Coordination Compounds

Section (A) : General introduction of complex salts and definitions to be used

Coordination Compounds :

Those addition compounds which retain their identity (i.e. doesn't lose their identity) in solution are called **coordination compounds**. For example, when KCN solution is added to $Fe(CN)_2$ solution, the species formed when dissolved in water no longer gives tests of Fe^{2+} and CN^-.

$$\boxed{Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2 \,.\, 4KCN \text{ or } K_4[Fe(CN)_6] \text{ (aq.)} \rightleftharpoons 4K^+ \text{ (aq.)} + [Fe(CN)_6]^{4-} \text{ (aq.)}}$$

Other examples are, $[Cu(NH_3)_4]SO_4 \text{ (aq.)} \rightleftharpoons [Cu(NH_3)_4]^{2+} \text{ (aq.)} + SO_4^{2-} \text{ (aq.)}$

$K_2[Zn(CN)_4] \text{ (aq.)} \rightleftharpoons 2K^+ \text{ (aq.)} + [Zn(CN)_4]^{2-} \text{ (aq.)}$

Coordination compounds are also acid-base adducts and are frequently called complexes or, if charged then complex ions.

D1 **Coordination compound is defined as a species in which metal atom or ion is attached to group of neutral molecules / ions by coordinate covalent bonds.**

Coordination Entity/Coordination Sphere :

A coordination entity constitutes a central atom/ion, usually of a metal, to which are attached a fixed number of other atoms or groups each of which is called a ligand. Ligand may be neutral or charged. Examples being: $[Co(NH_3)_6]^{3+}$, $[PtCl_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[NiCl_2(OH_2)_4]$.

D2 The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively called as **coordination sphere**.

Note : The remaining ions apart from complex ions i.e. outside the coordination sphere are called counter ions, free ions or ionisable ions. For example, in $K_4[Fe(CN)_6]$, the potassium is counter ion of coordination entity $[Fe(CN)_6]^{4-}$.

D3 **Central Atom/Ion :**

In a coordination entity–the atom/ion around which a fixed number of ligands are bound in a definite geometrical arrangement, is called the central atom or ion. For example, the central atom/ion in the coordination entities : $[NiCl_2(OH_2)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms / ions are also referred to as Lewis acids since they accept lone pairs from the ligands.

D4 **Ligands :**

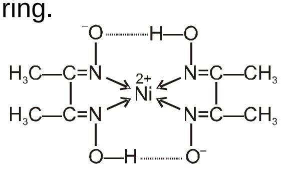
The neutral molecules, anions or cations which are directly linked with central metal atom or ion in the coordination entity are called ligands.

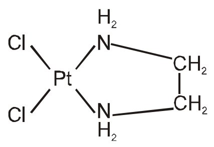
These may be simple ions such as Br^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules such as proteins.

When a ligand is attached to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be unidentate. Similarly when a ligand is bound through two donor atoms (in a single ligand), as in $H_2NCH_2CH_2NH_2$ (ethane-1, 2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be bidentate and when several donor atoms are present in a single ligand as in N $(CH_2CH_2NH_2)_3$ or ethylenediaminetetraacetic acid (EDTA), the ligand is said to be polydentate.

D5 **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.





D6 **Chelation :** 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 diaminetetracetate (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,

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

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

The five and six membered rings are more stable.

Denticity and Chelation :

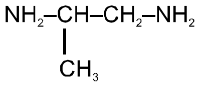
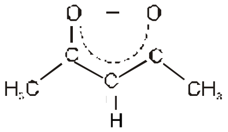
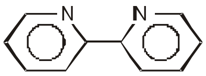
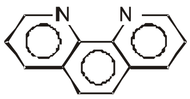
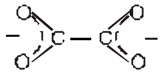
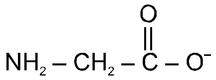
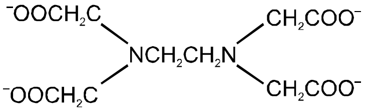
Tab1 Common Monodentate Ligands

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.

Tab2 Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
bidentate	ethylenediamine	1,2-ethanediamine/ ethane-1,2-diamine	en	$NH_2,CH_2CH_2NH_2$
bidentate	propanediamine	1,2-propanediamine	pn	 $NH_2–\underset{\displaystyle CH_3}{\underset{\mid}{CH}}–CH_2–NH_2$
bidentate	acetylacetonate	2,4-pentanediono or acetylacetonato	acac	
bidentate	2,2'-bipyridine	2,2'-bipyridyl	bipy	
bidentate	1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen,o-phen	
bidentate	oxalate	oxalato	ox	
bidentate	glycinate	glycinato	gly^-	 $NH_2 – CH_2 – \overset{\displaystyle O}{\overset{\|}{C}} – O^-$
hexadentate	ethylenediaminetetraacetate	1,2–ethanediyl (dinitrilo) tetraacetato or ethylenediaminetetraacetato	EDTA	

Flexidentate Ligand :

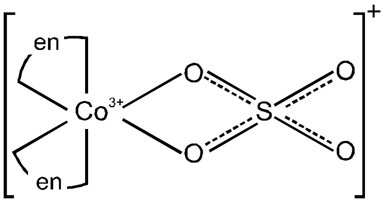
It is not necessary that all the donor items present in the polydentate ligands should form coordinate bonds with the central metal atom or ion i.e. a polydentate ligand which is found to have different denticity in different coordination compounds is called a flexidentate ligand. Note that in a particular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

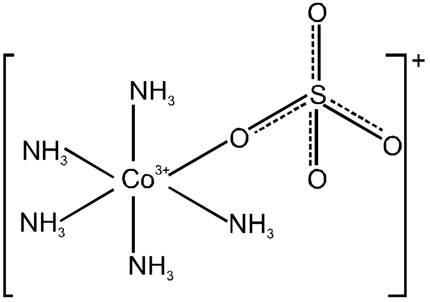
EDTA can act as **hexa, penta** as well as **tetra** dentate ligand.

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.

e.g. NO_3^-, CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$

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

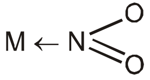




D7 Ambidentate Ligand :

Ligands which can ligate through two different sites present in it are called ambidentate ligands. Examples of such ligands are the CN^-, NO_2^- and SCN^- ions. NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds.

For example; Monodentate and ambidentate :



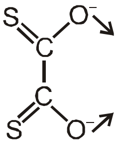
nitrito-N

M ← O—N=O nitrito-O

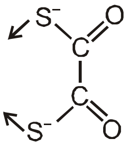
M ← SCN thiocyanato or thiocyanato-S

M ← NCS isothiocyanato or thiocyanato-N

Bidentate and ambidentate :



or



dithioxalate

Note : ***Although ambidentate ligands have two or more donor sites but during complex formation*** **different sites** ***can be used by them.***

D8 Coordination Number :

The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ion i.e. the number of ligand donor atoms to which the metal is directly attached. Pi-bonds, if any, between the ligating atom and the central atom/ion are not considered for the determination of **coordination number**. The sigma bonding electrons may be indicated by a pair of dots, preceding the donor atom in the ligand formula as in $[Co(:NH_3)_6]^{3+}$, $[Fe(:CN)_6]^{3-}$, $[Ni(:CO)_4]$, $[Co(:Cl_4)]^{2-}$.

Coordination number of 6 (most common), 4 (after 6) and 2 (after 4) are the most common coordination numbers and odd coordination numbers are generally not found (rare).

Some common co-ordination number of important metals are as given below.

Metal	**Coordination Number**	**Metal**	**Coordination Number**
Cu^+	2, 4	Ni^{2+}	4, 6
Ag^+	2	Fe^{2+}	6
Au^+	2, 4	Fe^{3+}	6
Cu^{2+}	4, 6	Co^{2+}	4, 6
Pt^{2+}	4	Co^{3+}	6
Pd^{2+}	4	Al^{3+}	6
Mg^{2+}	6	Pt^{4+}	6
		Pd^{4+}	6

D9 Oxidation number of Central Atom :

The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. Metal oxidation number is represented by a Roman numeral in parentheses following the name of the coordination entity. For example oxidation number of iron in $[Fe(CN)_6]^{3-}$ is +3 and it is written as Fe(III).

D10 Homoleptic and heteroleptic complexes :

Complexes in which a metal is bound to only one type of donor groups, e.g., $[Cr(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[Co(NH_3)_4Br_2]^+$, are known as heteroleptic.

Section (B) : Nomenclature of coordination compounds

Writing the formulas of Mononuclear Coordination Entities :

The following rules are followed while writing the formulas :

(i) The central atom is placed first.

(ii) The ligands are then placed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also placed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae is enclosed in parentheses. The abbreviations of the ligands are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Writing the name of Mononuclear Coordination Compounds :

The following rules are followed when naming coordination compounds :

(i) Like simple salts the cation is named first in both positively and negatively charged coordination entities.

Examples :

$[Ag(NH_3)_2]Cl$, diamminesilver(I) chloride. $K_3[Fe(CN)_6]$,potassium hexacyanidoferrate(III).

(ii) The ligands are named in an alphabetical order (according to the name of ligand, not the prefix) before the name of the central atom/ion.

Examples :

$[Pt(NH_3)BrCl(CH_3NH_2)]$, amminebromidochloridomethylamineplatinum(II).

$[Co(H_2O)_2(ox)_2]^-$, diaquabis(oxalato)cobaltate(III).

(iii) Names of the anionic ligands end in –o and those of neutral ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO, thiocarbonyl for CS and nitrosyl for NO. But names of cationic ligands end in–ium.

Some more important examples of neutral and cationic ligands are :

tetraphosphorus — P_4
dioxygen — O_2
octasulphur — S_8
urea — $CO(NH_2)_2$
hydrazinium — $N_2H_5^+$

(iv) Ambidentate ligands are named as follows :

(i) ← : ^{-}CN : cyanido or cyanido – C
← : NC^{-} : isocyanido or cyanido – N

(ii) ← : NO_2^{-} : nitro or nitrito – N
← : ONO^{-} : nitrito or nitrito – O

(v) Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix or are complicated or whenever the use of normal prefixes creates some confusion, it is set off in parentheses and the second set of prefixes is used.

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis

Examples : $[CoCl_2(NH_2CH_2CH_2NH_2)_2]^+$, dichloridobis(ethane-1,2-diamine)cobalt(III).
$[NiCl_2(PPh_3)_2]$, dichloridobis(triphenylphosphine)nickel(II).

(vi) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in the parentheses after the name of metal.

(vii) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix-ate. For example, Co in a complex anion, $[Co(SCN)_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions.

iron (Fe)	ferrate	lead (Pb)	plumbate
silver (Ag)	argentate	tin (Sn)	stannate
gold (Au)	aurate		

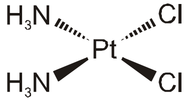
Examples ; $[Co(NH_3)_4Cl_2]^+$, tetraamminechloridocobalt(III).
$(NH_4)_2[Co(SCN)_4]$, ammonium tetrathiocyanato-S-cobaltate(II).

(viii) The neutral complex molecule is named similar to that of the complex cation.

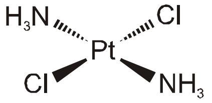
Example ; $[CrCl_3(py)_3]$, trichloridotris(pyridine)chromium(III).

(ix) The prefixes cis- and trans- designate adjacent and opposite geometric locations.

For examples, $[Pt(NH_3)_2Cl_2]$, cis- and trans-diamminedichloridoplatinum(II),
$[CoCl_2(NH_3)_4]^+$, cis- and trans-tetraamminedichloridocobalt(III).



cis–



trans–

(x) If there is any water of crystallization, it is to included in the name. For example,

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$: tetraaquadichlorido chromium(III) chloride-2-water or
tetraaquadichlorido chromium(III) chloride dihydrate.

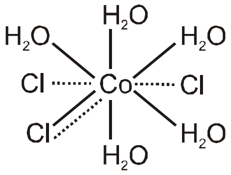
Section (C) : Werner's Theory

Several theories were proposed but none of them could satisfactorily explain the observed properties of Co(III) ammines and of other similar compounds like Pt(IV) ammines which had been prepared by them. It was only in 1893, that Werner presented a theory known as Werner's coordination theory which could explain all the observed properties of complex compounds. According to him most elements exhibit two types of valencies: (a) Primary valency and (b) Secondary valency.

(a) **Primary valency :** This corresponds to the oxidation state of the metal ion. This is also called as the principle, ionisable or ionic valency. It is satisfied by the negative ions and its attachment with the central metal ion is shown by dotted lines.

(b) **Secondary or auxiliary valency :** It is also termed as the coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e. coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules having lone pair of electrons (e.g., H_2O, NH_3 etc.) or even sometimes by some positive groups. The ligands which satisfy the coordination number are directly attached to the metal atom or ion and shown by thick lines.

Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e. it may satisfy both primary and secondary valencies since in every case the fulfillment of coordination number of the central metal ion appears essential. This dual behaviour is represented by both thick and dotted lines. For example, $[CoCl(H_2O)_5]Cl_2$ is represented as



Every metal has a fixed number of secondary valencies, e.g., cobalt(III) and platinum(IV) have six secondary valencies and copper(II) four. The coordination number of a metal in a particular oxidation state is generally fixed but certain oxidation states of certain metals have found to possess more than one coordination number.

The ions/groups bound by the secondary valencies have characteristic spatial arrangements corresponding to different coordination number. In the modern terminology, such spatial arrangements are called coordination polyhedra and various possibilities are

C.N. = 2	linear	C.N. = 3	Triangular
C.N. = 4	tetrahedral or square planar	C.N. = 6	octahedral.

To distinguish between the two types of valencies, Werner introduced the square brackets [ ] to enclose those atoms making up the coordination complex and which are, therefore, not ionized.

On the basis of the above postulates Werner formulated the coordination compounds, $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$ as : $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ respectively; the species within the square brackets being the coordination entities (complexes) and the ions outside the square brackets the counter ions. He further postulated that octahedral, square, planar and tetrahedral geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$, $[CoCl_2(NH_3)_4]^+$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square-planar respectively.

Tab4

S. No.	Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
1	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}$+3Cl^-	six (NH_3)	three (Cl^-)
2	$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+}$+2Cl^-	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
3	$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+$+ Cl^-	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
4	$CoCl_3.3NH_3$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3Cl_3]$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

From the above table it is clear that (i) the solution conductivities of complexes 1, 2 and 3 correspond to 1 : 3, 1 : 2 and 1 : 1 electrolyte respectively and thus the increasing order of the conductivity can be represented as $CoCl_3.3NH_3 < CoCl_3.4NH_3 < CoCl_3.5NH_3 < CoCl_3.6NH_3$ and (ii) the complexes 1, 2 and 3 will react with silver nitrate and give 3, 2 and 1 mole of the white precipitate of silver chloride respectively.

F1 **Effective Atomic Number Rule given by Sidgwick :**

Effective Atomic Number (EAN) = No. of electron present on the metal atom/ion + No. of electrons donated by ligands to it.

OR

Effective Atomic Number (EAN) = Atomic no. of central metal – Oxidation state of central metal + No. of electrons donated by ligands.

The complexes in which the EAN of the central atom equals the atomic number of the next noble gas, are found to be extra stable.

e.g. Cr(24) complex : $[Cr(CO)_6]$ O.S. of Cr^0 EAN = $24 - 0 + 2 \times 6 = 36$

Fe(26) complex : $[Fe(CN)_6]^{4-}$ O.S. of Fe^{+2} EAN = $26 - 2 + 2 \times 6 = 36$

Note : The EAN rule is generally found to be not valid in case of most of the complexes but in case of metal carbonyls this rule is found to be valid in all cases except one or two exceptions.

Section (D) & (E) : Valence Bond Theory + Crystal Field Theory (Part-I & II)

Bonding in coordination compounds :

Alfred-Werner described the bonding characteristic in coordination compounds. But this theory failed to explain certain basic questions like :

(a) Why only certain elements possess the remarkable property of forming compounds ?

(b) Why the bonds in coordination compounds have directional properties ?

(c) Why coordination compounds have the characteristic magnetic and optical properties ?

Many theories/approaches have been put forward to explain the nature of bonding in coordination compounds; these are valence bond theory (VBT), crystal field theory (CFT), ligand field theory (LFT) and molecular orbital theory (MOT).

Valence bond theory :

The valence bond theory, VBT, was extended to coordination compounds by Linus Pauling in 1931. The formation of a complex involves reaction between a lewis base (ligand) and a lewis acid (metal or metal ion) with the formation of a coordinate-covalent (or dative) bonds between them. The model utilizes hybridisation of (n – 1) d, ns, np or ns, np, nd orbitals of metal atom or ion to yield a set of equivalent orbitals of definite geometry to account for the observed structures such as octahedral, square planar and tetrahedral, and magnetic properties of complexes. The number of unpaired electrons, measured by the magnetic moment of the compounds determines which d-orbitals are used. These hybrid orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

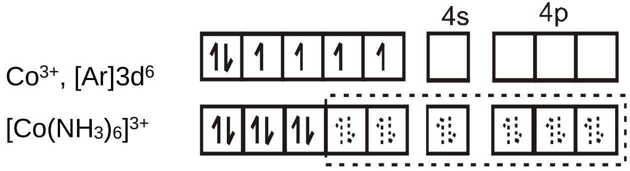
Tab5 Following table provides the types of hybridisation with different coordination number.

Coordination number of metal	Type of hybridisation	Shape of complex	Types of d-orbitals
2	**sp**	**Linear**	**–**
4	sp^3	Tetrahedral	–
4	dsp^2	Square planer	$d_{x^2-y^2}$
4	d^3s	Tetrahedral	d_{xy}, d_{yz}, d_{xz}
5	sp^3d	Trigonal bipyramidal	d_{z^2}
5	dsp^3	Square pyramidal	$d_{x^2-y^2}$
6	sp^3d^2	Octahedral	$d_{x^2-y^2}$ d_{z^2}
6	d^2sp^3	Octahedral	$d_{x^2-y^2}$ d_{z^2}

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.



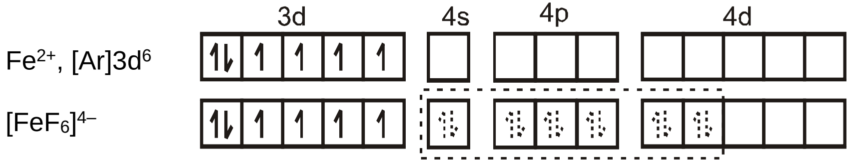
(inner orbital or low spin complex)

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,

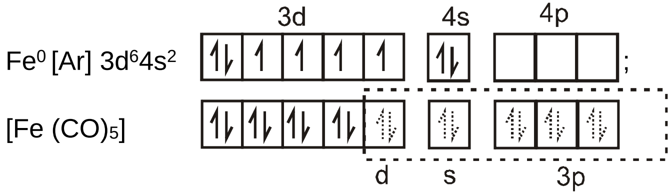


sp^3d^2 hybrid orbitals

Six pairs of electrons from six F^- ions.

Coordination Number Five :

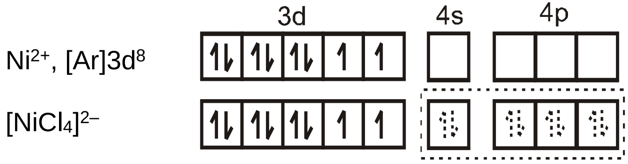
In the square pyramidal complex $[Fe(CO)_5]$, Iron is in 0 oxidation state



The compound is diamagnetic as it contains 0 unpaired electrons

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.

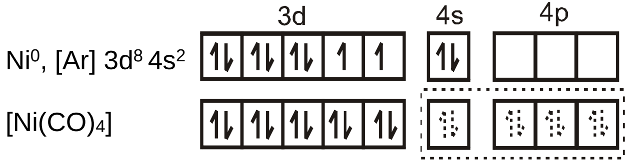


sp^3 hybrid orbitals

Four pairs of electrons from four Cl^- ions.

The compound is paramagnetic since it contains two unpaired electrons.

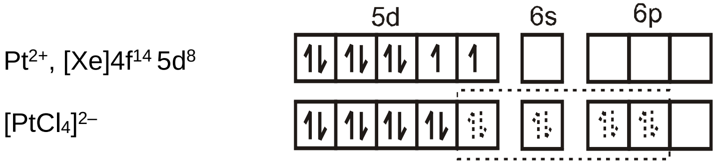
Similarly complex $[Ni(CO)_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.



sp^3 hybrid orbitals

Four pairs of electrons from four CO molecules.

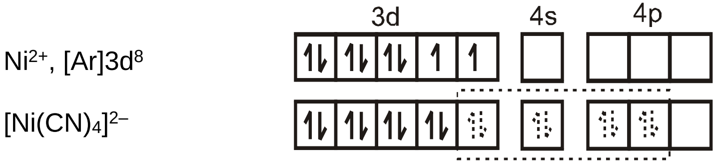
Complexes of Pd(II) and Pt(II) are usually four-coordinate, square planar, and diamagnetic and this arrangement is often found for Ni(II) complexes as well, e.g., in $[Ni(CN)_4]^{2-}$ (here nickel is in +2 oxidation state and has electronic configuration $3d^8$). In as much as the free ion is in the 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.

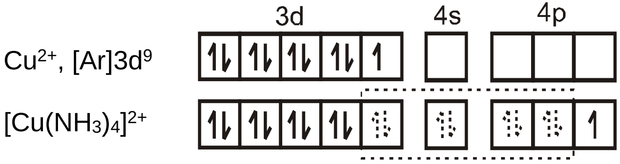
Similarly the hybridisation scheme for $[Ni(CN)_4]^{2-}$ is as shown in figure.



dsp^2 hybrid orbitals

Four pairs of electrons from four CN^- ions.

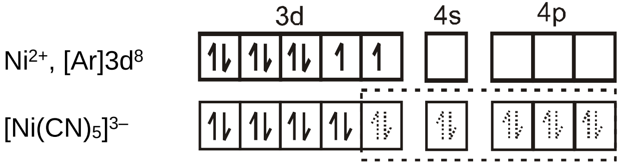
It is found that $[Cu(NH_3)_4]^{2+}$ is square planar and paramagnetic with one unpaired electron in 4p-orbital. The hybridisation scheme is as follow.



dsp^2 hybrid orbitals

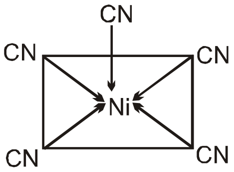
Four pairs of electrons from four NH_3 molecules.

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.



dsp^3 hybrid orbitals

Five lone pairs of electrons from five CN^- ions.



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 :

The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

(i) The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand.

(ii) Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules.

(iii) The five d orbitals is an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystals field.

(a) Crystal field splitting in octahedral coordination entities :

(i) In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands.

(ii) Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy ; and the d_{xy} , d_{yz} and d_{zx} orbitals (non-axial orbitals) which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field.

(iii) Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.

(iv) This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\ \Delta_0$.

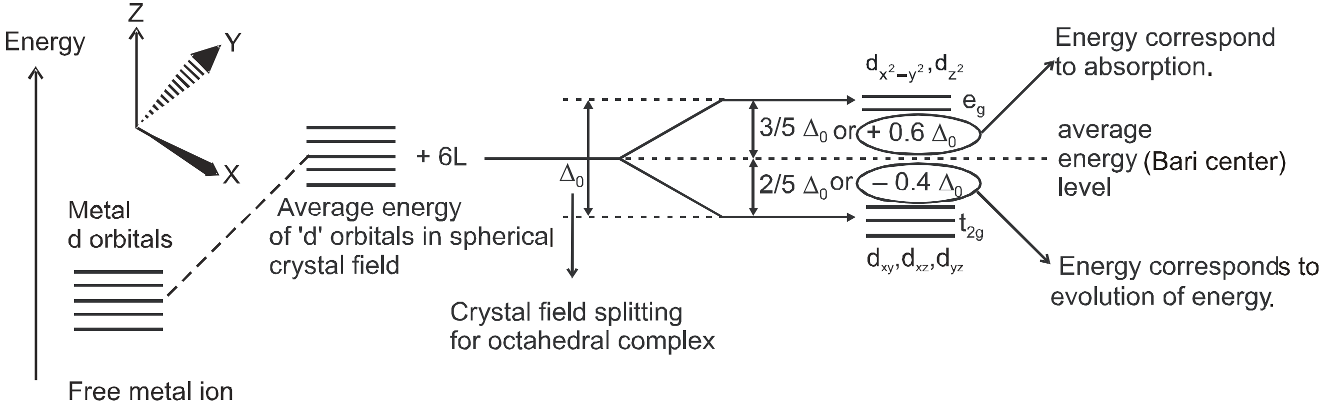


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0, depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in such a case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the orders of increasing field strength as given below :

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < EtOH < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < en < bipy$ (2, 2'-bipyridine) $< NO_2^- < PPh_3 < CN^- < CO$

* **Halide donors < O donors < N donors < C donors**

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For d^4 configuration, the fourth electron will singly occupy e_g orbital (according to Hund's rule) or will undergo pairing in t_{2g} orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_0 and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two possibilites are :

(i) If $\Delta_0 < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t^3_{2g}e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

(ii) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

CALCULATION OF CRYSTAL FIELD STABILISATION ENERGY (CFSE)

F2 **Formula :** CFSE = $[-0.4\ (n)\ t_{2g} + 0.6\ (n')\ e_g]\ \Delta_0 + {}^*nP$.

where n & n′ are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. *n represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

(b) Crystal field splitting in tetrahedral complexes :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_o$. This may attributes to the following two reasons.

(i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field spliting is also the two thirds the size and (ii) the direction of the orbitals does not concide with the direction of the ligands. This reduces the crystal field spliting by roughly further two third. So $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}\Delta_o$.

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

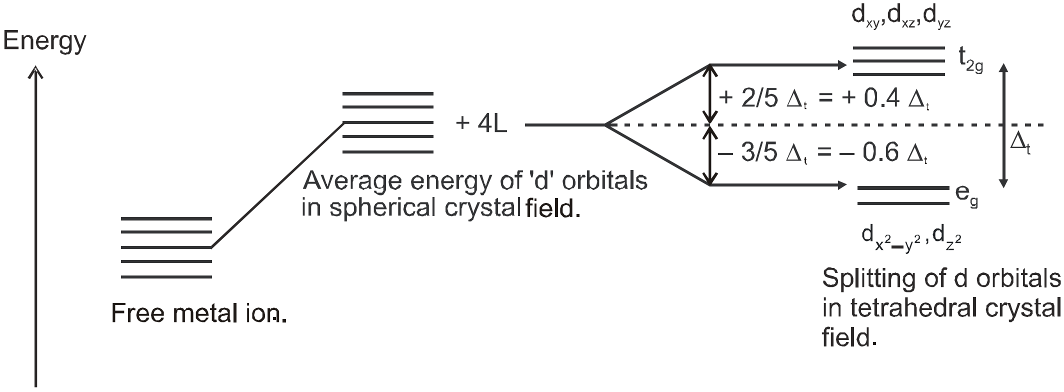


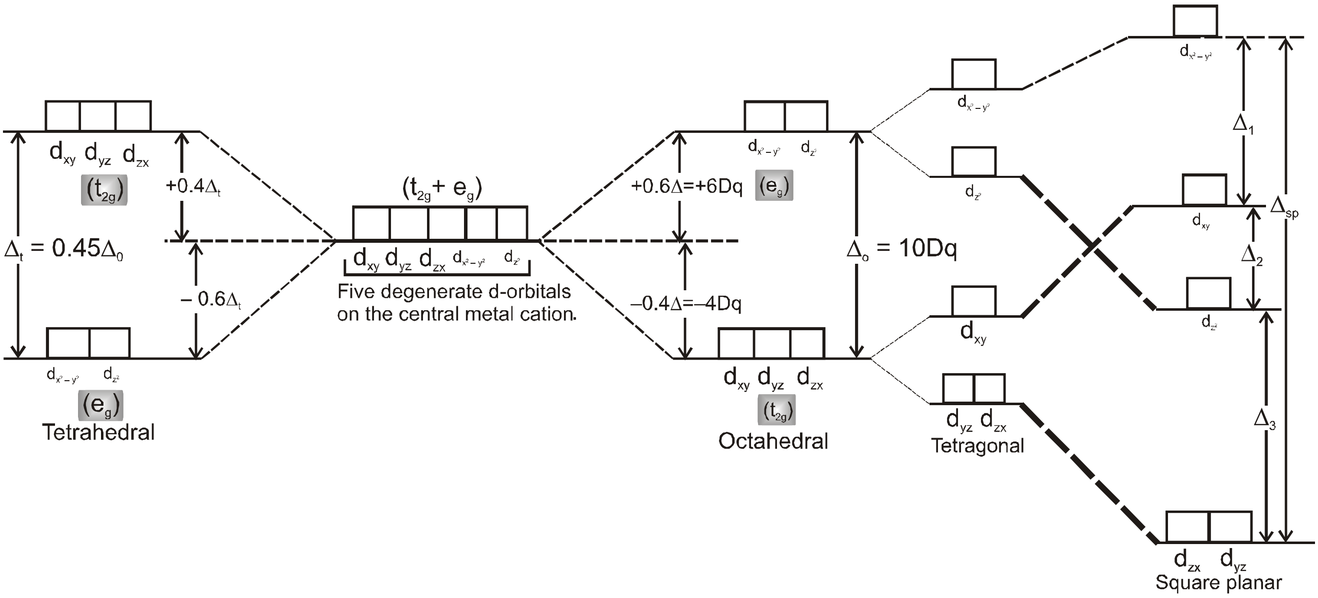
Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_o$ crystal field spliting favours the formation of octahedral complexes.

(c) Crystal field splitting in square planar complexes :

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the e_g and t_{2g} sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the axes, they would have greatest influence on d_{x2-y2} orbital, so the energy of this orbital, will be raised most. The d_{xy} orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the d_{x2-y2} orbital. On the other hand, due to absence of ligands along Z-axis, the d_{z2} orbital becomes stable and has energy lower than that of d_{xy} orbital. Similarly d_{yz} and d_{xz} become more stable. The energy level diagram may be represented as Figure along with tetrahedral and octahedral fields.



The value of Δ_{sp} has been found larger than Δ_o because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3\Delta_o$. Thus,

$$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o \qquad \text{and} \qquad \Delta_{sp} = 1.3\,\Delta_o.$$

Section (F) : Applications of crystal field theory

(Magnetic moment of complex, Colour of complex, Limitation, Stability of complex)

MAGNETIC PROPERTIES OF COORDINATION COMPOUNDS :

Additional information for understanding the nature of coordination entities is provided by magnetic susceptibility measurements. We have noted that coordination compounds generally have partially filled d orbitals and as such they are expected to show characteristic magnetic properties depending upon the oxidation state, electron configuration, coordination number of the central metal and the nature of the ligand field. It is experimentally possible to determine the magnetic moments of coordination compounds which can be utilized for understanding the structures of these compounds.

The number of unpaired electrons in any complex can be easily calculated from the configuration of the metal ion, its coordination number and the nature of the ligands involved (strong or weak from the spectrochemical series) and after that the magnetic moment of the complexes can be easily calculated using ;

F3 **Magnetic Moment =** $\sqrt{n(n+2)}$ **Bohr Magneton ;** **n = number of unpaired electrons**

For metal ions with upto three electrons in the d-orbitals like Ti^{3+}, (d^1); V^{3+} (d^2); Cr^{3+} (d^3); two vacant d-orbitals are easily available for octahedral hybridisation. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, like in Cr^{2+} and Mn^{3+} (d^4); Mn^{2+} and $Fe^{3+}(d^5)$; Fe^{2+} and $Co^{3+}(d^6)$; the required two vacant orbitals for hybridisation is not directly available (as a consequence of Hund's rules). Thus, for d^4, d^5 and d^6 cases, two vacant d-orbitals are only available for hybridisation as a result of pairing of 3d electrons which leaves two, one and zero unpaired electrons respectively.

Application of magnetic moment :

(i) The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ion. However, there are complications with the coordination compounds / species having d^4 and d^5 ions.

(ii) $[Mn(CN)_6]^{3-}$ has a magnetic moment equal to two unpaired electrons while $[MnCl_6]^{3-}$ has a magnetic moment equal to four unpaired electrons.

(iii) Similarly $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a magnetic moment of five unpaired electrons.

(iv) $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)]^{3-}$ is diamagnetic.

(v) This anomalous behaviour is explained by valence bond theory in terms of formation of inner orbitals and outer orbitals complexes.

(vi) $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_2]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two are paramagnetic and the latter diamagnetic. $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic having four, five and four electrons respectively.

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 ($d_{x^2y^2}$, 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.

Tab6 **Relationship between the wavelength of light absorbed and the colour observed In some coordination entities**

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.

Tab7

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

Limitations of crystal field theory

(1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, p_x, p_y and p_z orbitals).

(2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why H_2O is a stronger ligand than OH^- in the spectrochemical series.

(3) According to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.

(4) The CFT cannot account for the π-bonding in complexes.

Stability of coordination compounds :

(i) The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

F4 $\beta_n = [ML_n]/[M(H_2O)_n][L]^n$

For the overall reaction :

$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1, K_2, K_3, ... K_n for each step as represented below :

$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O$ $K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$

$ML_{n-1}(H_2O) + L \rightleftharpoons ML_n + H_2O$ $K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$

$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$ $\beta_n = K_1 \times K_2 \times K_3 \times \ldots\ldots \times K_n$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above. K_1, K_2, K_3 ..... K_n representing the stepwise stability (or formation) constants.

The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

Some important generalisation regarding stability constants :

(ii) For a given metal and ligand the stability is generally greater when the charge on the metal ion is greater. Thus, stability of coordination entities of ions of charge 3+ is greater than the entities of 2+ ions.

(iii) Further, for the divalent ions of the first row transition elements, irrespective of the ligand involved, the stabilities vary in the Irving-Williams order : $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$

(iv) This order is according to the size of the ions, smaller the size of the ion or greater the charge density on the metal greater is the stability of the complex.

In F^-, Cl^-, Br^-, I^- ; F^- forms strongest complexes due to small size & hence high charge density.

(v) (a) The stability also depends on the formation of chelate rings. If L is an unidentate ligand and L–L, a didentate ligand and if the donor atoms of L and L–L are the same element, then L–L will replace L. The stabilisation due to chelation is called the chelate effect. It is of great importance in biological systems and analytical chemistry.

(b) If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the **macrocyclic effect.**

Section (G) : Isomerism in Coordination compounds

(Structural Isomerism, Stereoisomerism, Geometrical Isomerism, Optical Isomerism)

ISOMERISM :

(1) STRUCTURAL ISOMERISM :

D11 (A) Ionisation isomerism :

This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand which can then become the counter ion. For example, following complexes show ionisation isomerism.

$[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$

$[Co(NH_3)_4(NO_2)Cl]Cl$ and $[Co(NH_3)_4Cl_2]NO_2$.

$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4BrCl]Br.H_2O$. [Also an example of hydrate isomers.]

$[Pt(NH_3)_4Cl_2]Br_2$, and $[Pt(NH_3)_4Br_2]Cl_2$.

$[CoCl(en)_2(NO_2)]SCN$, $[Co(en)_2(NO_2)SCN]Cl$ and $[Co(en)_2(SCN)Cl]NO_2$

D12 (B) Solvate / hydrate isomerism:

It occurs when water forms a part of the coordination entity or is outside it. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. For example, $CrCl_3.6H_2O$ exists in three distinct isomeric forms : $[Cr(H_2O)_6]Cl_3$, violet; $[CrCl(H_2O)_5]Cl_2.H_2O$, blue green : $[CrCl_2(H_2O)_4]Cl.2H_2O$, dark green. These three cationic isomers can be separated by cation ion exchange from commercial $CrCl_3.6H_2O$. A fourth isomer $[Cr(H_2O)_3Cl_3]$, yellow green also occurs at high concentration of HCl. Apart from their distinctive colours, the three isomers can be identified by the addition of excess of aqueous silver nitrate to their aqueous solutions, which precipitates chloride in the molar ratio of 3 : 2 : 1 respectively.

Complex	**Reaction with $AgNO_3$**	**Reaction with conc. H_2SO_4 (dehydrating agent)**
$[Cr(H_2O)_6]Cl_3$	in the molar ratio of 3 : 1	No water molecule is lost or no reaction
$[CrCl(H_2O)_5]Cl_2.H_2O$	in the molar ratio of 2 : 1	one mole of water is lost per mole of complex
$[CrCl_2(H_2O)_4]Cl.2H_2O$	in the molar ratio of 1 : 1	two mole of water are lost per mole of complex

Other examples are :

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$
$[Co(NH_3)_5(H_2O)](NO_3)_3$ and $[Co(NH_3)_5(NO_3)](NO_3)_2.H_2O$.

D13 (C) Linkage isomerism :

In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g.,NO_2 group can be bonded to metal ions through nitrogen ($–NO_2$) or through oxygen (–ONO). SCN too can be bonded through sulphur (–SCN) thiocyanate or through nitrogen (–NCS) isothiocyanate.

For example : $[Co(ONO)(NH_3)_5]Cl_2$ & $[Co(NO_2)(NH_3)_5]Cl_2$.

D14 (D) Coordination isomerism :

Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities. Some of the examples are :

(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
(ii) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
(iii) $[Co(NH_3)_6][Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2][Co(NH_3)_2(SCN)_4]$
(iv) $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$

Such isomers are expected to have significant differences in their physical and chemical properties.

D15 (E) Ligand isomerism :

Since many ligands are organic compounds which have possibilities for isomerism, the resulting complexes can show isomerism from this source.

For example; ligands 1,2-diaminopropane(propylenediamine or **pn)** and 1,3-diaminopropane (trimethylenediamine or **tn**) are such pairs. Similarly ortho-, meta- and para-toluidine ($CH_3C_6H_4NH_2$).

D16 (F) Polymerisation isomerism :

Considered to be a special case of coordination isomerism, in this the various isomers differ in formula weight from one another, so not true isomers in real sense.

For example $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$, $[Co(NH_3)_6][Co(NO_2)_6]$, $[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]_2$, $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$, $[Co(NH_3)_4(NO_2)_2]_3[Co(NO_2)_6]$ and $[Co(NH_3)_5(NO_2)_2]_3[Co(NO_2)_6]_2$.

These all have the empirical formula $Co(NH_3)_3(NO_2)_3$, but they have formula weights that are 2,2,3,4,4 and 5 times this, respectively.

(2) Stereoisomerism :

D17 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.

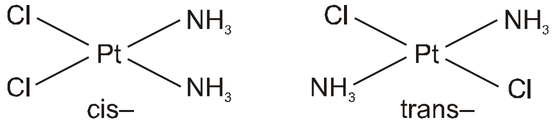
Geometrical Isomerism :

D18 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.

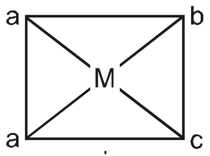
Square Planar Complex : In a square planar complex of formula $[Ma_2b_2]$ [a and b are unidentate], the two ligands ‘a’ may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted.



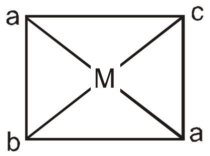
cis– trans–

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.

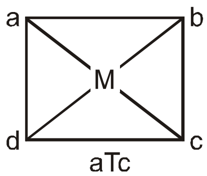


cis–

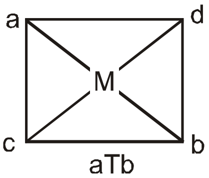


trans–

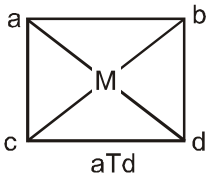
Square planar complex of the type Mabcd (where a,b,c,d are unidentates) shows three geometrical isomers.



aTc



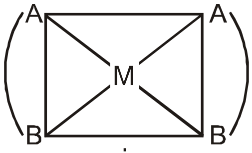
aTb



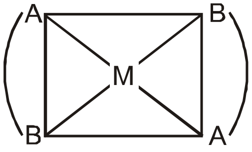
aTd

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–



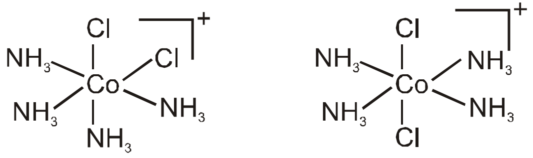
trans–

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 $[Co(NH_3)_4Cl_2]^+$

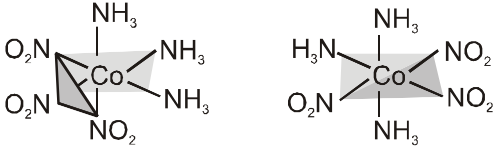
Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(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

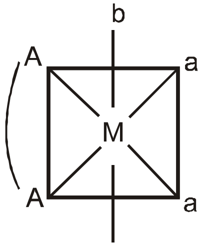
(viii) Ma_2bcde – 9

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

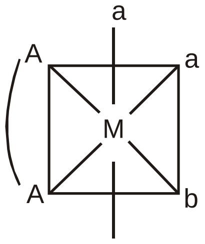
Note : Ma_6 and Ma_5b have only one form.

(II) Compounds containing bidentate ligand and unidentate ligands.

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

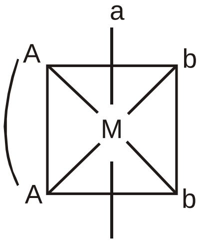


bTa

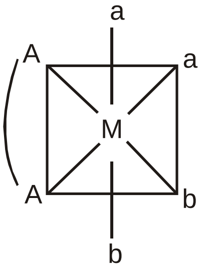


aTa

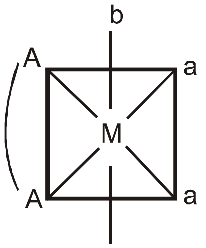
(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.



aTa



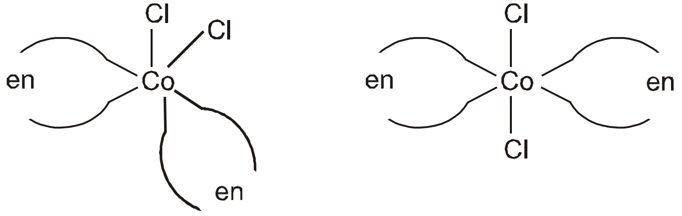
aTb



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.

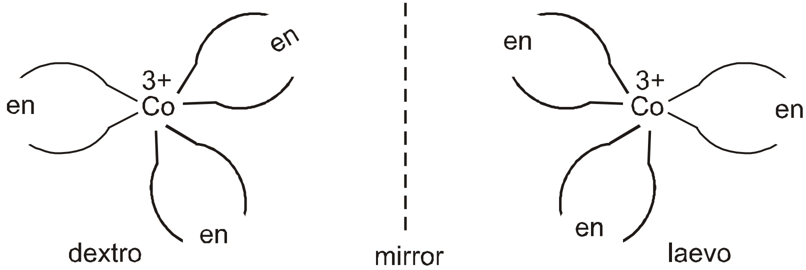


Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Optical Isomerism:

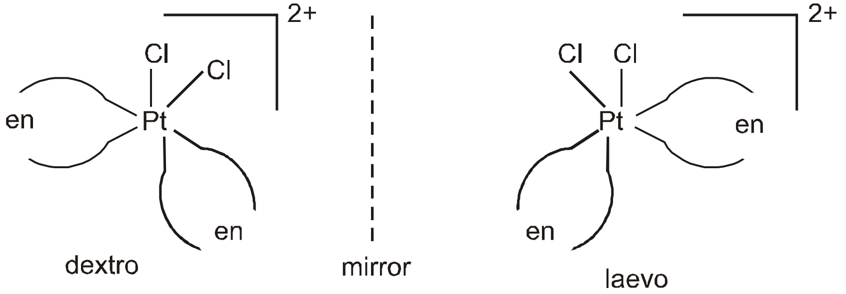
D19 A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical 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.



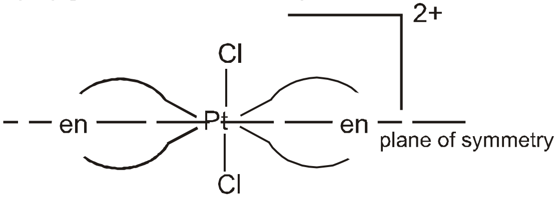
d and □ of $[Co(en)_3]^{3+}$

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.

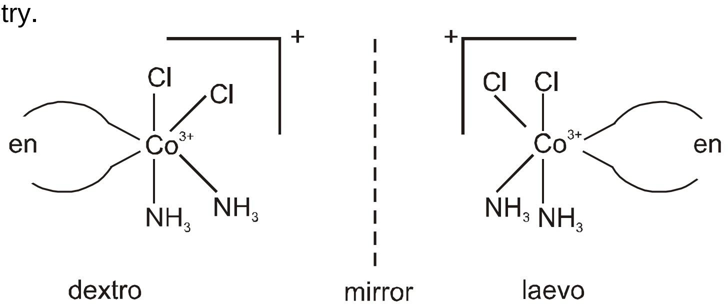


d and □ of cis-$[PtCl_2(en)_2]^{2+}$

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

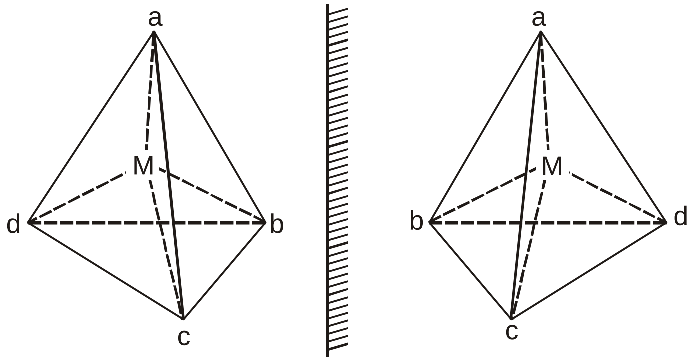


cis-$[Co(NH_3)_2Cl_2(en)]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.



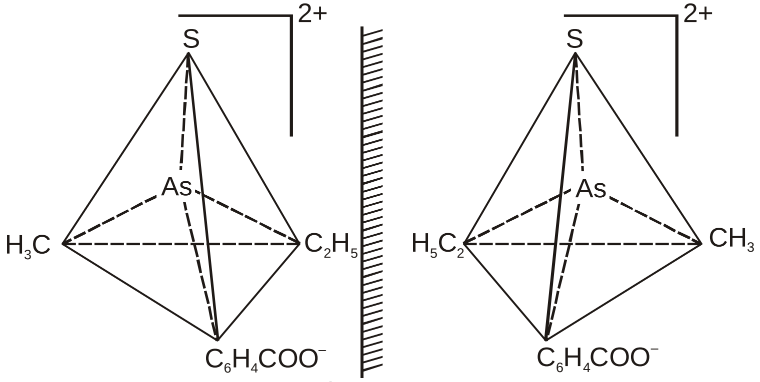
Tetrahedral complex :

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



Mirror plane

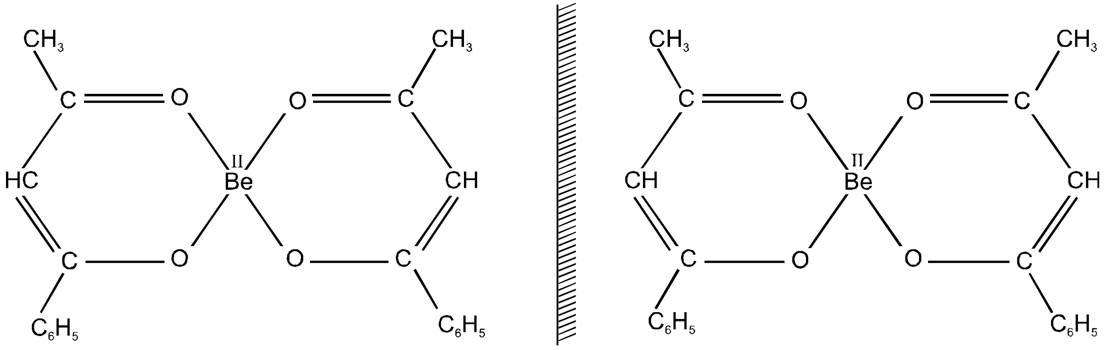
(i) For example $[As(III)(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$, shows optical isomerism as given below.



Mirror plane

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 ℓ-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), $[Pt(II)(NH_2 \cdot CH(C_6H_5) \cdot CH(C_6H_5NH_2) \cdot (NH_2 \cdot CH_2 \cdot C(CH_3)_2 \cdot NH_2)]^{2+}$ which has square-planar shape has been resolved into two forms by Mills and Quibell in 1935.

Determination of Stereoisomers in octahedral Coordination compounds

Table -1

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
Ma_6	1	0	0
Ma_5b	1	0	0
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	5	1	4
$Ma_2b_2c_2$	6	1	5
Ma_2b_2cd	8	2	6
Ma_5bcde	15	6	9
Mabcdef	30	15	15

Table -2

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[M(AA)_3]$	2	2	0
$[M(AA)_2a_2]$	3	1	2
$[M(AA)_2ab]$	3	1	2
$[M(AA)a_4]$	1	0	1
$[M(AA)a_3b]$	2	0	2
$[M(AA)a_2b_2]$	4	1	3
$[M(AA)a_2bc]$	6	2	4
$[M(AA)abcd]$	12	6	6

Table -3

Formula	Possible number of stereoisomers	Possible number of enantiomer pairs	Possible number of geometrical isomers
$[M(AB)_3]$	4	2	2
$[M(AB)_2a_2]$	8	3	5
$[M(AB)_2ab]$	11	5	6
$[M(AB)a_4]$	1	0	1
$[M(AB)a_3b]$	4	1	3
$[M(AB)a_2b_2]$	6	2	4
$[M(AB)a_2bc]$	12	5	7
$[M(AB)abcd]$	24	12	12

M is the metal ion and a, b, c, d, e and f represent monodentate ligands. AA is a bidentate symmetrical ligand. AB is a bidentate unsymmetrical ligand.

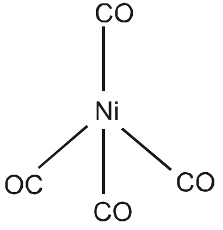
Section (H) : Organometallic Compounds

Organometallic compounds

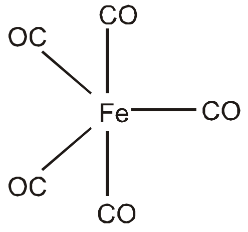
D20 Metal Carbonyls :

Compounds of metals with CO as a ligand are called metal carbonyls. They are of two types.

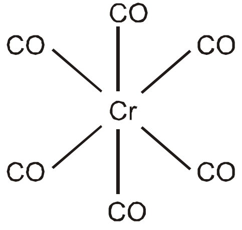
D21 (a) Monomeric: Those metal carbonyls which contain only one metal atom per molecule are called monomeric carbonyls. For examples: $[Ni(CO)_4]$ (sp^3, tetrahedral); $[Fe(CO)_5]$ (dsp^3, trigonal bipyramidal); $[Cr(CO)_6]$ (d^2sp^3, octahedral); $[V(CO)_6]$ (d^2sp^3, octahedral, only carbonyl which is paramagnetic having one unpaired electron ; this is least stable among all the four carbonyls)



$Ni(CO)_4$
Tetrahedral

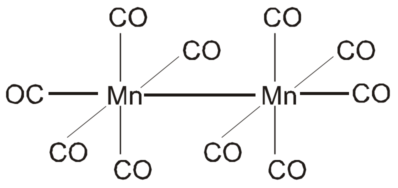


$Fe(CO)_5$
Trigonal bipyramidal

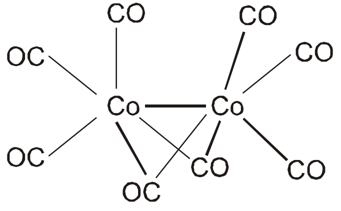


$Cr(CO)_6$
Octahedral

D22 (b) Polymeric : Those metal carbonyls which contain two or more than two metal atoms per molecule and they have metal-metal bonds are called polymeric carbonyl. For example: $Mn_2(CO)_{10}$, $CO_2(CO)_9$, etc.



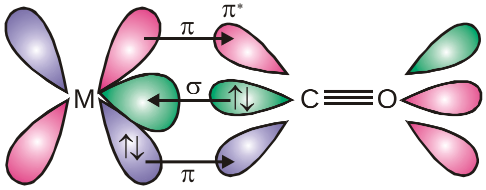
$[Mn_2(CO)_{10}]$



$[Co_2(CO)_8]$

Metal carbonyls are mostly solids at room temperature and atmospheric pressure. The mononuclear carbonyls are volatile and toxic. With the exception of $Fe_2(CO)_9$, carbonyls are soluble in hydrocarbon solvents. Mononuclear carbonyls are either colourless or light-coloured. Polynuclear carbonyls are more deeply coloured. $Fe_3(CO)_{12}$, dodecacarbonyltriiron(o), for example, is a deep grass green solid. Metal carbonyls find use as industrial catalysts and as precursors in organic synthesis.

The metal–carbon bond in metal carbonyls possess both s and p character. The M—C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon (CO is a weak base) into a vacant orbital of the metal. The M—Cπ bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. Thus carbon monoxide acts as σ donor (OC → M) and a π acceptor (OC ← M), with the two interactions creating a synergic effect which strengthens the bond between CO and the metal as shown in figure.



Synergic bonding

(i) As M—Cπ bonding increases, the C—O bond becomes weaken. The greater the positive charge on the central metal atom, the less readily the metal can donate electron density into the π^* orbitals of the carbon monoxide ligands to weaken the C—O bond.

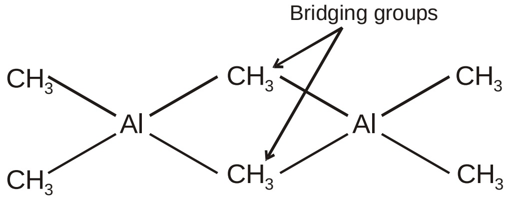
(ii) In contrast, in the anionic complex (i.e. carbonylate anion) the metal has a greater electron density to be dispersed, with the result that M—Cπ bonding is enhanced and the C—O bond is diminished in strength. For example; in isoelectronic complexes the strength of metal-ligand bond increases and strength of C—O bond in CO decreases (because bond order decreases) as the negative charge on the complexes increases.

Thus order of CO bond strengths ;

(a) $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$.   (b) $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$.

Sigma (σ) bonded organometallic compounds :

In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond in which ligand contributes one electron and is therefore called one electron donor. For example:



(a) Grignard's Reagent R–Mg–X where R is a alkyl or aryl group and X is halogen.
(b) $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$ etc.

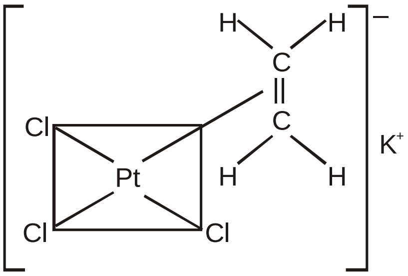
Pie (π)-bonded organometallic compounds :

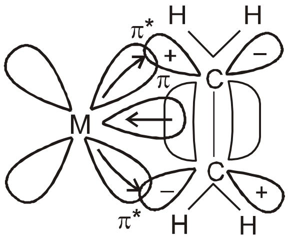
These are the compounds of metal with alkenes, alkynes, benzene and other ring compounds.

Zeise's salt :

In Zeise's salt structure, the ethylene occupies the fourth coordination site of the square planar complex with the C—C axis perpendicular to the platinum ligand plane. Relative to free ethylene the C—C bond is lengthened (from 133.77 pm to 137.5 pm), and the hydrogen are slightly tilted back from a planar arrangement. The bond between the ethylene molecule and the metal ion may be considered as a dative σ bond to an available orbital on the metal. The bonding scheme is analogous to that in carbon monoxide complexes in which there is a ligand metal σ donation and a reciprocal metal to ligand π bonding. The extent of back bonding varies depending on the metal, the substituents on ethylene, and the other ligands on the metal,

K $[PtCl_3(\eta^2 - C_2H_4)]$



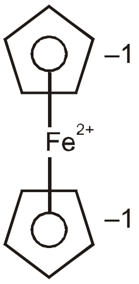


Ferrocene and bis(benzene)chromium **:**

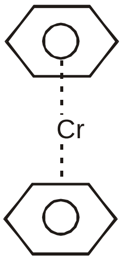
Ferrocene obeys 18-electrons rule. Depending on the electron counting method adopted, the cyclopentadienyl ligand may be viewed as either a five electron donor (neutral atom) or a six electron donor (oxidation state).

Similarly, the benzene ligand may be viewed as a six electron donor in neutral atom as well as in the oxidation state. Ferrocene show thermal stability and is not oxidised by air.

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



and $Cr(\eta^6 - C_6H_6)_2$



* For the π-donors, the prefix like η^x is to be used, where η indicates π-electron donation and x is known as the hapticity of the ligand, i.e. the number of atoms involved in the π-donation. For example:
(i) π-$C_5H_5^-$: η^5 – cyclopentadienyl or pentahaptocyclopentadienyl
(ii) π-$C_3H_5^-$: η^3 – allyl or trihaptoallyl

Applications of coordination and 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 :
ethylenediaminetetraaceticacid (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.

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. Give the order of chelating effect of following ligands.
(i) $C_2O_4^{2-}$ (ii) EDTA (iii) dien
(A) iii > ii > i (B) i > ii > iii (C) ii > iii > i (D) i > iii > ii

Ans. (C)

Sol. As number of donor atoms increases the number of bonds increase. So the chelating effect of ligands increase as oxalato, dien and EDTA has two, three and six donor atoms respectively.

2. Write the structural formula corresponding to each of the following IUPAC names :
(a) potassium tetracyanidozincate (II) (b) tetracarbonyl nickel (0)
(c) potassium tetracyanonickelate (0) (d) potassium tris(oxalato)aluminate (III)

Ans. (a) $K_2[Zn^{II}(CN)_4]$ (b) $[Ni^0(CO)_4]$ (c) $K_4[Ni^0(CN)_4]$ (d) $K_3[Al^{III}(C_2O_4)_3]$

Sol. Refer IUPAC rule.

3. Write IUPAC names of the following :
(a) $[Cr(acac)_3]$ (b) $[V(H_2O)_6]Cl_3$ (c) $(NH_4)_3[Co(C_2O_4)_3]$ (d) $K_2\,[CrO_4]$

Ans. (a) tris (acetylacetonato) chromium(III)
(b) hexaaquavanadium (III) chloride
(c) ammonium tris(oxalato)cobaltate(III) or ammonium trioxalatocobaltate(III)
(d) potassium tetraoxidochromate(VI)

Sol. Refer IUPAC nomenclature rule.

4. A solution containing 0.319 g of complex $CrCl_3.6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 ml of 0.125 M NaOH. The correct formula of the complex will be: [molecular weight of complex = 266.5]
(A) $[CrCl(H_2O)_5]Cl_2\ .\ H_2O$ (B) $[Cr(H_2O)_6]Cl_3$
(C) $[CrCl_2(H_2O)_4]Cl.\ 2H_2O$ (D) All are correct

Ans. (B)

Sol. $Cl^- = HCl = NaOH$

$nCl^- + nH^+ \longrightarrow nHCl$
Thus 1 mol of complex will form n mol of HCl
1 mole of complex = n mol of HCl = n mole of NaOH

mole of complex = $\dfrac{0.319}{266.5}$ = 0.0012; mole of NaOH used = $\dfrac{28.5 \times 0.125}{1000}$ = 0.0036

So 0.0012 mole of complex = 0.0036 mole of NaOH = 0.0036 mole of HCl

1 mole of complex = $\dfrac{0.0036}{0.0012}$ = 3 mole of HCl

$\therefore \quad n = 3$

So complex is $[Cr(H_2O)_6]Cl_3$.

5. Calculate the effective atomic number of the metal atoms in the following complexes / complex ions.

(a) $[Cr(CO)_6]$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Co(CN)_6]^{4-}$ (d) $[Ni(NH_3)_6]^{2+}$

[Cr = 24 ; Fe = 26; Co = 27 and Ni = 28 as atomic numbers]

Ans. (a) 36 (b) 35 (c) 37 (d) 38

Sol. EAN = Number of electrons in metal atom or ion + Number of electrons donated by ligands to metal.

(a) $[Cr^0(CO)_6]$; EAN = 24 + 12 = 36 ; (b) $[Fe^{III}(CN)_6]^{3-}$; EAN = 23 + 12 = 35

(c) $[Co^{II}(CN)_6]^{4-}$; EAN = 25 + 12 = 37 ; (d) $[Ni^{II}(NH_3)_6]^{2+}$; EAN = 26 + 12 = 38

6. Consider the following complexes :

(i) K_2PtCl_6 (ii) $PtCl_4 \cdot 2NH_3$ (iii) $PtCl_4 \cdot 3NH_3$ (iv) $PtCl_4 \cdot 5NH_3$

their electrical conductance in aqueous solutions are :

(A) 256, 0, 97, 404 (B) 404, 0, 97, 256 (C) 256, 97, 0, 404 (D) 404, 97, 256, 0

Ans. (A)

Sol. The electrical conductance of the complexes depend upon the number of ions given by them in the aqueous solutions.

(i) $K_2[PtCl_6] \overset{aq}{\rightleftharpoons} 2K^+ (aq) + [PtCl_6]^{2-} (aq)$ (ii) $[Pt(NH_3)_2Cl_4] \overset{aq}{\rightleftharpoons} [Pt(NH_3)_2Cl_4] (aq)$

(iii) $[Pt(NH_3)_3Cl_3]Cl \overset{aq}{\rightleftharpoons} [Pt(NH_3)_3Cl_3]^+ (aq) + Cl^- (aq)$ (iv) $[Pt(NH_3)_5Cl]Cl_3 \overset{aq}{\rightleftharpoons} [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$

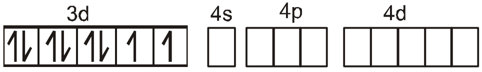
	Complex	**Number of ions**	**Expected electrical conductance**
(i)	$K_2[PtCl_6]$	3	256
(ii)	$[Pt(NH_3)_2Cl_4]$	0	0
(iii)	$[Pt(NH_3)_3Cl_3]Cl$	2	97
(iv)	$[Pt(NH_3)_5Cl]Cl_3$	4	404

7. Explain the following :

(i) All the octahedral complexes of Ni^{2+} must be outer orbital complexes.

(ii) $[CoF_6]^{3-}$ is paramagnetic but $[Co(CN)_6]^{3-}$ is diamagnetic.

Sol. (i) Ni^{2+} configuration

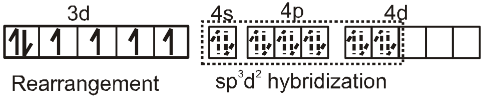


During rearrangement only one 3d-orbital may be made available for pairing of the electrons.

Thus, d^2sp^3 hybridization is not possible. So only sp^3d^2 (outer) hybridization can occur.

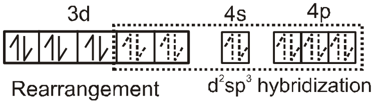
(ii) In $[CoF_6]^{3-}$, Co^{3+} undergoes sp^3d^2 hybridization. Four d-orbitals are singly occupied. Hence, it is paramagnetic.

$[CoF_6]^{3-}$



In $[Co(CN)_6]^{3-}$, Co^{3+} undergoes d^2sp^3 hybridization. All electrons are paired and thus it is diamagnetic.

$[Co(CN)_6]^{3-}$



8. You are given the following two complexes X and Y which are isomers of each other; X is Hg $[Co(SCN)_4]$. It is further given that ‘spin only’ magnetic moment of X is found to be 3.78 B.M. and that of Y is 1.73 B.M. Then which of the following is correct ?

(A) Anion of X will be tetrahedral and that of Y will be square planar.

(B) Anion of X will be square planar but that of Y will be tetrahedral

(C) Both the anions will be tetrahedral

(D) Both the anions will be square planar

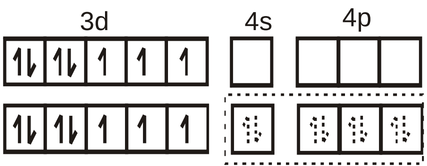
Ans. (A)

Sol. In Hg $[Co(SCN)_4]$ (X), the cobalt is in +2 oxidation state.

$\mu = \sqrt{n(n+2)}$; So, 3.78 B.M = $\sqrt{n(n+2)}$ or n = 3.

Co^{2+}, [Ar] $3d^7$

$[Co(SCN)_4]^{2-}$

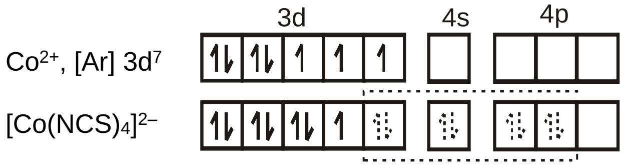


sp^3 hybrid orbitals

Four pairs of electrons from four SCN^- ions.

In Hg $[Co(NCS)_4]$ (Y), the cobalt is in +2 oxidation state. Further 'spin only' magnetic moment of complex,

$Hg[Co(NCS)_4]$ is 1.73 B.M. So, $\mu = \sqrt{n(n+2)}$; So, 1.73 B.M = $\sqrt{n(n+2)}$ or n = 1.



dsp^2 hybrid orbitals

Four pairs of electrons from four NCS^- ions.

So, X is tetrahedral and Y is square planar.

9. All the following complexes show a decreases in their weights when placed in a magnetic balance. Then which of the these has square planar geometry ?

(A) $Ni(CO)_4$ (B) $K[AgF_4]$ (C) $Na_2[Zn(CN)_4]$ (D) None of these

Ans. (B)

Sol. In K $[AgF_4]$, Ag(III) has $4d^8$ configuration. This has higher CFSE which favours pairing of electrons and thus complex is diamagnetic and square planar.

10. It is an experimental fact that $Cs_2[CuCl_4]$ is orange coloured but $(NH_4)_2[CuCl_4]$ is yellow. It is further known that total paramagnetic moment of a unpaired electron is due to spin as well as due to nature of orbital; 'd' orbital contributing more than 's' or 'p'. Thus the total paramagnetic moment of orange compound is found to be more than that of yellow compound. Then which of the following is correct ?

(A) Anion of orange compound is tetrahedral and that of yellow is square planar

(B) Anion of orange compound is square planar and that of yellow is tetrahedral

(C) Both the anions are tetrahedral

(D) Both the anions are square planar

Ans. (A)

Sol. Cs_2 $[CuCl_4]$ (orange) is tetrahedral because in Cu(II) the unpaired electron is in 3d. But $(NH_4)_2$ $[CuCl_4]$ (yellow) is square planar because the unpaired electron is not in 3d rather in some promoted state 's' or 'p'.

11. It is an experimental fact that : DMG + Ni(II)salt + $NH_4OH \longrightarrow$ Red precipitate

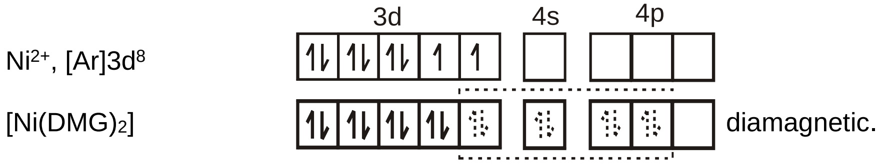
Which of the following is wrong about this red precipitate?

(A) It is a non–ionic complex. (B) It involves intra molecular H–bonding.

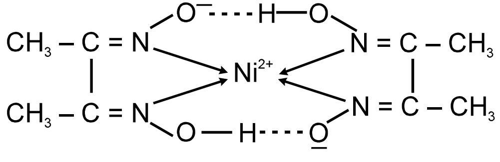
(C) Ni(II) is sp^3 hybridised. (D) It is a diamagnetic complex.

Ans. (C)

Sol. In complex $[Ni(DMG)_2]$, the nickel is in +2 oxidation state ; the ion has the electronic configuration $3d^8$ and dimethylglyoxime is a chelating ligand. So, the hybridisation scheme is as shown in figure.



dsp^2 hybrid orbitals



square planar

12. The correct order for the CFSE (numerical value) for the following complexes is :

Complex	P	Q	R	S
Formula	$[CoF_6]^{3-}$	$[Co(CN)_6]^{3-}$	$[Co(NH_3)_6]^{3+}$	$[Co(H_2O)_6]^{3+}$

(A) P > Q > R > S (B) Q > R > S > P (C) S > R > P > Q (D) R > Q > P > S

Ans. (B)

Sol. CFSE depends on the relative magnitude of crystal field splitting, Δ_o and pairing energy, p and in turns Δ_o depends upon the field produced by ligand and charge on the metal ion. So,the order of increasing crystal field strength is $F^- < H_2O < NH_3 < CN^-$. (Co is in +3 oxidation state in all complexes).
Thus the (B) option is correct.

13. Which of the following statements is not correct ?
(a) $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have same value of CFSE
(b) $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have same value of magnetic moment
(A) Only a (B) Only b (C) Both a and b (D) None of these

Ans. (A)

Sol. (a) Ammonia is a stronger field ligand than water. So $[Ni(NH_3)_6]^{2+}$ will have higher CFSE than $[Ni(H_2O)_6]^{2+}$.
(b) Both complexes $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have sp^3d^2 hybridisation with two unpaired electrons. So, they possess same magnetic moment ('spin only')

14. **Statement-1 :** $[Co^{II}(NH_3)_6]^{2+}$ is not readily oxidized to $[Co^{III}(NH_3)_6]^{3+}$ when air is bubbled through it.
Statement-2 : Crystal field stabilization energy of Co(+III) with a d^6 configuration is higher than for Co(+II) with a d^7 arrangement.
(A) Statement-1 is true, statement-2 is true; statement-2 is a correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

Ans. (D)

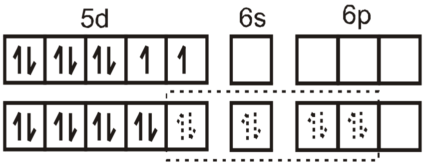
Sol. Statement 1 is false statement. $[Co^{II}(NH_3)_6]^{2+}$ is readily oxidised in $[Co^{III}(NH_3)_6]^{3+}$ in presence of air due to the higher CFSE value ($-2.4\Delta_o$) of d^6 configuration than d^7 configuration ($-0.8\ \Delta_o$).

15. Which of the following is true about the complex $[PtCl_2(NH_3)(OH_2)]$? [Atomic number of Pt = 78]
(i) It will have two geometrical isomeric forms, cis and trans.
(ii) The hybridisation state of Pt(II) is sp^3.
(iii) It is a square planar complex. (iv) It is a diamagnetic complex.
(v) It can show hydrate isomerism. (vi) It is a tetrahedral complex.
(A) (i), (iii),(iv) (B) (ii),(iv),(v) (C) (ii),(v),(vi) (D) (i),(v),(vi)

Ans. (A)

Sol. Pt^{2+}, $[Xe]4f^{14}\,5d^8$

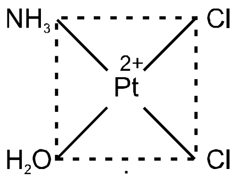
$[PtCl_2(NH_3)(OH_2)]$



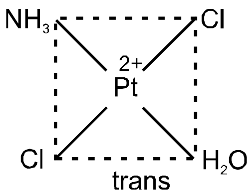
diamagnetic

dsp^2 hybrid orbitals
Four pairs of electrons from four Cl^- ions.

Ma_2bc have cis- and trans isomers.



cis



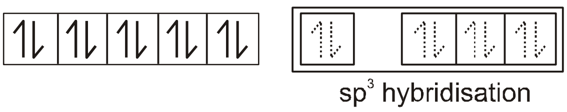
trans

16. Among $[Ni(CN)_4]^{4-}$, $[Ni(PPh_3)_3Br]$ and $[Ni(dmg)_2]$ species, the hybridisation states of the Ni-atoms are respectively :
(A) dsp^2, dsp^2, sp^3 (B) sp^3, sp^3, dsp^2 (C) sp^3, dsp^2, dsp^2 (D) dsp^2, sp^3, dsp^2

Ans. (B)

Sol. $[Ni(CN)_4]^{4-}$ - Ni is in zero oxidation state. The CN^- is strong field ligand and, therefore, rearrangement of electrons occur.

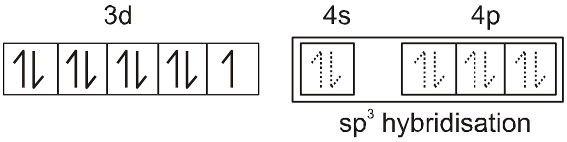
So, $[Ni(CN)_4]^{4-}$



sp^3 hybridisation

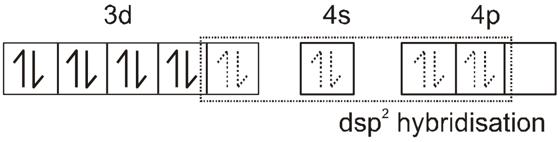
$[Ni(PPh_3)_3Br]$ - Ni is in +1 oxidation state with $3d^9$ configuration (PPh_3 is a strong field ligand).

So, $[Ni(PPh_3)_3Br]$



$[Ni(dmg)_2]$ - Ni is in +2 oxidation state with $3d^8$ configuration. (dmg is a chelating ligand).

So, $[Ni(dmg)_2]$



17. For the reaction $Ni^{2+} + 4NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$; at equilibrium, if the solution contains $1.6 \times 10^{-4}\%$ of nickel in the free state, and the concentration of NH_3 at equilibrium is 0.5 M. Then the instability constant of the complex will be approximately equal to :

(A) 1.0×10^{-5} (B) 1.5×10^{-16} (C) 1.0×10^{-7} (D) 1.5×10^{-17}

Ans. (C)

Sol. $Ni^{2+} + 4\,NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$ $\quad \therefore \quad k = \dfrac{[Ni(NH_3)_4]^{2+}}{[Ni^{2+}]\,[NH_3]^4}$

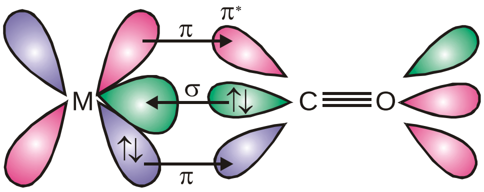
But $\dfrac{[Ni^{2+}]}{[Ni^{2+}] \; + [Ni(NH_3)_4]^{2+}} = 1.6 \times 10^{-6}$

or $\dfrac{Ni^{2+}}{[Ni(NH_3)_4]^{2+}} \approx 1.6 \times 10^{-6}$ $\quad \therefore \quad k = \dfrac{10^6}{1.6 \times (0.5)^4} = 10^7$

Hence instability constant = 10^{-7}

18. In metal carbonyls the metal carbon bond length is found to be less than the expected bond length. Explain why ?

Sol. It is due to synergic interaction between metal and CO which develops partial double bond character between metal and CO.



Synergic bonding

19. π-bonding is not involved in :

(A) ferrocene (B) dibenzenechromium

(C) Zeise's salt (D) Grignard's reagent

Ans. (D)

Sol. RMgX i.e. Grignard's reagent is σ bonded complex.

20. Wilkinson's catalyst contains :

(A) rhodium (B) iron (C) aluminium (D) cobalt

Ans. (A)

Sol. Wilkinson's catalyst is $[Rh(I)Cl(PPh_3)_3]$. So it contains rhodium.