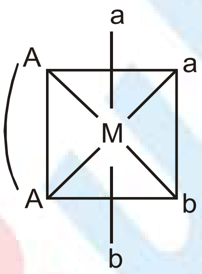


aTa

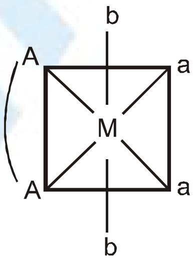
(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.



aTa



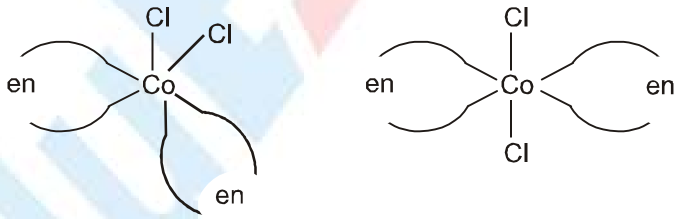
aTb



bTb

Note : With $[M(AA)b_4]$, only one form is possible. M(AA)abcd have six geometrical isomers.

(iii) $M(AA)_2a_2$ – Two geometrical isomers are possible.



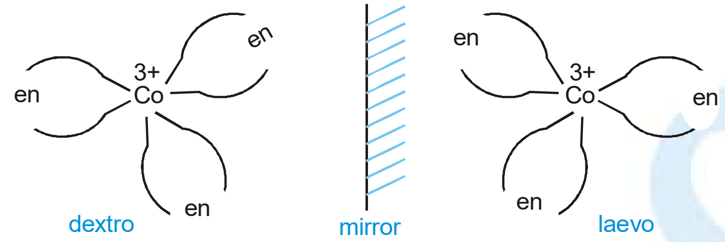
Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

OPTICAL ISOMERISM

A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. This is due to the absence of elements of symmetry in the complex. The two forms are called dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, ● to the left).

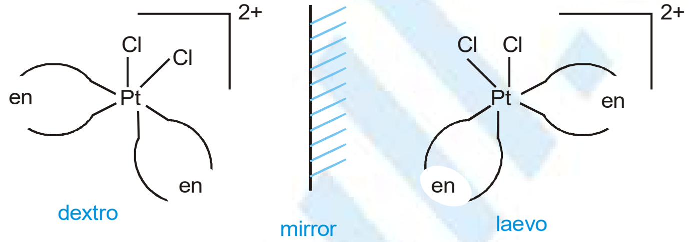
Octahedral complex :

Optical isomerism is common in octahedral complexes involving didentate ligands. For example, $[Co(en)_3]^{3+}$ has d and ● forms as given below.



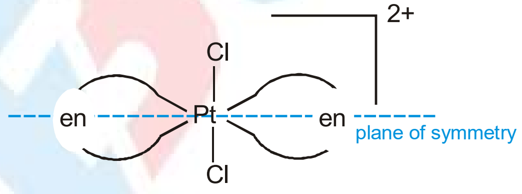
d and ● of $[Co(en)_3]^{3+}$

Cis-isomer of $[PtCl_2(en)_2]^{2+}$ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.

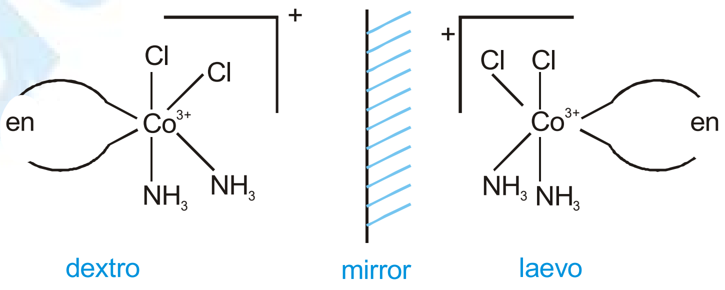


d and ● of cis-$[PtCl_2(en)_2]^{2+}$

But trans isomer of $[PtCl_2(en)_2]^{2+}$ does not show optical isomerism.

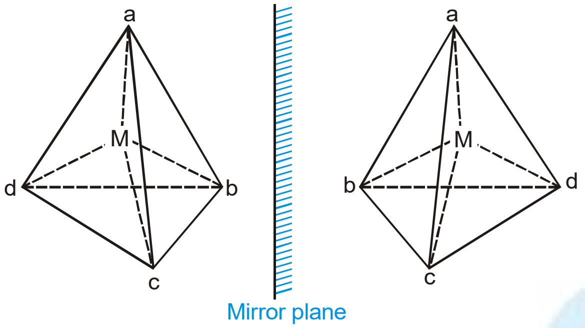


cis-$[Co(NH_3)_2Cl_2(en)]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.

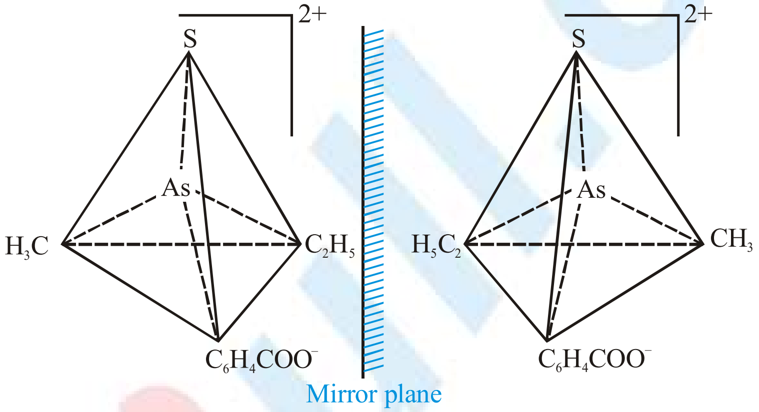


Tetrahedral complex :

Optical isomerism is expected in tetrahedral complexes of the type [Mabcd] analogous to tetrahedral carbon atom.

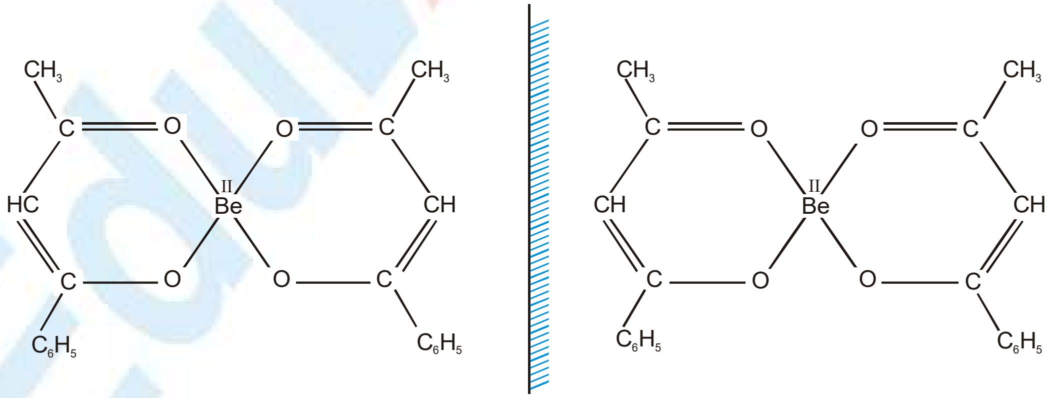


(i) For example [As**(III)**$(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$, shows optical isomerism as given below.



Here it may be noted that 4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric (i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

(ii) Tetrahedral complexes of Be, B, Cu(II) and Zn(II) with unsymmetrical bidentate ligands have been resolved into optical isomers. In order for the complex to be chiral, the chelating ligand must be unsymmetrical (not necessarily asymmetric or chiral, itself). An example is bis(benzoylacetonato) Be(II) complex, $[(C_6H_5COCHCOCH_3)_2Be]^0$ whose mirror-image isomers are shown in figure.



Here it may be noted from the figure that the complex has no centre or plane of symmetry and the two forms are not superimposable on each other. This explains the resolution of the complex into d-and ●-forms.

Square planar complex :

Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality. Although, square planar complexes seldom show optical isomerism, yet a four -coordinated complex of Pt(II), $[Pt(II)(NH_2.CH(C_6H_5).CH(C_6H_5NH_2).(NH_2.CH_2.C(CH_3)_2.NH_2)]^{2+}$ which has square-planar shape has been resolved into two forms by Mills and Quibell in 1935.

BONDING IN COMPLEXES

Werner's Co-ordination Theory :

Alfred Werner put forward his concept of secondary valency for advancing a correct explanation for the characteristics of the coordination compounds. The fundamental postulates of Werner's theory are as follows.

(i) Metal possess two types of valencies, namely, primary (principal or ionisable) valency and secondary (auxillary or non-ionisable) valency.

In modern terminology, the primary valency corresponds to oxidation number and secondary valency to coordination number. According to werner primary valencies are shown by dotted lines and secondary valencies by thick lines.

(ii) Every metal cation in complex compound has a fixed number of secondary valencies for example Pt^{4+} cation has its six secondary valency.

(iii) Primary valency is satisfied by negative ions, whereas secondary valency is satisfied either by negative ions or by neutral molecules.

(iv) Primary valency has non-directional character, where as secondary valency has directional character, there fore a complex ion has its definite geometry eg. $[Co(NH_3)_6]^{3+}$ – octahedron.

(v) It is the directional nature of secondary valency due to which co-ordination compound exhibits the phenomenon of isomerism.

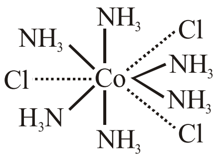
Werner's Representation of Complexes

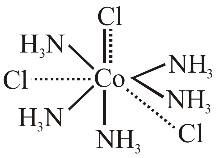
Consider the case of $CoCl_3.xNH_3$ where primary valency = +3 and secondary valency = 6.

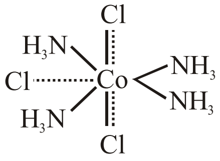
Various structures are summarised in Table.

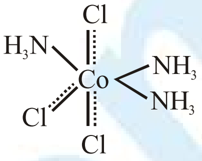
	Werner complexes	Modern formula	Ionisation	Secondary valency satisfied by	Primary valency staisfied by
(A)	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^-$	six (NH_3)	three (Cl^-)
(B)	$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+}+2Cl^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
(C)	$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^{+}+Cl^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
(D)	$CoCl_3.3NH_5$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3]Cl_3$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

- From Table , It is clear that conduction of the complexes will be in the order D < C < B < A.
- They are represented as


(A)


(B)


(C)


(D)

VALENCE BOND THEORY

It was developed by Pauling. The salient features of the theory are summarised below :

(i) Under the influence of a strong field ligands, the electrons of central metal ion can be forced to pair up against the Hund's rule of maximum multiplicity.

(ii) Under the influence of weak field ligands, electronic configuration of central metal atom / ion remains same.

(iii) If the complex contains unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons, then it is diamagnetic in nature and magnetic moment is calculated by spin only formula.

Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

where n is the number of unpaired electrons in the metal ion.

Relation between unpaired electrons and magnetic moment

Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

Thus, the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

(iv) When ligands are arranged in increasing order of their splitting power then an experimentally determined series is obtained named as spectrochemical series.

$$\underbrace{I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < EtOH < CH_3COO^- \approx C_2O_4^{2-} < H_2O}_{\text{Weak field ligands}}$$

$$< \underbrace{EDTA < NH_3 \approx py < en < dipy < phen < NO_2^-\ CN^- < CO}_{\text{Strong field ligands}}$$

(v) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the co-ordination number of the metal ion for a particular complex.

(vi) The atomic orbital (s, p or d) of the metal ion hybridise to form hybrid orbitals with definite directional properties. These hybrid orbitals now accept e^- pairs from ligands to form coordination bonds.

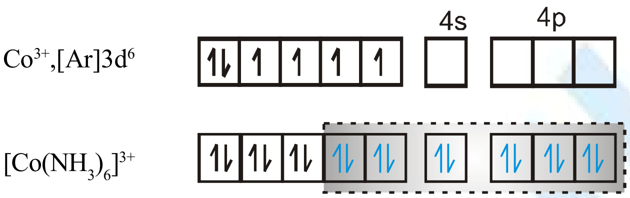
(vii) The d-orbitals involved in the hybridisation may be either inner (n – 1) d orbitals or outer n d-orbitals. The complexes formed in these two ways are referred to as inner orbital complexes and outer orbital complexes, respectively. Following table provides the types of hybridisation with different coordination number.

Coordination number of metal	Type of hybridisation	Shape of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planer
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

It is to be noted that the type of hybridisation of metal and shape of complex involved can be predicted conveniently, if some characteristic of the complex like magnetic nature, geometry or whether exhibits isomerism or not, etc., be known.

Coordination Number Six.

In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.

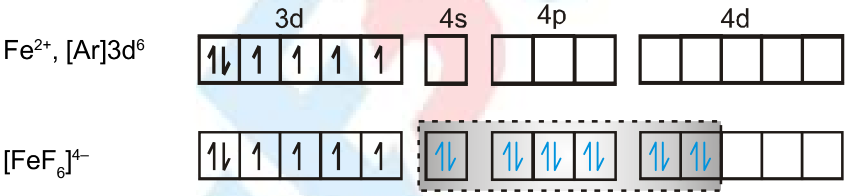


(inner orbital or
low spin complex)

d^2sp^3 hybrid orbital
Six pairs of electrons from six NH_3 molecules.

Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. Since in the formation of complex the inner d-orbital (3d) is used in hybridisation, the complex is called an inner orbital or low spin or spin paired complex.

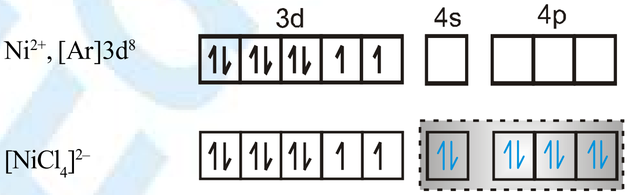
The complex $[FeF_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So,



sp^3d^2 hybrid orbitals
Six pairs of electrons from six F^- ions.

Coordination Number Four :

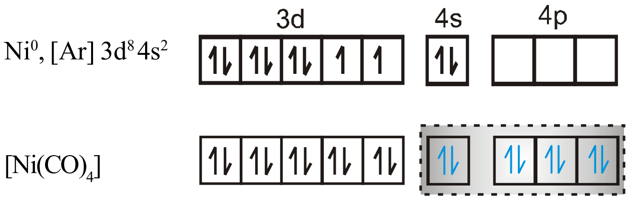
In the paramagnetic and tetrahedral complex $[NiCl_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.



sp^3 hybrid orbitals
Four pairs of electrons from four Cl^- ions.

The compound is paramagnetic since it contains two unpaired electrons.

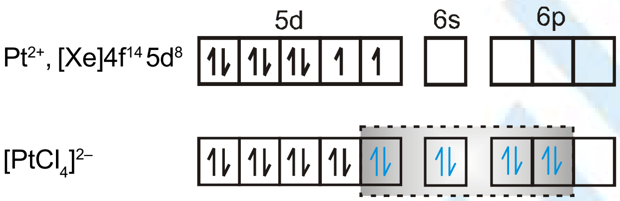
Similarly complex $[Ni(CO)_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.



sp^3 hybrid orbitals

Four pairs of electrons from four CO molecules.

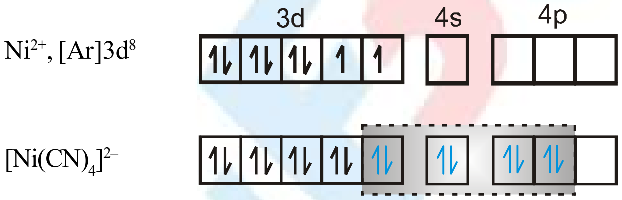
Complexes of Pd(II) and Pt (II) are usually four-coordinate, square planar, and diamagnetic and this arrangement is often found for Ni(II) complexes as well, e.g., in $[Ni(CN)_4]^{2-}$ (here nickel is in +2 oxidation state and has electronic configuration $3d^8$). In as much as the free ion is in the ground state each case is paramagnetic, the bonding picture has to include pairing of electrons as well as ligand-metal-ligand bond angles of 90º and this occurs via hybridisation of one (n–1) d, one ns and two np orbitals to form four equivalent dsp^2 hybrid orbitals directed toward the corners of a square. These orbitals then participate in covalent coordinate σ bonds with the ligands, the bonding electron pairs being furnished by the ligands. The hybridisation scheme for $[PtCl_4]^{2-}$ is as shown in figure.



dsp^2 hybrid orbitals

Four pairs of electrons from four Cl^- ions.

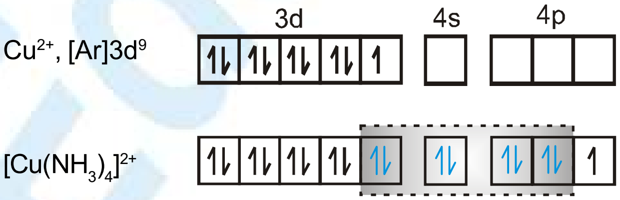
Similarly the hybridisation scheme for $[Ni(CN)_4]^{2-}$ is as shown in figure.



dsp^2 hybrid orbitals

Four pairs of electrons from four CN^- ions.

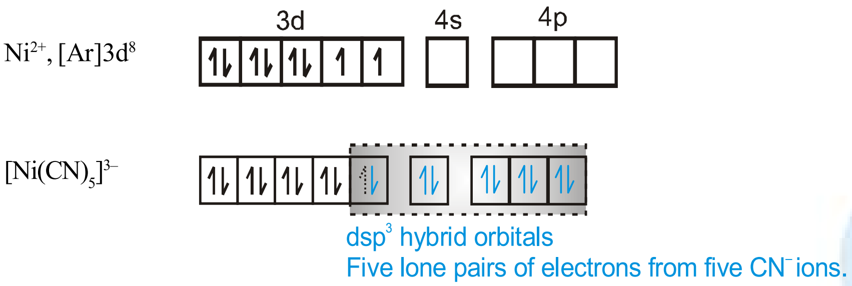
It is found that $[Cu(NH_3)_4]^{2+}$ is square planar and paramagnetic with one unpaired electron in 4p-orbital. The hybridisation scheme is as follow.

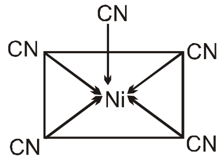


dsp^2 hybrid orbitals

Four pairs of electrons from four NH_3 molecules.

Note. $[Ni(CN)_5]^{3-}$ is found to be diamagnetic with 2 types of Ni – C bond lengths, out of which four bond lengths are found to be equal and the fifth one is different. The hybridisation scheme for $[Ni(CN)_5]^{3-}$ is as shown in figure.





square pyramidal.

While the valence bond theory, to a large extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following **shortcomings** :

1. A number of assumptions are involved.
2. There is no quantitative interpretation of magnetic data.
3. It has nothing to say about the spectral (colour) properties of coordination compounds.
4. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
5. It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
6. It does not distinguish between strong and weak ligands.

CRYSTAL FIELD THEORY (CFT) :

Crystal field theory is now much more widely accepted than the valence bond theory. It is assumed that the attraction between the central metal and ligands in a complex is purely electrostatic. The transition metal which forms the central atom cation in the complex is regarded as a positive ion of charge equal to the oxidation state. It is surrounded by negative ligands or neutral molecules which have a lone pair of electrons If the ligand is a neutral molecule such as NH_3, the negative end of the dipole in the molecule is directed toward the metal cation. The electrons on the central metal are under repulsive forces from those on the ligands. Thus, the electrons occupy the d orbital remain away from the direction of approach of ligands.

In the crystal field theory, the following assumptions are made.

(i) Ligands are treated as point charges.

(ii) There is no interaction between metal orbitals and ligands orbitals.

(iii) All the d orbitals on the metal have the same energy (that, is degenerate) in the free atom. However, when a complex, is formed, the ligands destroy the degeneracy of these orbitals, that is , the orbitals now have different energies. In an isolated gaseous metal ion, all five d orbitals have the same energy and are termed degenerate. If a spherically symmetrical field of ligands surrounds the metal ion, the d orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field of ligands and electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both these cases, the field produced by the ligands is not spherically symmetrical. Thus, the d orbitals are not all affected equally by the ligand field.

In the an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The direction x, y and z point to three adjacent corners of the octahedron as shown fig.

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x,y and z. The lobes of the t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}) point in between the axes. If follows that the approach of six ligands along the x,y,z, –x, –y, and –z directions will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals (which point along the axes) than it increases the energy of the dxy, dxz and dyz orbitals (which points between the axes). Thus, under the influence of an octahedral ligand field the d orbitals split into two groups of different energies.

Rather than referring to the energy level of a isolated metal atom. The difference in energy between the two d levels is given by the symbols Δ_0 or 10 Dq.

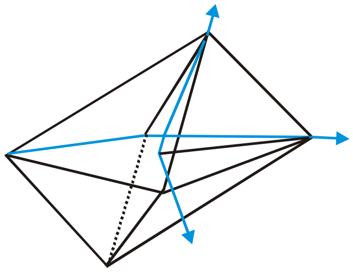
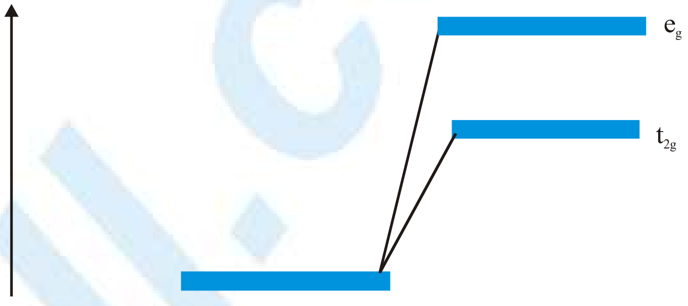


Fig. The directions in an octahedral complex



Free metal ion
(five degenerate d orbitals)
Fig Crystal field spliting of energy levels in an octahedral field

metal ion in
octahedral field

It follows that the e_g orbitals are $+0.6\ \Delta_0$ above the average level, and the t_{2g} orbitals $-0.4\ \Delta_0$ below the average level.

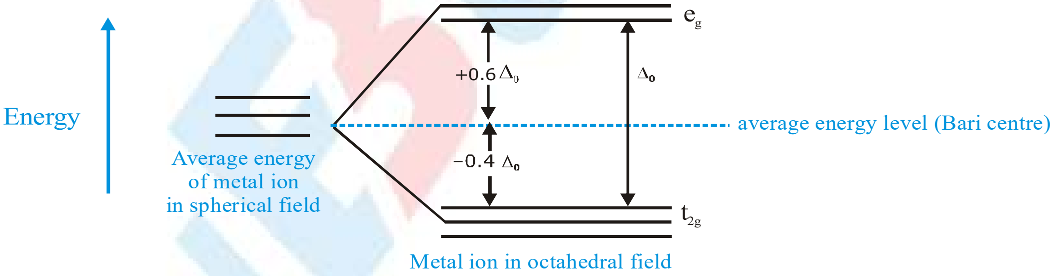
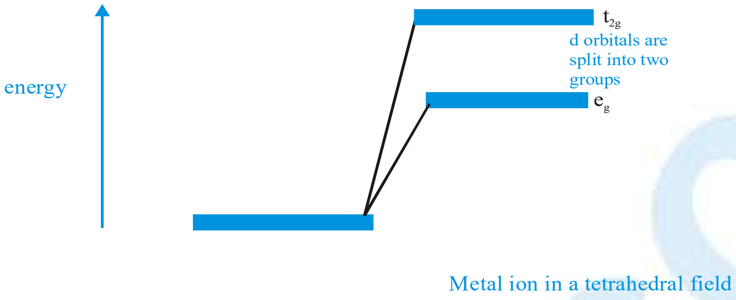


Fig. Diagram of the energy levels of d -orbitals in a octahedralfield

Tetrahedral Complexes A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Fig. The direction x,y and z point to the centres of the faces of the cube. The e_g orbitals point along x,y and z (that is , to centres of the faces.)

Fig. Relation of tetrahedron to a cube

The approach of the ligands raised the energy of both sets of orbitals. The energy of the t_{2g} orbital raised most because they are closest to the ligands. This crystals field splitting is opposite to that in octahedral complexes. The t_{2g} orbitals are 0.4 Δ_t above the average energy of the two groups (the Bari centre) and the e_g orbitals are 0.6 Δ_t below the average level.



Free metal ion
(five degenerate d orbitals)
Fig Crystal field splitting of energy levels in a tetrahedral field

Stability of complexes

A co-ordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex, ML_n (M = central metal cation, L = monodentate ligand and n=co-ordination number of metal ion) supposed to take place by the following n consecutive steps.

$$M + L \rightleftharpoons ML;\ K_1 = \frac{[ML]}{[M][L]}$$

$$M + L \rightleftharpoons ML_2;\ K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3;\ K_3 = \frac{[ML_3]}{[ML_2][L]}$$

……………………………………………………………

……………………………………………………………

$$ML_{n-1} + L \rightleftharpoons ML_n;\ K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

K_1, K_2, K_3........K_n are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n. The overall stability constant K is given as

$$M + nL \rightleftharpoons ML_n;$$

$$K = K_1K_2K_3....K_n = \frac{[ML_n]}{[M][L]^n}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively, 1/K values called instability constant explain the dissociation of the complex into metal ion and ligands in the solution. The value of the stability constant for some of the complexes are given in Table.

Stability constants of complexes

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$[Ag(NH_3)_2]^{+}$	1.6×10^{7}
$[Co(NH_3)_6]^{2+}$	1.12×10^{6}
$[Co(NH_3)_6]^{+}$	5.0×10^{33}
$[AgCl_2]^{-}$	1.11×10^{5}
$[AgBr_2]^{-}$	1.28×10^{7}
$[Ag(CN)_2]^{-}$	1.0×10^{22}
$[Cu(CN)_4]^{2-}$	2.0×10^{27}
$[Fe(CN)_6]^{3-}$	7.69×10^{43}

COLOUR IN COORDINATION COMPOUNDS

Coordination compounds of transition metals have fascinating colours. According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black. The mechanism of light absorption in coordination compounds is that photons of appropriate energy can excite the coordination entity from its ground state to an excited state. Consider the Ti(III) ion in solution, that is $[Ti(H_2O)_6]^{3+}$. This is a violet colour octahedral complex, where in the ground state of the complex a single electron is present in t_{2g} level. The next higher state available for the transition is the empty e_g level. If the light corresponding to the energy of yellow-green is absorbed by the complex, it would excite the electron from t_{2g} level to e_g level. Consequently the complex appears violet in colour. In case of copper (II) ions in solution, for example, it can be imagined that one of the d-electrons from the t_{2g} set (d_{xy}, d_{yz}, d_{xz} orbitals) gets excited to the e_g set ($d_{x^2-y^2}$, d_{z^2} orbitals). In this case since high energy light is transmitted it means that low energy light (red region) is absorbed. For copper (II) ions in aqueous solution, the energy gap Δ_t is relatively small. Table below gives the relationship of the wavelength of light absorbed and the colour observed.

Relationship between the wavelength of light absorbed and the colour observed In some coordination entitles

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Purple

Note : **(a)** In absence of ligand, crystal field splitting does not occur and as a consequence the substance appears colourless. For example ; (i) removal of water from violet coloured complex $[Ti(H_2O)_6]Cl_3$ on heating makes it colourless, (ii) similarly anhydrous copper sulphate ($CuSO_4$) is white, but hydrated copper sulphate ($CuSO_4.5H_2O$) is blue coloured.

(b) The nature of the ligand and the molar ratio of metal : ligands also influence the colour of the complex. For example ; in the pale green complex of $[Ni(H_2O)_6]$, the colour change is observed when ethylenediamine is progressively added to it.

Molar ratio of en : Ni	Coloured observed
1 : 1	Pale blue
2 : 1	Blue/Purple
3 : 1	Violet

Note : Ruby is Al_2O_3 in which 0.5–1% Cr^{3+} ions (d^3 electron system) are randomly distributed in the positions normally occupied by Al^{3+}. We may consider Cr(III) species as octahedral Cr(III) complexes incorporated into the alumina lattice ; d-d transition of electron at these centres/points give rise to the colour (red).

Emerland is the mineral beryl ($Be_3Al_2Si_6O_{18}$) in which Cr^{3+} ions occupy octahedral sites, but in this case low energy corresponding to yellow red and blue is absorbed and light corresponding to green region is transmitted.

FACTORS AFFECTING STABILITY OF COMPLEX COMPOUNDS

(i) The values of stability constant differ widely depending on the nature of the metal ion and the ligand In general higher the charge density on the central ion. The greater the stability of its complexes.

(ii) the more basic a ligands, the greater is the ease with which it can donate its lone pairs of electrons and therefore, greater is the stability of the complexes formed by it.

Ex. The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that NH_3 and CN^- are strong Lewis bases.

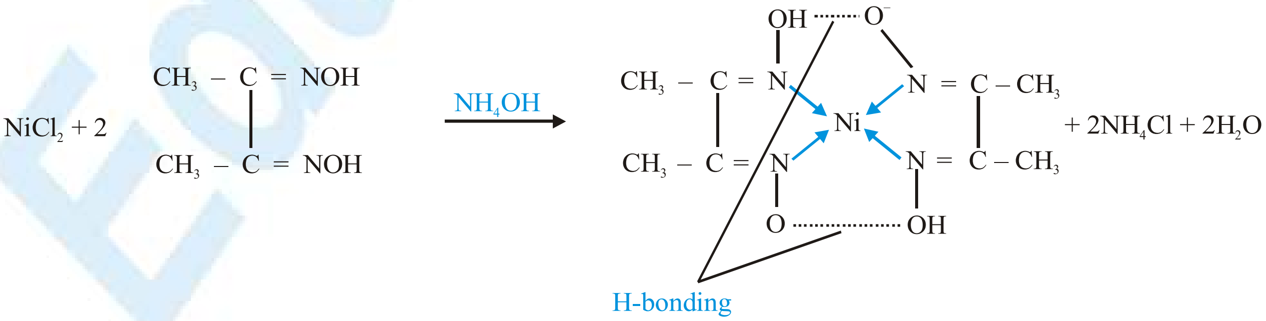
(iii) The higher the oxidation state of the metal, the more stable is the complex. The charge density of Co^{3+} ion is more than Co^{2+} ion and thus, $[Co(NH_3)_6]^{3+}$ is more stable than $[Co(NH_3)_6]^{2+}$. Similarly, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$.

(iv) Chelating ligands form more stable complexes as compared to mondentate ligands.

APPLICATION OF COMPLEXES

The complexes are of immense importance on account of their applications in various fields. During complex formation there are drastic changes in the properties of metal atom/ion these changes in properties are made use of in the application of metal complexes.

(i) The detection and estimation of Ni^{2+} is based on the formation of a scarlet red complex with dimethyl glyoxime.



(a) Fe^{3+} is detected by formation of a blood red coloured complex with KSCN.

$$Fe^{3+} + 3KSCN \longrightarrow \underset{\text{blood red colour}}{Fe(SCN)_3} + 3K^{+}$$

or

$$[Fe(H_2O)_5(SCN)]^{2+}$$

(b) Many ligands (organic reagents) are used for the gravimetric estimation of number of metal ions.

Metal ion to be estimated	Cu^{2+}	Ni^{2+}	Fe^{3+}	Al^{3-}	Co^{2+}
Organic reagents used	Benzoin oxime	Dimethyl glyoxime	1,20-phena-nthroline	8-hydroxy quinoline	α-nitroso β-naphthol

(c) EDTA is used as a compelexing agent in volumeter analysis of metal ions like Ca^{2+}, Mg^{2+} and Zn^{2+}.

(d) The co-ordination compounds of the transition metals exhibit a variety of colours. This property is utilised in colorimetric analysis for the estimation of many metals.

(ii)

(a) Metallurgical process : Silver and gold are extracted by the use of complex formation. Silver ore is treated with sodium cyanide solution with continuous passing of air through the solution. Silver dissolves as a cyanide complex and silver is precipitated by the addition of scrap zinc.

$$\underset{\text{argentine}}{Ag_2S + 4NaCN} \xrightleftharpoons{\text{Air}} \underset{\text{sodium argentocyanide}}{2N[Ag(CN)_2] + NaS} \xrightarrow{O_2(\text{Air})} Na_2SO_4 + S$$

$$2Na[Ag(CN)_2] + Zn \xrightleftharpoons{\text{Air}} \underset{\text{sodium tetracyanozincate(II)}}{Na_2[Zn(CN)_4]} + 2Ag$$

(b) Native Gold and Silver also dissolve in NaCN solution in presence of the oxygen (air).

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 3Na[Ag(CN)_2] + 3NaOH$$

Silver and Gold are precipitated by addition of scrap zinc. Nickel is extracted by converting it into a volatile complex, nickel carbonyl, by use of carbon monoxide (Mond's process). The complex decomposes on heating again into pure nickel and carbon monoxide.

$$Ni + 4CO \longrightarrow Ni(CO)_4 \xrightarrow{\text{heating}} Ni + 4CO$$

(iii) **Photography** In photography, the image on the negative is fixed by dissolving all the remaining silver bromide with hypo solution in the form of a soluble complex.

$$AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{(soluble)}}{Na_3[Ag(S_2O_3)_2]} + \underset{\text{(soluble)}}{NaBr}$$

(iv) **Electroplating** Metal complexes release metal slowly and give a uniform coating of the metal on the desired object Cyano complexes of silver, gold copper and other metals are used for the electrodeposition of these metals,

(v) **Biological processes** Metal complexes are of immense importance in biological processes. Haemoglobin, the red blood pigment, which acts as oxygen carrier to different parts of the body is a complex of iron (II). Vitamin B_{12} is a complex of cobalt metal. The green colouring matter of plants, called chlorophyll, is a complex of magnesium. It acts as a catalyst in photosynthesis.

ORGANOMETALLIC COMPOUNDS

Introduction

Organometallic compounds are defined as those compounds in which the carbon atoms of organic (usually alkyl or aryl) groups are directly bonded to metal atoms. The compounds of elements such as boron, phosphorus, silicon, germanium and antimony with organic groups are also included in organometallics. Many organometallic compounds are important reagents which are used for the synthesis of organic compounds.

Classification of Organometallic Compounds

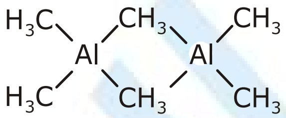
Organometallic compounds are classified in three classes.

(i) **Sigma bonded organometallic compounds:** In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, For Examples:

(a) Grignard reagents, R – Mg – X where R is an alkyl or aryl group and X is a halogen.

(b) Zinc compounds of the formula R_2Zn such as $(C_2H_5)_2Zn$. (isolated by Frankland).

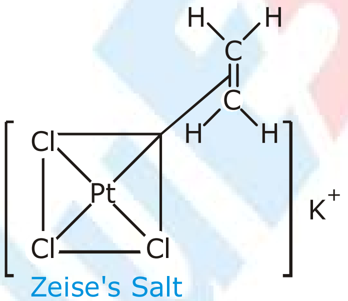
Other similar compound are $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$, $Pb(CH_3)_4$ etc.



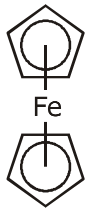
$Al_2(CH_3)_6$ is a dimeric compound and has a structure similar to diborane, (B_2H_6). It is an electron deficient compound and two methyl groups act as bridges between two aluminium atoms.

(ii) **Pi-bonded organometallic compounds :** These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the π-electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium.

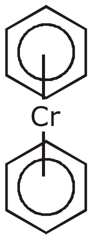
These are shown below.



Zeise's Salt
$K\{PtCl_3(\eta^2-C_2H_4)\}$



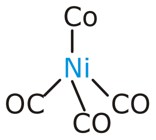
Ferrocene
$Fe(\eta^5-C_5H_5)_2$



Dibenzene chromium
$Cr(\eta^6-C_6H_6)_2$

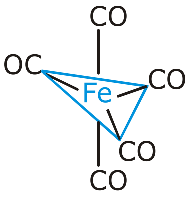
The number of carbon atoms bonded to the metal in these compounds is indicated by the Greek letter η(eta) with a number. The prefixes η^2, η^5 and η^6 indicate that 2, 5 and 6 carbon atoms are the metal in the compound.

(iii) **Sigma and Pi bonded organometallic compounds :** Metal carbonyl compounds formed between metal and carbon monoxide, belong to this class. These compounds possess both σ-and π-bonding. Generally oxidation state of metal atoms in these compounds is zero. Carbonyls may be mononuclear, bridged or polynuclear.



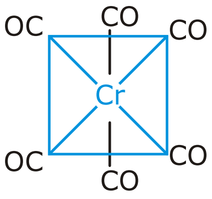
Tetracarbonyl nickel(0)

$Ni(CO)_4$



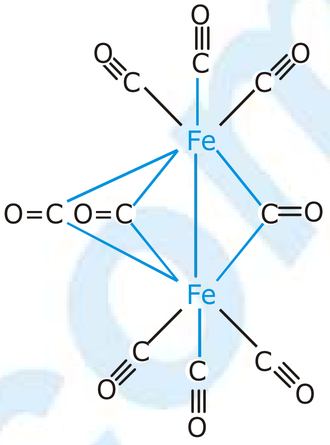
Pentacarbonyl iron(0)

$Fe(CO)_5$



Hexacarbonyl chromium(0)

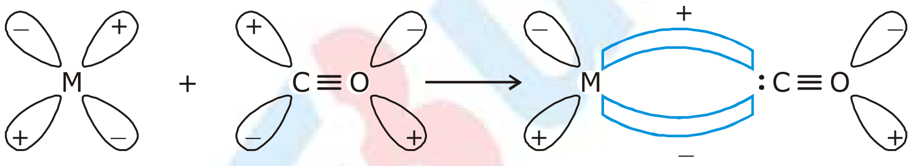
$Cr(CO)_6$



$Fe(CO)_9$

In a metal carbonyl, the metal-carbon bond possesses both the σ-and π-character. A σ-bond between metal and carbon atom is formed when a vacant hybrid orbital of the metal atom overlap with an orbital on C atom of carbon monoxide containing a lone pair of electrons.

Formation of p-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon.



The π-overlap is perpendicular to the nodal plane of σ-bond.

In olefinic complexes, the bonding π-orbital electrons are donated to the empty orbital of the metal atom and at the same time to the back bonding p-orbital of the olefin.

APPLICATIONS OF CO-ORDINATION & ORGANOMETALLIC COMPOUNDS

(i) Coordination compounds are of great importance in biological systems. Example being – chlorophyll (the green pigment in plants); haemoglobin (the red pigment of blood, which acts as oxygen carrier) along with myoglobin (which stores oxygen and is a regulator of respiration); Vitamin B_{12}, cyanocobalammine, the anti-pernicious anaemia factor. All of these, respectively, are the coordination compounds of magnesium, iron and cobalt with the macrocyclic porphyrin and corrin ligands.

(ii) There are many examples of the use of coordination compounds in qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially the chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Familiar examples of such reagents are :

ethylenediaminetetraacetic acid (EDTA), dimethylglyoxime, α-nitroso β-naphthol, cupron, etc.

(iii) Some important extraction processes of metals, like those of extraction of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be precipitated from this solution by the addition of Zinc.

(iv) Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

(v) EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumors. Examples are : cis-platin (cis-$[Pt(NH_3)_2Cl_2]$ and related compounds.

(vi) Organometallic compounds are used as catalysts. These catalysts are either of the homogeneous type (soluble in the reaction medium) or of the heterogeneous type (insoluble in the reaction medium). The catalysed polymerisation of alkenes at atmospheric pressure and ambient temperature using Ziegler-Natta catalyst (titanium tetrachloride plus triethylaluminium) is one of the important discoveries of organometallic chemistry. The first effective homogeneous catalyst chloridotris(triphenylphosphine) rhodium(I), $[RhCl(PPh_3)_3]$ for hydrogenation was given by Wilkinson.

(vii) Tetra ethyl lead (TEL) is used as antiknock compound in gasoline.

1. $CH_3B(OCH_3)$ is an organometallic compound but $B(OCH_3)$ is not.

2. The closed ring complexes formed by polydenatate ligands are called Chelates. Chelation leads to stability.

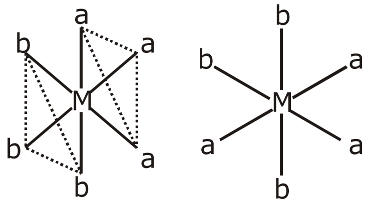
3. Estimation of nickel (II) is done by complexing with dimethyl glyoxime (DMG) whereas that of Ca^{+2} and Mg^{2+} ions is done by titrating against EDTA.

4. Complex in which ligands can be substituted by other ligands are called labile complexes. For example $[Cu(NH_3)_4]^{2+}$ is a labile complex because NH_3 ligands can be substituted by CN^- ligands.

$$\underset{\text{(less stable)}}{[Cu(NH_3)_4]^{2+}} + 4\,CN^- \rightarrow \underset{\text{(more stable)}}{[Cu(CN)_4]_2} + 4NH_3$$

5. Another type of geometrical isomerism is also shown by octahedral complexes of the type Ma_3b_3.

   if each trio of donor atoms occupy adjacent positions at the corner of an octahedral face, then it is called facial (fac) isomer and when the position are around the meridian of the octahedron, then it is called meridional (mer) isomer.



fac-form Mer-form

6. Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg, vitamin B_{12} is a complex of Co.

7. σ-bond organometallic compounds generally contains a non-transition metal linked to carbon atom of alkyl group by σ bond. For example eg. R-MgX.

8. p-bonded organometallics are formed by donation of p-electrons of double bond to the metal atom. For example Zeise's salt $K[PtCl_3\eta^2\,C_2H_4]$ and Ferrocene $Fe(\eta^5\text{-}C_5H_5)_2$

9. Grignard's reagent is one of the most useful organometallic compounds. Due to the high polarity of $(C^{\delta}–Mg^{\delta+})$ bond, it can be used to synthesise many organic compounds.