09

Coordination Compounds

We have already discussed in the last chapter that one of the important characteristic of the transition metals is their ability to form complexes which are known as coordination compounds. These are chemical compounds that consist of metal atom or ion surrounded by anions, neutral molecules or sometime positive molecules (known as ligands) through coordinate bonds.

IN THIS CHAPTER ....

Double Salts and Complex Compounds

(i) **Doble salt** (Compounds which loose their identity in solution) In aqueous solution, these compounds break down into simpler ions, thus, exhibit the properties of their constituent, e.g. an aqueous solution of carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ shows the properties of K^+, Mg^{2+} and Cl^- simpler ions. Such compounds, which loose their identity in solution, are called **'double salts.'** They only exist in the crystalline state. Some other examples of double salts are potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and Mohr salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

(ii) **Complex compounds** (Compounds which retain their identity in solution) In aqueous solution, these compounds do not furnish all simple ions but instead give more complex ions having complicated structure, e.g. potassium ferrocyanide does not give properties of simple K^+, Fe^{2+} and CN^- ions but gives the properties of K^+ ions and complex ferrocyanide ions, $[Fe(CN)_6]^{4-}$. In other words, in these compounds, the **complex ions** retain their identity in the solution which is different from their constituents. Other example of coordination compounds are $[Co(NH_3)_6]Cl_3$, $K_2[PtCl_6]$, etc.

Actually, complexes or coordination compounds are the result of acceptance of lone pair of electrons of ligands by the empty orbitals of the metal atom or ion.

Difference between Double Salt and Complex Compounds

Double salt	Complex compound
They exist only in the solid state. In aqueous solution, they dissociate completely into ions.	They exist in solid state as well as in aqueous solution, because the complex ion does not dissociate into ions.
They usually contain two simple salts in equimolar proportions.	The simple salts from which they are formed may or may not be in equimolar proportions.
They are ionic compounds and do not contain any coordinate bond.	They may or may not be ionic but the complex part always contains coordinate bonds.
The metal ions show their normal valency.	The metal ion satisfies its two types of valencies called primary and secondary valencies.
They lose their identity in the solution.	They retain their identity in the solution.
The properties of double salts are same as those of their constituent compounds.	The properties of these compounds are different from its constituents.

Terminology Used in Coordination Compounds

The important terms used to define a complex completely are as follows

1. Complex Ions

A complex ion may be defined as an electrically charged entity which is formed by the combination of a simple cation with one or more neutral molecules or one or more simple anions or in some cases positive groups also. It exists as a single entity and is usually indicated within square bracket, i.e. [ ].

e.g. $[Cu(NH_3)_4]^{2+}$ is a complex ion, which is formed by the combination of four neutral molecules of ammonia with a simple Cu^{2+} cation.

Similarly, $[Fe(CN)_6]^{4-}$ is a complex ion formed by the combination of six CN^- anions with a simple Fe^{2+} cation. In nitroprusside ion, $[Fe(CN)_5NO]^{2+}$, five CN^- ions and one NO^+ (a positively charged ligand) ion are coordinated to Fe^{2+} ion.

The complex ion carrying a positive charge, e.g. $[Cu(NH_3)_4]^{2+}$, is called **cationic complex.**

The one with a negative charge e.g. $[Fe(CN)_6]^{4-}$ is called **anionic complex**. The one with no charge, e.g. $[PtCl_2(NH_3)_2]$ is called a **neutral complex.**

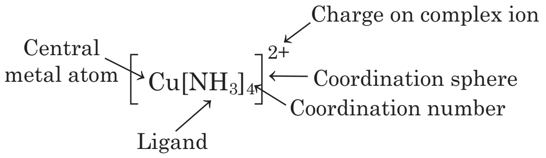
Homoleptic complex have only one type of ligands linked to the central metal atom/ion. e.g. $[Co(NH_3)_6]^{3+}$.

Heteroleptic complex have more than one type of ligands linked to the central metal atom/ion, e.g. $[Co(NH_3)_4Cl_2]$.

Remember Complex ions do not give tests of their constituent ions. e.g. $[Cu(NH_3)_4]^{2+}$ does not give test of Cu^{2+} or NH_3.

2. Representation of a Complex Ion

The terms such as ligand, central metal, charge on complex ion and coordination number can be illustrated as,



A complex Ion

3. Ligands

The central metal ion is surrounded by a number of the anions or the neutral molecules or sometimes positively charged ions possessing at least one lone pair. These surrounded ions are called **ligands.**

The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage. In the formation of coordination complexes, the ligands act as the **electron-pair donors** or **Lewis bases.**

e.g. In the complex ions $[Cu(NH_3)_4]^{2+}$ and $[Fe(CN)_6]^{4-}$, NH_3 and CN^- are the ligands. Ligands invariably contain one or more atoms (called **donor atoms**) having lone pairs of electrons.

The number of donor groups, from a given ligand, attached to the same central atom, is called the **denticity of the ligand.** Ligands like NH_3, CH_3NH_2, PH_3 can form only one coordinate bond with the central metal ion. So, their denticity is one. $H_2N—CH_2—CH_2—NH_2$, $NH_2CH_2COO^-$ have two donor atoms in each molecule or ion and each can form two coordinate bonds with the central metal ion and hence, their denticity is two.

Depending upon the number of donor atoms (or sites), the ligands may be classified into various categories as follows

(i) Unidentate or Monodentate Ligands

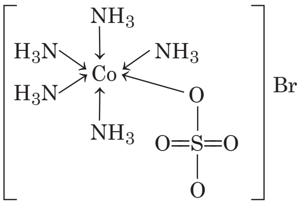
These ligands contain only one donor atom (or site) which is capable of donating an electron pair and thus, attach to the central metal ion only at one point, e.g. CN^-, F^-, Cl^-, Br^-, OH^-, H_2O, NH_3, NO_2^-, C_5H_5N (pyridine) etc.

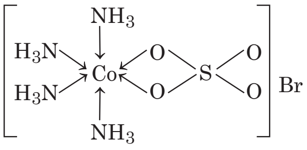
(ii) Polydentate or Multidentate Ligands

Ligands containing two or more such atoms which can simultaneously serve as donor atoms are called **polydentate or multidentate ligands.** Such ligands attach to the central metal ion at more than one point. Polydentate ligands with two donor sites are called bidentate, and with three, four, five and six donor sites are called tri (or ter), tetra (or quadri), penta and hexa-(or sexi) dentate ligands respectively.

Certain polydentate ligands have flexi dentate character, i.e. they do not use all the donor atoms to form a complex e.g. EDTA is a hexadentate ligand but it can also act as a pentadentate or a tetradentate ligand.

Remember Some ligands like SO_4^{2-} ion etc., can act both as a monodentate as well as a bidentate ligand. This is clear from the following examples.

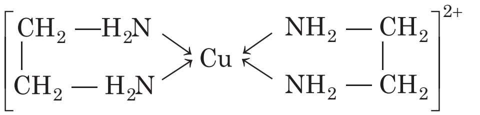

SO_4^{2-} as monodentate


SO_4^{2-} as bidentate

(iii) Chelating Ligands

Polydentate ligands, the structures of which permeates the attachment of two or more donor sites at the terminals of a chain to the same metal ion simultaneously thus, closing one or more rings are called **chelating ligands** and the compounds formed are known as **chelate compounds.**

Thus, a chelate may be defined as a ring structure formed by the combination of a polydentate ligand having two or more donor atoms at the terminals with a metal ion forming part of the ring. The process of formation of chelates is called **chelation.**


Chelate formation

Chelate complexes are more stable than ordinary complexes in which the ligand is monodentate. This increased stability of the compound due to chelation is called the chelate effect.

Generally, the chelate complexes with five or six membered rings are more stable. Out of these, five membered rings are very stable when these involve saturated ligands.

On the other hand, six membered ring structures acquire maximum stability when these involve unsaturated ligands containing conjugate double bonds. This is due to the resonance effects involving metal d-orbitals and ligand π-orbital electrons.

The stability of the chelate complex is explained on the basis of **entropy effect.**

When one end of en (ethylenediamine) is coordinated, the probability of the coordination of the other end is high because this end is bound to stay close to the cation. This shows that it is easier to form a chelate ring than coordinate to two independent molecules.

Thermodynamically, the increased stability due to chelation can be attributed to an increase in the degree of freedom of the system. A large entropy change but only small heat of reaction generally accompany the chelation process.

The complex compound having maximum number of rings formed with the ligands, is most stable. A complex $[M(\text{en})_3]^{3+}$ is less stable than a complex $[M(\text{EDTA})]^-$ because in the former there are three rings while, the latter involves five rings.

Example 1. *The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?* ***(NCERT Exemplar)***

(a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

Sol. (c) $(C_2O_4)^{2-}$ is a chelating agent $\left[\begin{array}{l}\text{COO}^-\\ |\\ \text{COO}^-\end{array}\right]$, so its complex is more stable than the other given, due to chelation.

(iv) Ambidentate Ligands

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

$M \leftarrow NO_2$ (Nitro) $M \leftarrow ONO$ (Nitrito)
$M \leftarrow CN$ (Cyano) $M \leftarrow NC$(Isocyano)
$M \leftarrow SCN$ (Thiocyano) $M \leftarrow NCS$ (Isothiocyano)

(v) Bridging Ligands

Certain ligands like N_2, $NH_2—NH_2$, NH_2^-, NH^{2-}, O^{2-}, Cl^-, SO_4^{2-}, NO_2 etc., can act as bidentate ligands when these are attached to two separate metal atoms making a bridge between them.

Such ligands are called bridging ligands and the complex formed is given the name as bridged complex. A bridging ligand must have at least two lone pairs of electrons which the ligand uses to get coordinated to two or more metal atoms.

Ligands having no lone pair of electrons : certain ligands have no lone pair of electrons but have π-bonding electrons. Such ligands are $H_2C{=}CH_2$, benzene, cyclopentadienyl ion etc.

4. Central Metal Atom or Ion

Every complex ion contains a metal atom or ion to which one or more neutral molecules or ions are attached. This is known as the **central metal atom** or **ion.** It is sometimes known as the **nuclear atom.** In a complex, the central metal atom or ion behaves as the **electron pair acceptor** or **Lewis acid.**

5. Coordination Sphere

The central atom and ligands which are directly attached to it, are enclosed in square brackets, called the coordination sphere. The ligands and the metal atom shown inside the square bracket actually behave as a single constituent unit.

The bonding between the central metal ion/atom, and the ligands in its coordination sphere is non-ionisable. The part outside coordination sphere is called ionisation sphere.

6. Coordination Number

The total number of ligands attached to the central metal ion through coordinate bond is called the **coordination number** (CN) of the metal ion. e.g. In the complex ion $[Cu(NH_3)_4]^{2+}$, the coordination number of Cu^{2+} is 4 and that of Fe^{2+} ion in $[Fe(CN)_6]^{4-}$ is 6.

The coordination numbers of most common metals are 4 and 6. $Ag^+, Pt^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{3+}$ and Pt^{4+} ions show only one coordination number, Ag^+ shows C.N. = 2, Pt^{2+} CN = 4 and Cr^{3+} $Fe^{2+}, Fe^{3+}, Co^{3+}$ and Pt^{4+} show C.N. = 6 only.

In case of polydentate ligands,

Coordination number = No. of ligand × its denticity

e.g. In $[CoBr_2(en)_2]^+$. CN w.r.t. Br = 2

CN w.r.t. en = 2 × 2 = 4

Total CN = 2 + 4 = 6

7. Oxidation Number or Oxidation State

It is a number that represents an electric charge in which a metal atom or ion has or appears to have when combined with ligands.

e.g. Oxidation number of copper in $[Cu(NH_3)_4]^{2+}$ is +2 but its coordination number is 4. Similarly, the oxidation number of Fe in $[Fe(CN)_6]^{4-}$ is +3 but its coordination number is 6.

8. Charge on the Complex Ions

The charge carried by a complex ion is the algebraic sum of the charges carried by central metal ion and the ligands coordinated to the central metal ion.

e.g. In the complex ion, $[Ag(CN)_2]^-$, Ag ion carries a charge of +1. Therefore, the net charge on the complex ion $[Ag(CN)_2]$ is $+1-2=-1$.

Similarly, in the complex ion, $[Cu(NH_3)_4]^{2+}$, Cu ion carries charge equal to +2 and as NH_3 molecules are neutral, therefore, the net charge on the complex is +2.

9. Effective Atomic Number [EAN]

In order to explain the stability of the complex **Sidgwick** proposed effective atomic number abbreviated as EAN, which is defined as the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligand.

The effective atomic number (EAN) generally coincides with the atomic number of next inert gas except in some cases.

Calculation of EAN EAN can be calculated by the following relation,

EAN = Z (atomic number of the metal) – number of electrons lost in the ion formation + number of electrons gained from the donor atoms of the ligands

EAN of Some Species

Complex	Oxidation state of metal ion	Atomic number of metal (Z)	Coordination number	Effective atomic number
$[Co(NH_3)_6]Cl_3$	+3	27	6	$(27-3)+(6\times2)$ = 36 (Kr)
$K_4[Fe(CN)_6]$	2	26	6	$(26-2)+(6\times2)$ = 36 (Kr)
$Ni[CO]_4$	0	28	4	$(28-0)+(4\times2)$ = 36 (Kr)
$K_2[PtCl_6]$	+4	78	6	$(78-4)+(6\times2)$ = 86 (Rn)
$K_3[Fe(CN)_6]$	+3	26	6	$(26-3)+(6\times2)$ = 35

Example 2. *The pair having the same magnetic moment is* [*at. no.* Cr = 24, Mn = 25, Fe = 26 and Co = 27] ***[JEE Main 2016 (offline)]***

(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
(c) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$
(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

Sol. (a)

Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (n)	
$[Cr(H_2O)_6]^{2+}$	Cr^{2+} ; [Ar] $3d^4$	↑ ↑ ↑ ↑ □	4
$[Fe(H_2O)_6]^{2+}$	Fe^{2+} ; [Ar] $3d^6$	↑↓ ↑ ↑ ↑ ↑	4
$[Mn(H_2O)_6]^{2+}$	Mn^{2+} ; [Ar] $3d^5$	↑ ↑ ↑ ↑ ↑	5
$[CoCl_4]^{2-}$	Co^{2+} ; [Ar] $3d^7$	↑↓ ↑↓ ↑ ↑ ↑	3

Werner's Theory

Werner proposed a theory called **Werner's coordination theory** for which he was awarded Nobel prize in 1913. It was the first successful theory, which explained the properties of complexes.

The main postulates of this theory are

- **Primary linkages** (valencies) **are ionisable** and are exhibited by a metal in the formation of its simple salts such as $CoCl_3$, $CuSO_4$ and AgCl.

  In these salts, the primary valencies of Co, Cu and Ag are 3, 2 and 1 respectively. Now a days, **primary valency** is referred to as **oxidation state** of the metal ion.
- **Secondary linkages** (valencies) **are non-ionisable** and are exhibited by a metal in the formation of its complex ions such as $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$.

  In these complexes, the secondary valencies of Co^{3+}, Cu^{2+} and Ag^+ are 6, 4 and 2 respectively. The secondary valency is also referred to as **coordination number** (CN) of the metal cation.

- Primary linkages (valencies) are satisfied by negative ions while, secondary linkages (valencies) can be satisfied by neutral molecules or negative ions or in some cases positive ions (ligands) also.
- Every metal atom or ion has a fixed number of secondary linkages. In other words, the coordination number of the metal atom is fixed. Thus, the coordination number gives the total number of neutral molecules of negative or positive groups, which may be directly linked to the metal cation in the formation of its complexes.
- Every metal has a tendency to satisfy both its primary and secondary linkages (valencies).
- The ligands satisfying secondary linkages (valencies) are always directed towards fixed positions in space about the central metal atom or ion. Thus, the coordination compounds have a definite geometry (structure or shape).

Werner's Representation

Consider the case of $CoCl_3 \cdot xNH_3$

where, maximum value of x = CN of Co(III) = 6

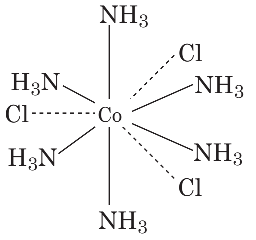
and minimum value of x = CN − ON = 3

Werner's Coordination Compounds

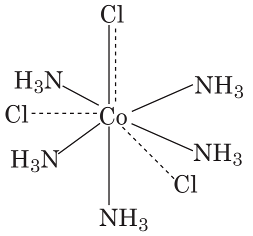
Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^-$	six (NH_3)	three (Cl^-)
$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+} + 2Cl^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with **dual nature**
$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+ + Cl^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with **dual nature**
$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3Cl_3]$ (single species)	three (NH_3) and three (Cl^-)	three (Cl^-) all with **dual nature**

From the table, it is clear that conduction of the complexes which depends on the number of ions will be in order

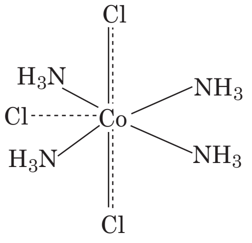
$$D < C < B < A$$



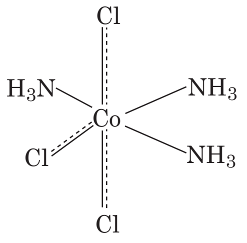
(A)



(B)



(C)



(D)

Example 3. *On treatment of* 100 mL *of* 0.1 M *solution of* $CoCl_3 \cdot 6H_2O$ with excess of $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is ***(JEE Main 2017)***

(a) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$

(b) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

(c) $[Co(H_2O)_6]Cl_3$

(d) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

Sol. (*d*) Molarity (M) $= \dfrac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$

∴ Number of moles of complex

$$= \frac{\text{Molarity} \times \text{volume (in mL)}}{1000} = \frac{0.1 \times 100}{1000} = 0.01\,\text{mol}$$

Number of moles of ions precipitate $= \dfrac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02$ mole

∴ Number of Cl^- present in ionisation sphere

$$= \frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}} = \frac{0.02}{0.01} = 2$$

∴ 2 Cl^- are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$.

IUPAC Nomenclature of Coordination Compounds

The various rules are applied in naming the coordination compounds according to the IUPAC (International Union of Pure and Applied Chemistry) system.

Order of Naming Ions

If the complex compound is ionic, the positive ion (cation) whether simple or complex, is named first followed by the negative ion (anion). e.g. $K[BF_4]$ ionises to K^+ and BF_4^- ions. Here cation (K^+) is simple and it is named first followed by anionic part. Thus, $K[BF_4]$ is named as potassium tetrafluoroborate (III). The complex $[Ag(NH_3)_2]Cl$ ionises as

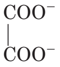
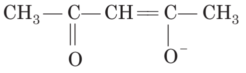
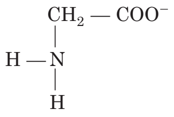
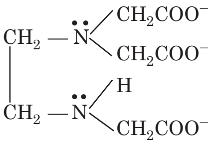
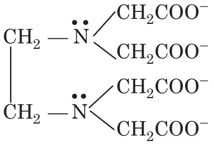
$$[Ag(NH_3)_2]Cl \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$$

Here, the cation $[Ag(NH_3)_2]^+$ is not a simple one but a complex. Therefore, it is named first and then the anionic part. Thus, $[Ag(NH_3)_2]Cl$ is named as diamminesilver (I) chloride. But one word name is given to non-ionic and molecular complexes.

Naming Ligands

The number of each kind of ligand is specified using the Greek **prefixes** like di, tri, tetra, penta, and hexa. The term mono is generally not mentioned. If the name of ligand itself is complex, i.e. it includes a numerical prefix. e.g. In case of organic molecules such as dipyridyl or ethylenediamine, then the terms **bis** (for two), **tris** (for three), **tetrakis** (for four), **pentakis** (for five), etc., are used followed by the name of the ligand placed without brackets. e.g. $[Cu(NH_3)_4]^{2+}$ is named as tetramminecopper (II) ion and $[Co(en)_3]^{3+}$ is named as tris (ethylenediamine) cobalt (III) ion.
Negative ligands are normally end in –o, e.g.

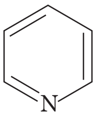
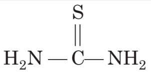
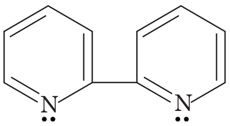
Different Negative Ligands, their Charge and Donor Atoms

	Name	Formula	Charge	Name of ligand in the complex	Donor atom/ atoms
Monodenate ligands with one unit negative charge	Halide ion	(X = Cl, Br, I)	–1	Halido	X
	Hydroxide ion	$:OH^-$	–1	Hydroxo	O
	Cyanide ion	$-C\equiv N$	–1	Cyano	C
	Isocyanide	$N^+\equiv C^-$	–1	Isocyano	N
	Nitro ion	NO_2^-	–1	Nitro	N
	Nitrito ion	ONO^-	–1	Nitrito	O
	Thiocyanate ion	SCN^-	–1	Thiocyanato	S
	Isothiocyanate ion	NCS^-	–1	Isothiocyanato	N
	Hydride ion	H^-	–1	Hydrido	H
	Amide ion	NH_2^-	–1	Amido	N
	Acetate ion	CH_3COO^-	–1	Acetato	O
	Nitrate ion	NO_3^-	–1	Nitrato	O
	Cyanate	ONC^-	–1	Cyanato	O
Monodentate ligands with two negative charges	Isocyanate	NCO^-	–1	Isocyanato	N
	Sulphate ion	SO_4^{2-}	–2	Sulphato	O
	Oxide ion	O^{2-}	–2	Oxo	O
	Peroxide ion	O_2^{2-}	–2	Peroxo	O
	Carbonate ion	CO_3^{2-}	–2	Carbonato	O
	Sulphite ion	SO_3^{2-}	–2	Sulphito	O
	Sulphide ion	S^{2-}	–2	Sulphido	S
Bidentate ligands with one/two negative charges	Thiosulphate ion	$S_2O_3^{2-}$	–2	Thiosulphato	S
	Imide ion	NH^{2-}	–2	Imido	N
	Oxalate ion (o*x)	 $\begin{array}{c}COO^-\\ \vert\\ COO^-\end{array}$	–2	Oxalato	Two O-atoms
	Acetyl acetonate (a*cac)	 $CH_3-\underset{\underset{O}{\Vert}}{C}-CH=\underset{\underset{O^-}{\vert}}{C}-CH_3$	–1	Acetyl acetonato	Two O-atoms
	Glycinate ion (g*ly)		–1	Glycinato	One N-atom and one O-atom
Polydentate ligands with high negative charges	Ethylenediamine triacetate ion (a pentadentate ligand)		–3	$EDTA^{3-}$	Two N-atoms and three O-atoms
	Ethylenediamine tetra-acetate ion (a hexadentate ligand)		–4	$EDTA^{4-}$	Two N-atoms and four O-atoms

* Symbol used

- **Neutral ligands** have no special ending e.g.

Neutral Ligands

	Name and symbol of ligand	Formula	Charge	Name of ligand on the complex	Donor atom
Neutral monodentate ligands	Ammonia	NH_3	Zero	Ammine	N
	Water	H_2O	Zero	Aqua	O
	Phosphine	PH_3	Zero	Phosphine	P
	Nitrogen oxide	NO	Zero	Nitrosyl	N
	Carbon monoxide	CO	Zero	Carbonyl	C
	Pyridine (py)	C_6H_5N or 	Zero	Pyridine	N
	Thiourea (tu)	 $H_2N-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2$	Zero	Thiourea	S
	Triphenyl phosphine	$(C_6H_5)_3P$	Zero	Triphenyl phosphone	P
	Thiocarbonyl	CS	Zero	Thiocarbonyl	S
	Ethylenediamine (en) (a bidentate ligand)	$NH_2CH_2CH_2NH_2$	Zero	Ethylene diamine	Two N-atoms
Neutral polydentate ligands	2,2-dipyridyl (dipy) (a bidentate ligand)		Zero	Dipyridyl	Two N-atoms
	Diethylene triamine (dien) (a tridentate ligand)	$NH_2CH_2CH_2NHCH_2CH_2NH_2$	Zero	Diethylene triamine	Three N-atoms
	Triethylene tetramine (trien) (a tetradentate ligand)	$NH_2(CH_2)_2NH(CH_2)_2$ $—NH — (CH_2)_2NH_2$	Zero	Triethylene tetramine	Four N-atoms

- **Positive ligands** (which are very few) end in -ium e.g.

Positive Ligands

Name and symbol of ligand	Formula	Charge	Name given in the complex	Donor atom
Nitronium ion	NO_2^+	+1	Nitronium	N
Nitrosonium ion	NO^+	+1	Nitrosonium	N
Hydrazinium ion	$NH_2NH_3^+$	+1	Hydrazinium	N

There should be no hyphen in between. In case, there are more than one negative or positive ligands, they are listed alphabetically. Thus, Cl^-, NO_2^- are written in the order as chlorido, nitro etc. IUPAC rules recommended that all ligands whether anions, neutral or positive be arranged alphabetically without any preference order. Some examples are as,

Formula of the complex	Old IUPAC name	Latest IUPAC name
$[PtCl(NO_2)(NH_3)_4]SO_4$	Chloronitrotetrammine platinum (IV) sulphate	Tetramminechloridonitro platinum (IV) sulphate
$[CoCl(NH_3)_4(H_2O)]Cl_2$	Chloroaquatetrammine cobalt (III) chloride	Tetrammineaquachloridocobalt (III) chloride

Certain ligands like NO can act as a neutral as well as unipositive (NO^+) ligand. In such case, it is very difficult to find the oxidation state and the charge on the ligand from the given formula of the complex.

Naming of the Complex Ion

While naming the complex ion, number and name of the ligands are given first, then the central metal atom followed by its oxidation state indicated by Roman numeral in parenthesis.

(i) **If the complex ion is a cation,** the name of the central metal ion is given as such followed by its oxidation state indicated by numerals (such as II, III, IV) in the parenthesis at the end of the name of the complex without a space between the two. Some examples are as follows

$[Ni(DMG)_2]$ Bisdimethylglyoximatonickel (II)

$[Pt(NH_3)_2Cl_4]$ Diamminetetrachloridoplatinum (IV)

(ii) **If the complex ion is an anion,** the name of the central atom, is made to end in –ate followed by the oxidation number in brackets without any space between them, e.g.

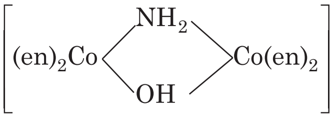
$Na_3[AlF_6]$ Sodium hexafluoridoaluminate (III)

$[Ag(CN)_2]^-$ Dicyanoargentate (I) ion

$[Pb(OH)_4]^{2-}$ Tetrahydroxoplumbate (II) ion

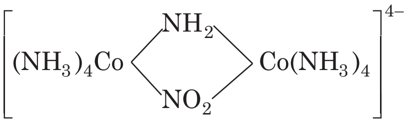
For an acid we have a characteristic ending, (ic) e.g. $H_4[Pt(CN)_6]$ Hexacyanoplatinic (II) acid. If the complex contains two or more metal ions, it is termed as polynuclear complex.

The ligands, which link the two metal atoms, are called bridge groups and are separated from the rest complex by hyphens and denoted by the prefix μ placed before their names, e.g.



$\left[(en)_2Co\begin{matrix}NH_2\\ OH\end{matrix}Co(en)_2\right](SO_4)_2$ is named as *bis* (ethylenediamine) cobalt (III) -μ -amido -μ -hydroxo *bis* (ethylenediamine) cobalt (III) sulphate

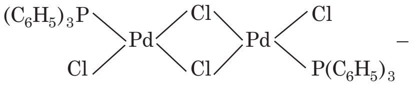
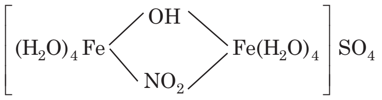
[It can also be named as tetrakis (ethylenediamine) μ-amido-μ-hydroxocobalt (III) sulphate.]

Similarly, 

$\left[(NH_3)_4Co\begin{matrix}NH_2\\ NO_2\end{matrix}Co(NH_3)_4\right]^{4-}$

is named as octaammine-μ-amido-μ-nitrodicobalt (III) ion It can also be named as [tetramminecobalt (III)-μ-amido-μ-nitrotetrammine cobalt (III) ion].

The following examples illustrates the nomenclature of complex

- $[Cr(H_2O)_4Cl_2]Cl$ – Tetraaquadichloridochromium (III) chloride
- $[Co(NH_3)_5CO_3]Cl$ – Pentaamminecarbonatocobalt (III) chloride
- $[Ag(NH_3)_2]Cl$ – Diamminesilver (I) chloride
- $[Co(en)_2Cl_2]_2SO_4$ – Dichloridobis (ethylenediamine) cobalt (III) sulphate
- $[Co(NH_3)_4(NO_2)Cl]NO_3$ – Tetraamminechloridonitrocobalt (III) nitrate
- $[Co(NH_3)_3(NO_2)_3]$ – Triamminetrinitrocobalt (III)
- $[Pt(NH_3)_6]Cl_4$ – Hexaammineplatinum (IV) chloride
- $[Cr(H_2O)_3(NH_3)_3]Cl_3$ – Triamminetriaquachromium (III) chloride
- $[CoF_2(en)_2]ClO_4$ – Bis (ethylenediammine) difluoridocobalt (III) perchlorate
- $Na_2[SiF_6]$ – Sodium hexafluoridosilicate (IV)
- $Fe_4[Fe(CN)_6]_3$ – Iron (III) hexacyanoferrate (II) or ferric hexacyanoferrate (II)
- $Na_2[CrF_4O]$ – Sodium tetrafluoridooxochromate (IV)
- $K[BF_4]$ – Potassium tetrafluoridoborate (III)
- $K_2[OsCl_5N]$ – Potassium pentachloridonitridoosmate (VI)
- $Ni(CO)_4$ – Tetracarbonyl nickel (0)
- $K_4[Ni(CN)_4]$ – Potassium tetracyanonickelate (0)
- $[Ni(dmg)_2]$ – Bis (dimethylglyoximato) nickel (II)
- $[Pt(NH_3)_2Cl_2]$ – Diamminedichloridoplatinum (II)
- $[Cr(PPh_3)(CO)_5]$ – Pentacarbonyltriphenylphosphinechromium (0)
- $[Co(NH_3)_4Cl_2]_3[Cr(CN)_6]$ – Tetraamminedichloridocobalt (III) hexacyanochromate (III)
- $[Pt(NH_3)_4Cl_2][PtCl_4]$ – Tetraammine dichloridoplatinum (IV) tetrachloridoplatinate (II)
- $[(NH_3)_5Cr — OH — Cr(NH_3)_5]Cl_5$ – Pentaamminechridomium (III)-μ-hydroxopentaamminechromium (III) chloride
-  – Chloridotriphenylphosphinepalladium (II)-μ-dichloro chloridotriphenylphoshinepalladium (II)
- $[(NH_3)_5Co — NH_2 — Co(NH_3)_5](NO_3)_5$ – Decammine-μ-amidodicobalt (III) nitrate
-  $\left[(H_2O)_4Fe\begin{matrix}OH\\ NO_2\end{matrix}Fe(H_2O)_4\right]SO_4$ – Octaaqua-μ-hydroxo-μ-nitrodiiron (III) sulphate
- $[Mn_3(CO)_{12}]$ – Dodecacarbonyltrimanganese (0)
- $[Fe(C_5H_5)_2]$ – Bis(cyclopentadienyl)iron (II) or ferrocene
- $[PtBrClI(NO_2)(NH_3)(Py)]$ – Amminebromidochloridoiodidonitropyridineplatinum (IV)
- $[VO(acac)_2]$ – Bis(acetylacetonato)oxovanadium (IV)
- $Na_3[Ag(S_2O_3)_2]$ – Sodium bis(thiosulphato) argentate (I)
- $Na_2[Ni(EDTA)]$ – Sodium ethylenediaminetetraacetatonickelate (II)
- $Hg[Co(SCN)_4]$ – Mercuric tetrathiocyanatocobaltate (II)

Remember During naming of ligands, when organic free radicals act as ligands, the ligands are named as usual, e.g. CH_3 as methyl, C_2H_5 as ethyl etc.

Formula Writing of Complexes

From the IUPAC name for writing the formula of complexes, following rules may be observed

- Cation whether simple or complex is written first followed by the anion.
- The order of formulating a complex ion is reverse to that adopted in naming, i.e. the central metal atom is written first followed by the ligand.
- When there are more than one type of ligands present these are named, alphabetically according to the first symbol of their formulae.
- Whole of the complex ion is enclosed in a square bracket.
- The charge on the complex species is equal to the charge on the central metal atom, i.e. its oxidation state plus the total charge carried by all the ligands coordinated to the metal atom thus the formula of tetraamminecopper (II) chloride is $[Cu(NH_3)_4]Cl_2$.

Example 4. *Which among the following will be named as dibromidobis- (ethylenediamine) chromium* (III) *bromide?*

(a) $[Cr(en)_3]Br_3$
(b) $[Cr(en)_2Br_2]Br$ ***(AIEEE 2012)***
(c) $[Cr(en)Br_4]^-$
(d) $[Cr(en)Br_2]Br$

Sol. (*b*) Two Br, two (en) and one Cr are parts of complex.

$$\text{Charge on the complex is } \left.\begin{array}{l} 2(\text{Br}) = -2 \\ 2(\text{en}) = \;\;0 \\ 1(\text{Cr}) = +3 \end{array}\right\} = +1$$

Thus, complex ion is $[Cr(en)_2Br_2]^+$.

Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]Br$.

Isomerism

It is a phenomenon, in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. These compounds are called **isomers.**

There are two main types of isomerism as seen in coordination compound namely

(i) Structural isomerism, (ii) Stereoisomerism

Structural Isomerism

Structural isomerism is mainly of the following types,

1. Ionisation Isomerism

Ionisation isomers yield different ions in solution although they have same composition. This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it, e.g. $[Co(NH_3)_5Br]SO_4$ is red-violet and in solution gives a precipitate of $BaSO_4$ with $BaCl_2$ confirming the presence of SO_4^{2-} ion. On the other hand, $[Co(NH_3)_5SO_4]Br$ is red, and does not give test for sulphate ion in the solution, but instead gives a precipitate of AgBr with $AgNO_3$.

Other examples are

(i) $[Pt(NH_3)_4(OH)_2]SO_4$ and $[Pt(NH_3)_4SO_4](OH)_2$
(ii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
(iii) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

2. Hydrate Isomerism

Since, water is one of the most effective coordinating agents, therefore the number of water molecules, which may enter into the coordination sphere, may vary resulting in the formation of hydrate isomers, e.g. there are three different hexa-hydrates of chromic chloride with an empirical formula of $CrCl_3 \cdot 6H_2O$.

One of these hydrates is violet and the other two are green in colour. All the three differ in the number of molecules of water in the coordination sphere. The formulae, which have been assigned to these hydrate isomers, are

$$[Cr(H_2O)_6]Cl_3$$

Violet (three ionic chlorine)

$$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$$

Bluish green (two ionic chlorine)

$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$$

Dark green (one ionic chlorine)

Similarly, other compounds in which hydrate isomerism is observed are

(i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl \cdot H_2O$
(ii) $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Cl \cdot Br]Br \cdot H_2O$

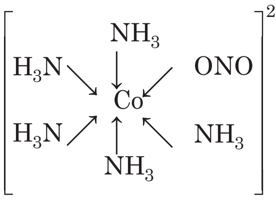
3. Linkage Isomerism

Isomerism of this type occurs when two or more atoms in a monodentate ligand may function as a donor i.e. when an ambidentate ligand is present.

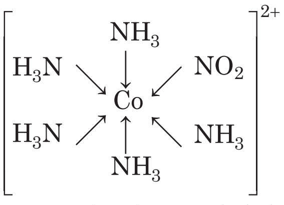
For example, in the case of NO_2^- ion either a nitrogen or an oxygen atom may act as donor giving two different isomers. Thus, two different isomers with molecular formula $[Co(NO_2)(NH_3)_5]^{2+}$ have been prepared.

One isomer has N-atom of NO_2 group linked to cobalt atom and the other has O-atom linked to cobalt.

This behaviour is analogous to the behaviour of organic nitrites *R*—ONO and nitro compounds *R*— NO_2. The two isomers are represented below



Pentaamminenitrito-O-cobalt (III) ion



Pentaamminenitro-N-cobalt (III) ion

4. Coordination Isomerism

This type of isomerism is possible when both positive and negative ions of a salt are complex ions.

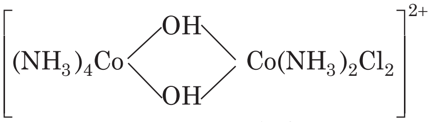
The two isomers differ in the **distribution of ligands** in the cation and the anion. Some important examples are

- $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
- $[Cr(NH_3)_6][Co(C_2O_4)_3]$ and $[Co(NH_3)_6][Cr(C_2O_4)_3]$

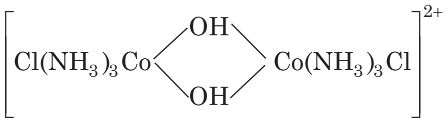
This type of isomerism may be caused by **interchange of ligand between the two complex ions.**

5. Coordination Position Isomerism

This type of isomerism is due to the difference in the distribution of ligands in two coordination centres. Generally, the bridged complexes involving different ligands show this isomerism. e.g.



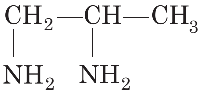
Unsymmetrical



Symmetrical

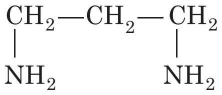
6. Ligand Isomerism

This isomerism arises in those complexes in which the two ligands are isomers themselves. e.g.



1,2-diamino propane

and



1,3-diamino propane

When these form the complexes, we get ligand isomers. e.g. $[Co(1,2\text{-diaminopropane})_2 Cl_2]^+$, $[Co(1,3\text{-diaminopropane})_2Cl_2]^+$. This type of isomerism is quite rare.

Stereoisomerism

This is due to the different relative positions of the ligands. It is of two types

- Geometrical isomerism,
- Optical isomerism

1. Geometrical Isomerism

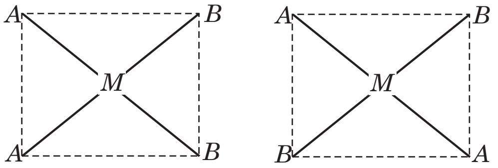
Geometrical isomers differ in the spatial distribution of atoms or groups about the central atom or atom in polynuclear compounds. Those complexes in which the identical two ligands occupy adjacent positions to each other or opposite to each other (*cis* or *trans* respectively) are able to show this isomerism.

This isomerism cannot be exhibited by coordination compounds having 2 or 3 coordination number as it is not possible to have more than a single arrangement of ligands in space around the central ion in these cases. Geometrical isomerism with respect to the metal has also not been found among **tetrahedral** complexes of type MA_4 or MA_3B or MA_2B_2 because all the four ligands are equidistant from each other.

Only square planar and octahedral complexes show this type of isomerism.

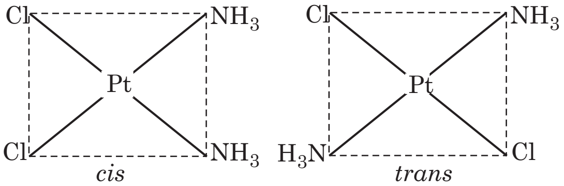
I. ***cis-trans* isomerism in square planar complexes are as follows**

(i) Any complex of the type MA_2B_2 can exist in *cis-trans* form.



cis *trans*

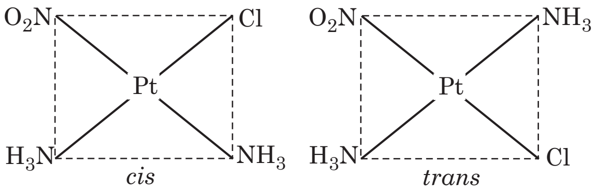
Dichlorodiammineplatinum (II), $[Pt(NH_3)_2Cl_2]$ can exist as under



cis *trans*

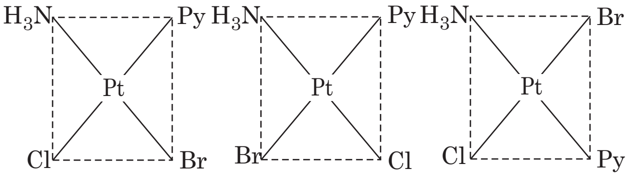
Remember Square planar complexes of the type $[M(AA)_2]$, MA_4, MA_3B and MAB_3 do not show this isomerism since, all possible spatial arrangements for any of these complexes are identical.

(ii) In a complex of the type MA_2BC, also there are *cis*- and *trans*-isomers, e.g. $[Pt(NH_3)_2ClNO_2]$ can exist as

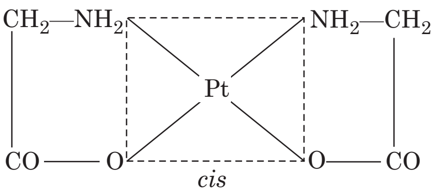


cis *trans*

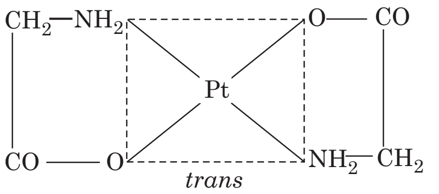
(iii) For a complex of the type *MABCD*, three geometrical isomers are possible, e.g. $[Pt(Py)(NH_3)BrCl]$ can exist as



(iv) The geometrical isomerism can also occur in square planar complexes if the chelate group is not symmetrical, e.g. complex of glycine (NH_2CH_2COOH) and platinum, i.e. $[Pt(gly)_2]$

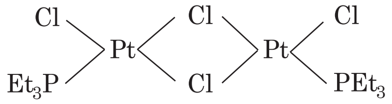


cis

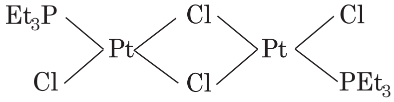


trans

(v) Geometrical isomerism is also shown by **bridged binuclear** planar complexes of the type, $M_2A_4X_2$, e.g. $[PtCl_2PEt_3]_2$



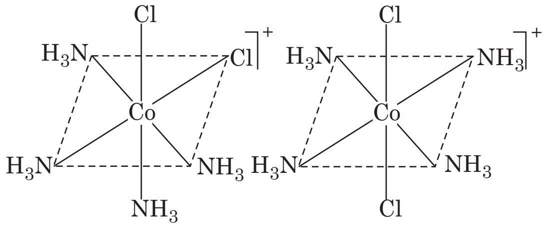
cis



trans

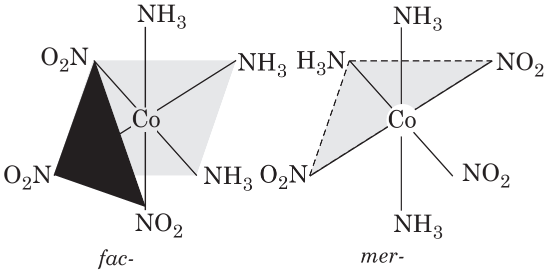
II. **Various octahedral complexes that show geometrical isomerism are as follows**

(i) Octahedral complexes of MA_4B_2 type show *cis-trans* isomerism, e.g. dichlorotetramminecobalt (III) complex ion, $[Co(NH_3)_4Cl_2]^+$ shows *cis-trans* isomerism as



cis (violet) *trans* (green)

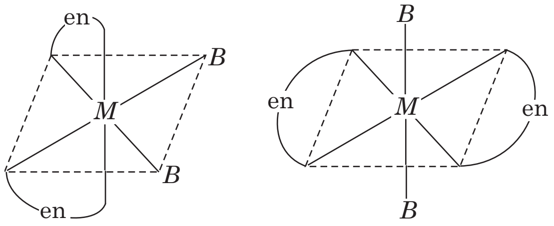
(ii) An another type of geometrical isomerism called by *fac*-and *mer*-isomerism also occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial** (*fac*) **isomer.** When the positions are around the meridian of the octahedron, we get **meridional** (*mer*) **isomer.**



fac- *mer-*

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

(iii) Even $M(AA)_2B_2$ type octahedral complexes also show *cis* and *trans* isomerism where, *A—A* can be any symmetrical bidentate ligand like ethylenediamine (en) and *B* can be any anionic ligand, such as Cl^-, CN^-, NO_2^- etc.



cis *trans*

An example of this type is $[Pt(en)_2Cl_2]$.

Octahedral complexes of $[MA_5\ B]$ or $M(AA)_3$ (where, AA = symmetrical bidentate ligand) do not exhibit geometrical isomerism.

(iv) Complexes having six different ligands $[M(ABCDEF)]$ shall exhibit geometrical isomerism. Theoretically, fifteen different isomers should be possible. In practice, three isomers of the complex $[Pt(C_5H_5N)(NH_3)(NO_2)(Cl)(Br)(I)]$ have actually been isolated.

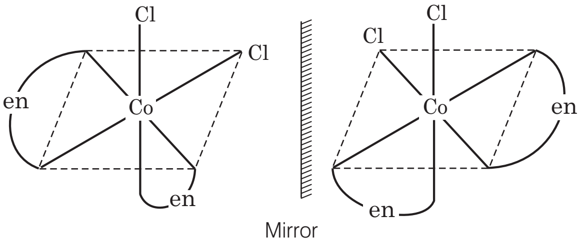
(v) As was observed in square planar complexes, unsymmetrical bidentate ligands also give rise to geometrical isomerism in octahedral complexes of the type $[M(AB)_3]$.

2. Optical Isomerism

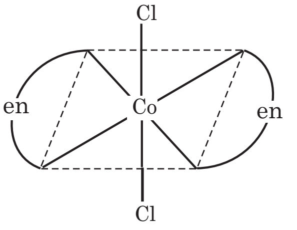
Optical isomerism arises when a compound can be represented by two asymmetrical structures (known as optical isomers). The two isomers are structurally the mirror images of each other (just as in the organic chemistry). Further, it has been found that these mirror image compounds are non-superimposable on each other and these do not possess the plane of symmetry.

Optical isomerism is common in octahedral complexes involving 2 or 3 symmetrical bidentate groups (i.e. a group attached to the central atom by two coordinate bonds of the type $[M(AA)_2X_2]$ and $[M(AA)_3]$ where, AA = bidentate ligand. This is illustrated as under :

(i) **Example of $M(AA)_2X_2$ type** *cis*-dichloridobis (ethylenediamine) cobalt (III) ion, $[Co(en)_2Cl_2]^+$, the *cis*-form of this complex is optically active and exists in *d* and *l*-forms. Its *trans* form is optically inactive due to the presence of a plane of symmetry as shown below.



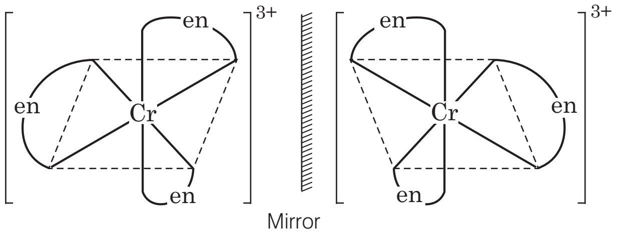
(a) optically active forms



(b) Optically inactive form

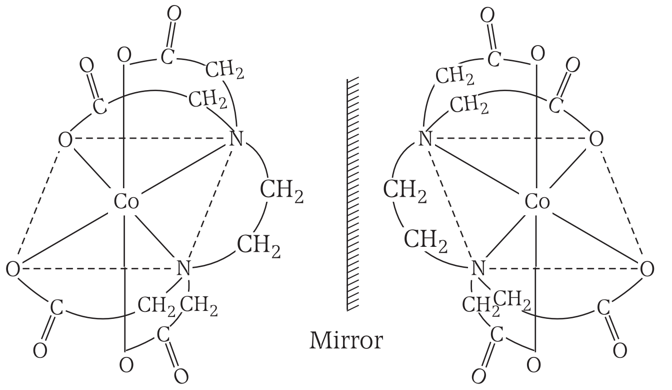
(a) *cis*-dichlorobis(ethylenediamine) cobalt (III) ion
(b) *trans*-dichlorobis(ethylenediamine) cobalt (III) ion

(ii) **Example of $M(AA)_3$ type** octahedral complexes $[Cr(en)_3]^{3+}$, *tris* (ethylenediamine) chromium (III) ion and $[Cr(C_2O_4)_3]^{3-}$, trioxalatochromate (III) ion etc.

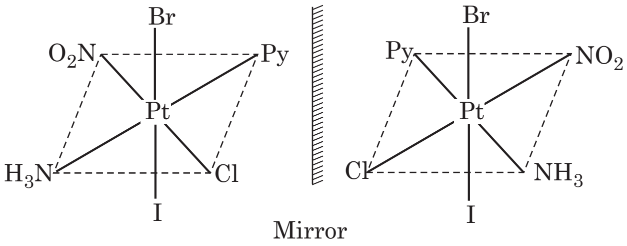


(iii) **Examples of $[M(AA)B_2X_2]$ type** octahedral complexes are optically active, e.g. $[CoCl_2(NH_3)_2(en)]^+$.

(iv) **Complexes containing hexadentate ligand** (e.g. ethylenediaminetetraacetic acid) show optical activity, e.g. the anion $[Co(EDTA)]^-$ exists in two forms.

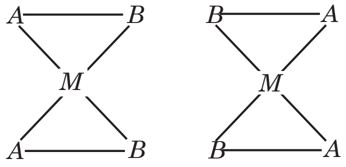


(v) **Example of $ML_aL_bL_cL_dL_eL_f$ type** is $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$. The optical activity in such complexes is due to the presence of six different ligands around the central atoms.

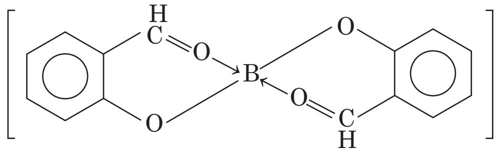


In such a compounds fifteen geometrical isomers are possible which can be resolved into optical isomers. Resolution of all the isomers is not achieved. The optical activity has been observed for chelated tetrahedral and square planar complexes but only rarely found.

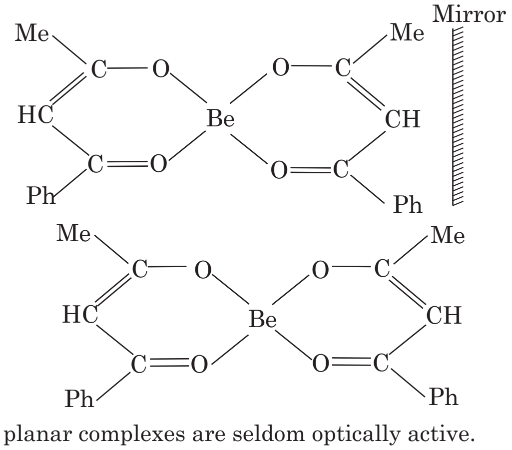
In tetrahedral complexes only the type, which occurs in bis-chelates with unsymmetrical ligand has been detected. These have been found in Be(II), B(III), Zn(II) and Cu(II) complexes. They are of the general type as represented below :



Thus, bis(salicylaldehyde) boron (III) cation has been found to be racemic and resolution has been accomplished.



The two enantiomers of *bis* (benzoylacetonato) beryllium (II) are shown below



Square planar complexes are seldom optically active.

Finding Number of Stereoisomers

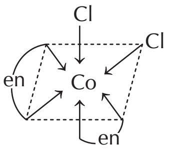
In order to find number of stereoisomers or whether a compound exhibit stereoisomerism or not, first find the general formula of the complex, and then compare with the following facts.

- Geometrical isomerism is possible in square planar complexes of the type MA_2BC, MA_2B_2 , $MABCD$. It is also possible in bridged binuclear planar complexes of the type $M_2A_4X_2$. Octahedral complexes of the type MA_3B_3 , MA_4B_2, $M(AA)_2B_2$, $[M(ABCDEF)]$ exhibit geometrical isomerism.
- Geometrical isomerism is not possible in square planar complexes of type MA_4 and MA_3B, tetrahedral complexes of type MA_4, MA_2B_2 and $MABCD$ and octahedral complexes of type MA_6 and MA_5B. In case of octahedral complexes of the types MA_3B_3 , the *cis-trans* isomers are also called *fac-mer* isomers.
- Octahedral complexes of the type $[M(AA)_2X_2]$, $[M(AA)_3]$, $[M(AA)B_2X_2]$ [where, AA = bidentate ligand] generally exhibits optical isomerism. $[M(\text{EDTA})]$ and $MABCDEF$ also exhibit optical isomerism. (*A, B, C, D, E, F* are different monodentate ligands)

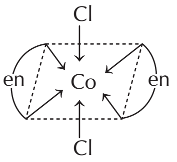
Example 5. *Which one of the following complexes shows optical isomerism?* ***[JEE Main 2016 (Offline)]***

(a) *cis*-$[Co(en)_2Cl_2]Cl$
(b) *trans*-$[Co(en)_2Cl_2]Cl$
(c) $[Co(NH_3)_4Cl_2]Cl$
(d) $[Co(NH_3)_3Cl_3]$

Sol. (*a*)

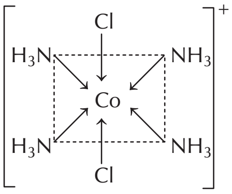


cis-$[Co(en)_2Cl_2]Cl$
(optically active)

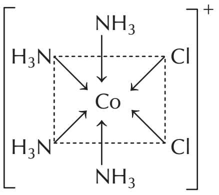


trans-$[Co(en)_2Cl_2]Cl$
(optically inactive due to plane of symmetry)

$[Co(NH_3)_4Cl_2]Cl$ can exist in both *cis* and *trans* forms that are given below

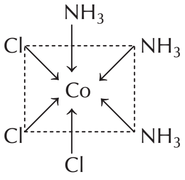


trans-$[Co(NH_3)_4Cl_2]Cl$
(optically inactive)

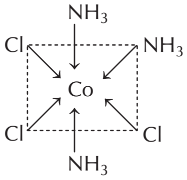


cis-$[Co(NH_3)_4Cl_2]Cl$
(optically inactive)

$[Co(NH_3)_3Cl_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.



fac-isomer
(optically inactive)



mer-isomer
(optically inactive)

Example 6. *Which of the following complex species is not expected to exhibit optical isomerism?* ***(JEE Main 2013)***

(a) $[Co(en)_3]^{3+}$
(b) $[Co(en)_2Cl_2]^+$
(c) $[Co(NH_3)_3Cl_3]$
(d) $[Co(en)(NH_3)Cl_2]^+$

Sol. (*c*) Optical isomerism is exhibited by only those complexes which lacks elements of symmetry. $[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

Theories in Coordination Compounds

The formation of coordination compounds can be explained electronically by a number of theories like

(i) Valence bond approach (ii) Crystal field theory

Valence Bond Approach

This was evolved largely through the efforts of **Linus Pauling** based on attempted **Lewis-Sidgwick** ideas of the coordinate covalent bond.

In this approach, the basic assumption made is that the metal ligand bonds arise by the donation of pairs of electron from ligands to the metal , i.e. through forming the coordinate covalent bond.

In order to accommodate these electrons, the metal ion must possess requisite number of vacant orbitals of similar energy.

These metal orbitals undergo hybridisation to give a set of hybrid orbitals of equal energy with the approach of the ligands.

The main assumptions of valence bond approach are

- The ions of the transition elements have some incompletely filled d-orbitals.
- Some or all the electrons in the incompletely filled d-orbitals are unpaired.

- It was suggested that sometimes, the unpaired $(n-1)$ d-electrons couple as fully as possible prior to bond formation. In this process some $(n-1)$ d-orbitals become vacant. The central metal atom thus, makes available a number of empty orbitals equal to its coordination number for the formation of coordinate bonds with suitable ligand orbitals.
- Since, the energy of the $(n-1)$ d-orbitals is only slightly less than that of s-and p-orbitals of the nth orbitals, these vacant orbitals mix together to form new equivalent orbitals, called **hybrid orbitals.**
- Each ligand has at least one lone pair of electrons.
- The hybrid orbitals formed, take part in the formation of hybrid bonds with the ligands by overlapping. The bond formation takes place by accepting the lone pair of electrons by the hybrid orbitals of the metal from the ligands. Especially the orbitals that would be used for a metal ion of the first series, are the two $3d$, one $4s$ and the three $4p$-orbitals.
- The rest $3d$ or **inner orbitals on the metal ion do not** participate in the bonding. When $(n-1)$ d-orbitals are used in bond formation, the complex formed is called **inner orbital complex.**
- Sometimes, in place of $(n-1)$ d-orbitals, outer nd-orbitals are used for hybridisation. The complex, thus, formed is called **outer orbital complex.**

  The bond hybridisation involved and the resulting geometrical shapes of the complexes are given in the following table

Relation Between Hybridisation and Geometry of Complexes

Bond hybridisation	Geometrical shape	d-orbital used	Typical example
d^2sp^3	Octahedral (inner orbital complex)	d_{z^2} and $d_{x^2-y^2}$	$[Fe(CN)_6]^{3-}$
sp^3d^2	Octahedral (outer orbital complex)	$d_{x^2-y^2}$ and d_{z^2}	$[FeF_6]^{3-}$
sp^3	Tetrahedral		$[Zn(NH_3)_4]^{2+}$
dsp^2 or sp^2d	Square planar	$d_{x^2-y^2}$	$Ni(CN)_4]^{2-}$

- A given complex is **paramagnetic**, if one or more unpaired electrons are present in the d-subshell. However, if there is no unpaired electrons, then complex is termed as **diamagnetic**.
- Pauling made extensive use of magnetic measurements to discover the number of unpaired electrons in a complex and he also differentiated between complexes in which the bonding could be considered as ionic or those in which it was probably covalent.

  In deciding whether the hybridisation at the central metal ion of octahedral complexes is sp^3d^2 (outer orbital) or d^2sp^3 (inner orbital) we must know the results of magnetic measurements. These indicate the number of unpaired electrons (N). Magnetic moment is given by,

$$\mu = \sqrt{N(N+2)}\ \text{BM} \qquad \text{(BM is Bohr Magneton)}$$

Finding Geometry and Magnetic Character of Complexes

In order to find the geometry, hybridisation and magnetic character, follow the following steps

***Step* I** Find the oxidation number of central metal atom and write the electronic configuration of **central metal ion.**

***Step* II** Find the nature of ligand,

- If it is CN^-, NH_3^-, CO, pair up the unpaired electrons of the metal ion (if they are more than 4 and less than 8 in case of octahedral complex.)
- If it is Cl^-, Br^-, I^-, H_2O, etc., leave the unpaired electrons of the metal ion as such.

***Step* III** Now fill the ligand's electrons in empty available orbitals. The orbitals occupied by ligands give an idea about the hybridisation.

***Step* IV** From the hybridisation, find geometry (see table).

***Step* V** Also see whether unpaired electrons are present, or not. If they are present, species is paramagnetic, otherwise diamagnetic.

***Step* VI** If inner $[(n-1)\,d]$-orbital takes part in hybridisation, the complex is inner orbital, otherwise outer orbital.

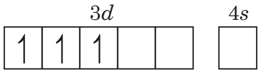
The above procedure can be best understood by following examples.

1. $[Cr(NH_3)_6]^{3+}$ Ion

In this ion, oxidation state of Cr is +3.

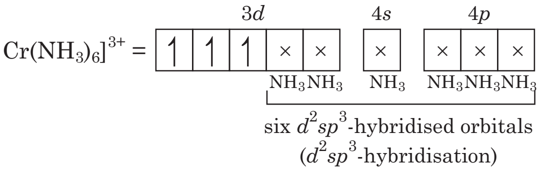
$$[x + 6 \times 0 = +3 \quad \text{or } x = +3]$$

$$Cr^{3+} = [Ar]\,3d^3\,4s^0$$



NH_3 is a strong field ligand but unpaired electrons are < 4. So, pairing does not occur.

Since, there are six NH_3 ligands, fill their electrons as



(Here, x = a pair of electrons from ligand, i.e. from NH_3)

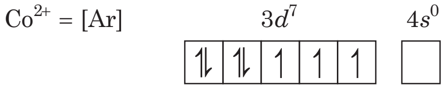
Since, hybridisation is d^2sp^3, geometry is octahedral.

Because of the presence of three unpaired electrons, it is a paramagnetic complex. Since, $(n-1)\,d$ ($3d$-orbital) takes part in hybridisation, it is an inner orbital complex.

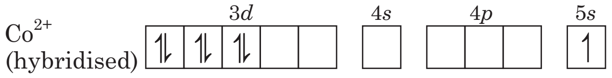
Other complexes of Cr with similar inner structure are $[Cr(CN)_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$. In a similar way, structure of $[V(H_2O)_6]^{3+}$ with d^2-configuration of V^{3+} ion can be explained.

2. $[Co(NH_3)_6]^{2+}$

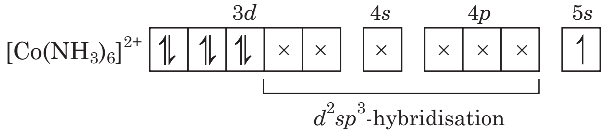
Co is present in +2 oxidation state, so



NH_3 being strong field ligand pair up the unpaired electrons of Co and also transfers one remained unpaired electron into higher energy state, as



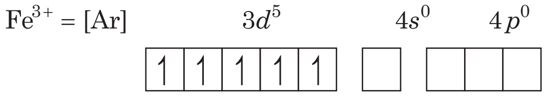
The inner two *d*-orbitals are made available for the required d^2sp^3-hybridisation after maximum pairing of electrons within the 3*d* level followed by promotion of one *d*-electrons to the higher energy level (5*s*). This is shown below



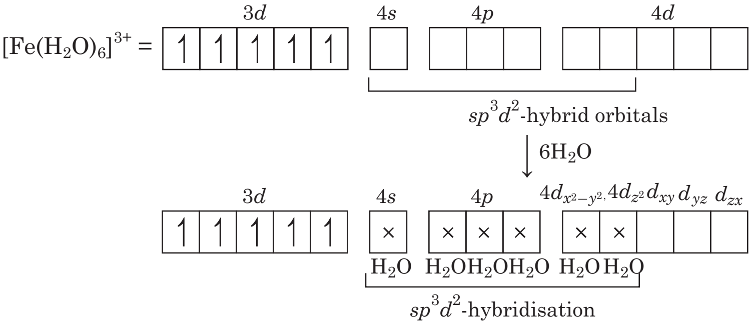
Thus, its geometry is octahedral. It is a paramagnetic complex. Moreover, it is an inner orbital complex. As the promoted electron (shown above) has low ionisation energy, the complexed central metal ion Co^{2+} has a tendency to undergo oxidation easily to Co^{3+}. Thus, the paramagnetic complex changes to diamagnetic after oxidation. It should be noted however, that the formation of such inner orbital complex and promotion of electron can be brought about only by very strong ligands.

3. $[Fe(H_2O)_6]^{3+}$

Here, Fe is present as Fe^{3+}.

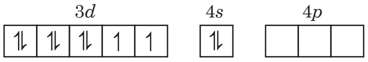
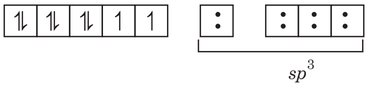
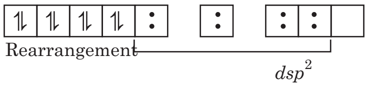
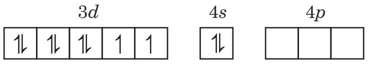
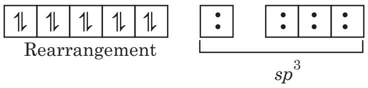
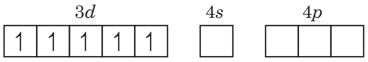
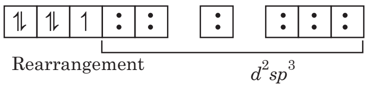
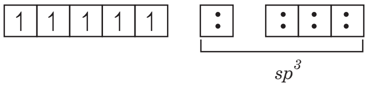


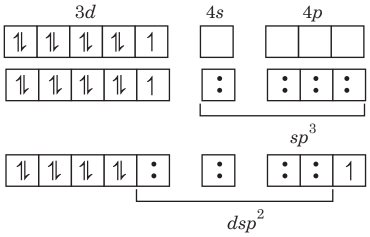
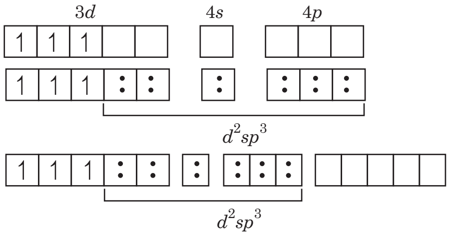
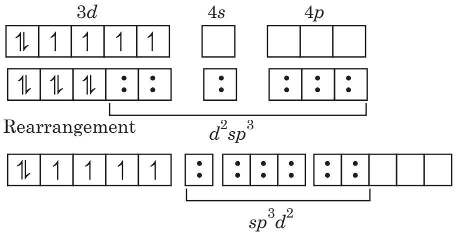
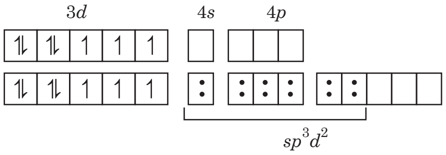
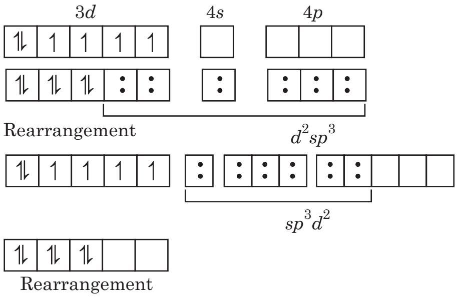
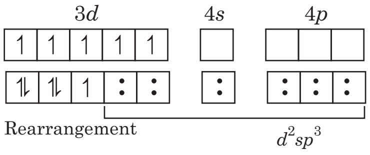
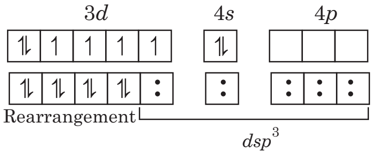
H_2O being weak field ligand is unable to pair up its unpaired electrons, thus, occupy the 4*s*, 4*p* and 4*d* empty orbitals as



Thus, its geometry is octahedral. Because of the presence of five unpaired electrons, it is paramagnetic. Since *nd* orbitals (4*d*-orbitals) take part in hybridisation (bonding), it is an **outer orbital or high spin complex.**

Geometry and Hybridisation of Some Other Complexes on the Basis of VBT

Atom/Ion complex	Configuration	Oxidation state of metal	Type of hybridisation	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
Ni^{2+} (d^8)		+2			2	Paramagnetic
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2-}$		+2	dsp^2	Square planar	0	Diamagnetic
Ni (d^8s^2)		0			2	Paramagnetic
$[Ni(CO)_4]$		0	sp^3	Tetrahedral	0	Diamagnetic
$[Mn^{2+}(d^5)]$		+2			5	Paramagnetic
$[Mn(CN)_6]^{4-}$		+2	d^2sp^3 (Inner)	Octahedral	1	Paramagnetic
$[MnCl_4]^{2-}$		+2	sp^3	Tetrahedral	5	Paramagnetic

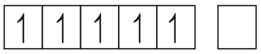
Atom/Ion complex	Configuration	Oxidation state of metal	Type of hybridisation	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
Cu^{2+} (d^9)		+2			1	Paramagnetic
$[CuCl_4]^{2-}$		+2	sp^3	Tetrahedral	1	Paramagnetic
$[Cu(NH_3)_4]^{2+}$	One electron is shifted from 3*d* to 4*p*-orbital	+2	dsp^2 (inner)	Square planar	1	Paramagnetic
Cr^{3+} (d^3)		+3			3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$		+3	d^2sp^3(Inner)	Octahedral	3	Paramagnetic
$[Cr(H_2O)_6]^{3+}$		+3	d^2sp^3(Inner)	Octahedral	3	Paramagnetic
Co^{3+} (d^6)		+3			4	Paramagnetic
$[Co(NH_3)_6]^{3+}$		+3	d^2sp^3(Inner)	Octahedral	0	Diamagnetic
$[CoF_6]^{3-}$		+3	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
Co^{2+} (d^7)		+2			3	Paramagnetic
$[Co(H_2O)_6]^{2+}$		+2	sp^3d^2(Outer)	Octahedral	3	Paramagnetic
Fe^{2+} (d^6)		+2			4	Paramagnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3(Inner)	Octahedral	0	Diamagnteic
$[Fe(H_2O)_6]^{2+}$		+2	sp^3d^2(Outer)	Octahedral	4	Paramagnetic
$[Fe(NH_3)_6]^{2+}$		+2	d^2sp^3(Inner)	Octahedral	0	Diamagnetic
Fe^{3+} (d^5)		+3			5	Paramagnetic
$[Fe(CN)_6]^{3-}$		+3	d^2sp^3 (Inner)	Octahedral	1	Paramagnetic
Fe(d^6, s^2)						
$[Fe(CO)_5]$		0			4	Paramagnetic
		0	dsp^3 (Inner)	Trigonal bipyramidal	0	Diamagnetic

Example 7. *Which of the following options are correct for* $[Fe(CN)_6]^{3-}$ *complex?* ***(NCERT Exemplar)***

(i) d^2sp^3-hybridisation	(ii) sp^3d^2-hybridisation
(iii) Paramagnetic	(iv) Diamagnetic
(a) (i) and (iii)	(b) (i) and (iv)
(c) (ii) and (iii)	(d) (ii) and (iv)

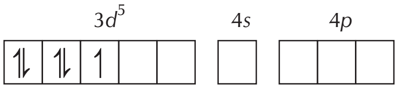
Sol. (*a*) In $[Fe(CN)_6]^{3+}$, Fe is present as Fe^{3+}.

Fe^{3+} = [Ar] $3d^5$ $4s^0$



CN^- being strong field ligand pair up these unpaired electrons, so that now the complex have only one unpaired electron as

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



Now, the two $3d$, one $4s$ and three $4p$-orbitals hybridise to give six d^2sp^3-hybridised orbitals which are occupied by electrons of CN^- Since, the complex contain one unpaired electron, it is paramagnetic in nature.

Limitations of Valence Bond Theory

Although this theory explained the formation, shape, structure and magnetic behaviour of complexes sucessfully but it suffers from the following short comings

- It involves a number of assumptions.
- It describes bonding in coordination compounds only qualitatively.
- It does not offer any explanation for the optical absorption spectra of complexes or in other words. It could not give any satisfactory explanation for the colour of the complexes.
- It does not describe the detailed magnetic properties of coordination compounds.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- It does not distinguish between weak and strong ligands, i.e. It can not explain why some complexes are low spin and others as high spin.

Crystal Field Theory

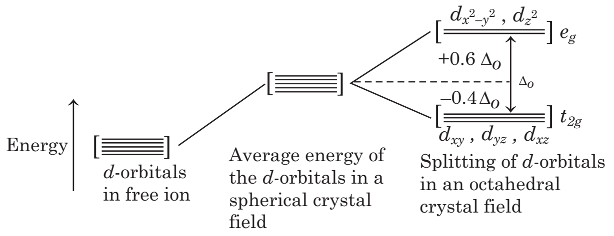
Most of the shortcomings of VBT of coordination compounds were removed in **Crystal Field Theory** (CFT). It attributes partial covalent character and partial ionic character to bonds. This **theory** was developed by **H. Bethe** and **V. Vleck** (1935) and proved to be more successful in explaining the bonding and properties of coordination complexes.

The theory is based upon the fact that the degenerate (meaning energetically alike) d-orbitals of metal ions are splitted energy wise due to the concentration of point charges in certain specific positions. This is seen because the energy of the orbitals lying in the direction of point charges increases more in comparison to orbitals lying in between the point charges as the electrons in former case experience greater repulsion than in latter case.

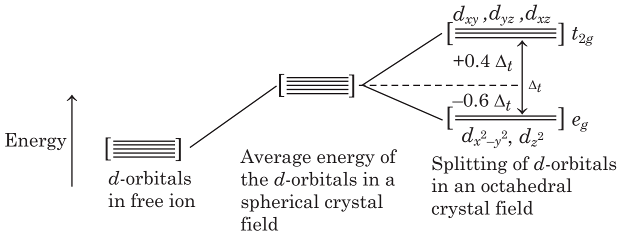
Thus, energy wise, two groups of orbitals are seen now, one with higher energy and other with lower energy. This splitting of 5 degenerate orbitals of metal ion into two sets of orbitals having different energies is called **crystal field splitting.**

In case of octahedral complexes, e_g set $(d_{x^2-y^2}, d_{z^2})$ is of higher energy while in case of tetrahedral complexes t_{2g} set (d_{xy}, d_{yz}, d_{zx}) has higher energy.

The splitting of d-orbitals in octahedral and tetrahedral complexes is shown in given figure,



d-orbital splitting in an octahedral crystal field.



d-orbital splitting in a tetrahedral crystal field

The difference in energy levels is arbitrarily taken to be Δ. The set of lower energy stabilises the complex ion by 0.4 units and that with higher energy destabilises the ion by 0.6 units. The gain in energy achieved by preferential filling of electrons in orbitals is called crystal field stabilisation energy (CFSE). Higher the amount of CFSE, greater is the stability of the complex.

The tetrahedral crystal field splitting is only 4/9 of the octahedral splitting and there is no known low spin tetrahedral complex.

Here, one point must always be kept in mind that **crystal field theory** considers purely electrostatic attractions between central metal ion and ligands.

Factors Affecting the Magnitude of Crystal Field Splitting

- Nature of ligands (the ligands with smaller size, large negative charge, with good σ donor and π acceptor properties will give large crystal field splitting). The ligands are arranged in **spectro chemical series** on the basis of their crystal field splitting power as

$$\mathrm{I^- < Br^- < Cl^- < F^- < ox^- \approx H_2O < Py \approx NH_3 < en < NO_2^- < CN^- < CO}$$

- It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the *d*-orbitals of metal ion in octahedral coordination entities. Obviously, the single *d* electron occupies one of the lower energy t_{2g} orbitals.
- In d^2 and d^3 coordination entities, the *d*-electrons occupy the t_{2g}-orbitals singly in accordance with the Hund's rule.
- For d^4 ions, two possible patterns of electron distribution arise (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the e_g level, which of these posibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are
- If $\Delta_o < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as **weak field ligands** and form high spin complexes.
- If $\Delta_o > P$, 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.
- Oxidation state of metal ion (more crystal field splitting is seen in metal ions with higher oxidation states).
- Size of *d*-orbital (larger the size, more crystal field splitting is seen).
- Geometry of the complex (as splitting is different for tetrahedral and octahedral complexes).
- Whereas valence bond theory considers metal-ligand bond to be covalent, crystal field theory considers the bond to be ionic arising out of electrostatic interaction between the metal ions and ligands. If the ligand is an anion. Then metal ion is a cation.
- In CFT, each ligand is treated as a point of negative charge. The arranagement of the ligands around the central metal ion is such that the repulsions between these negative points are minimum.

Calculation of Crystal Field Stabilisation Energy (CFSE)

Each electron occupying t_{2g}-orbital results in lowering of energy by $-0.40\,\Delta_o$ (or $-4Dq$). Similarly, each electron occupying e_g orbital results in increase of energy by $+0.6\,\Delta_o$ (or $+6Dq$). Thus if x is the number of electrons occupying t_{2g} orbitals any y electrons occupy e_g orbitals.

$$\text{CFSE} = (-0.4x + 0.6y)\,\Delta_o$$

For d^1 configuration (t_{2g}^1)

$$\text{CFSE} = -0.4\,\Delta_o \text{ (or } -4Dq)$$

For $d^8 = t_{2g}^6 \cdot e_g^2$

$$\text{CFSE} = 6\ (-0.4) + 2(+0.6) = -1.2\,\Delta_o$$

The number of unpaired electrons in octahedral and tetrahedral complex having different configuration, can be summarised in table.

Number of Unpaired Electrons in Octahedral and Tetrahedral Complexes

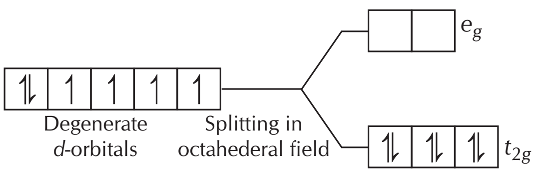
Electronic configuration	Octahedral complex		Number of unpaired electrons	Tetrahedral complex		Number of unpaired electrons
	(t_{2g} set)	(e_g set)		(e_g set)	(t_{2g} set)	
d^1	t_{2g}^1	e_g^0	1	e^1	t_2^0	1
d^2	t_{2g}^2	e_g^0	2	e^2	t_2^0	2
d^3	t_{2g}^3	e_g^0	3	e^2	t_2^1	3
d^4 (a)*	t_g^3	e_g^1	4	e^2	t_2^2	4
(b)*	t_g^4	e_g^0	2	e^4	t_2^0	0
d^5 (a)*	t_{2g}^3	e_g^2	5	e^2	t_2^3	5
(b)*	t_{2g}^5	e_g^0	1	e^4	t_2^1	1
d^6 (a)*	t_{2g}^4	e_g^2	4	e^3	t_2^3	4
(b)*	t_{2g}^6	e_g^0	0	e^4	t_2^2	2
d^7 (a)*	t_{2g}^5	e_g^2	3	e^4	t_2^3	3
(b)*	t_{2g}^6	e_g^1	1	e^4	t_2^3	3
d^8	t_{2g}^6	e_g^2	2	e^4	t_2^4	2
d^9	t_{2g}^6	e_g^3	1	e^4	t_2^5	1
d^{10}	t_{2g}^6	e_g^4	0	e^4	t_2^6	0

*[(a) is the configuration for high spin and (b) is the configuration for low spin complexes]

Example 8. *The electronic configuration of central matal atom/ion in* $[Co(CN)_6]^{3-}$ *is*

(a) $t_{2g}^5 e_g^0$ (b) $t_{2g}^4 e_g^2$ (c) $t_{2g}^6 e_g^0$ (d) $t_{2g}^4 e_g^3$

Sol. (c) $[Co(CN)_6]^{3-}$, i.e. Co^{3+}



$Co^{3+} = 3d^6$ (or $t_{2g}^6 e_g^0$)

There is no unpaired electron, so it is diamagnetic.

Example 9. *Arrange the following complex ion in increasing order of crystal field splitting energy.* (Δ_o).

I. $[Cr(Cl)_6]^{3-}$, II. $[Cr(CN)_6]^{3-}$, III. $[Cr(NH_3)_6]^{3+}$

(NCERT Exemplar)

(a) I < II < III (b) II < I < III
(c) III < II < I (d) I < III < II

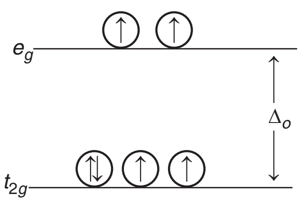
Sol. (*d*) CFSE is higher when the complex contains strong field ligand. Thus, crystal field splitting energy increases in the order $[Cr(Cl)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$.

Because the order of field strength is $Cl^- < NH_3 < CN^-$.

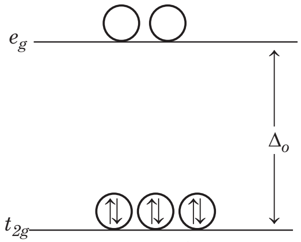
Magnetic Properties

The **diamagnetic** (repulsion from applied magnetic field due to paired electrons) and **paramagnetic** (attraction from applied magnetic field due to unpaired electron) behaviour of coordination compounds can be explained on the basis of crystal field theory, e.g. Co (III) shows diamagnetic properties in $[Co(NH_3)_6]^{3+}$ complex and paramagnetic properties in $[CoF_6]^{3-}$ complex.

Such a difference in behaviour show that there must be some unpaired electrons in latter while former have all paired electrons (magnetic measurement shows the presence of four unpaired electrons in latter). This can be explained on the basis of crystal field theory if you observe the diagrams given below carefully.



(a) $[CoF_6]^{3-}$ complex



(b) $[Co(NH_3)_6]^{3+}$ complex

In fig. (a) as Δ_o is small, the energy required to pair up the 4th and 5th electron with the electrons in lower *d*-orbitals (t_{2g}) is higher as compared to that required to place the electron in higher *d*-orbital (e_g).

In fig. (b) as Δ_0 is higher, the energy required to pair up the 4th and 5th electron with the electrons in lower *d*-orbitals (t_{2g}) is lower as compared to that required to place the electron in higher *d*-orbitals (e_g).

Magnetic moment (μ) is related to number of unpaired electrons '*n*' as, $\mu \;\; \mu = \sqrt{n(n+2)}$ BM

Remember The values of *n* calculated by applying the above formula for different magnetic moments are given in the following table

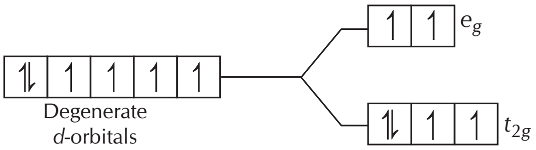
Magnetic moment (BM)	Number of unpaired electrons
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

Example 10. *The magnetic moment of* $[CoF_6^{3-}]$ *by using* CFT *is*

(NCERT Exemplar)

(a) 0 (b) 4.9 (c) 5.9 (d) 1.73

Sol. (*b*) $[CoF_6]^{3-}$, i.e. Co^{3+}



Configuration of $Co^{3+} = 3d^6$ (or $t_{2g}^4 e_g^2$)

Number of unpaired electrons (n) = 4

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)} = \sqrt{4\,(4+2)}$$

$$= \sqrt{24} = 4.9 \text{ BM}$$

Colour of the Complexes

- A substance appears coloured because it absorbs light at specific wavelengths in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmits or reflects the rest of the wavelength. Each wavelength of visible light represents a different colour. White light, such as sunlight, is a combination of all colours; an object that absorbs all visible light appears black.
- The CFSE for most of the complexes is of the same order of magnitude as the energy of a photon of visible light. It is therefore, possible for a transition metal complex to absorb visible light which thereby excites electron from the lower energy *d*-orbitals into the higher energy ones. For example, in the complex $[Ti(H_2O)_6]^{3+}$, Ti(III) has only one 3*d*-electron.

  Its spectrum shows a single absorption peak at about 5000 Å which corresponds to an energy of about 240 kJ mol^{-1}, i.e. greater than Δ_o value and is sufficient to excite the electron from t_{2g} to e_g-orbital. This means that green and yellow portions of the light are absorbed and it makes the colour of the compound purple, which is a complementary colour radiation absorbed.

- When the energy of the photon ($h\nu$) is equal to the difference between the lower and higher d-orbital energy levels, an electron is promoted from a lower to higher level. If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same as the incident light white and the ion appears colourless.
- The coloured nature of solutions of coordination compounds can also be explained on the basis of crystal field theory, because in coordination compounds the energy difference between two sets of d-orbitals is usually small (as explained by crystal field splitting) thus, excitation of an electron from lower energy to higher energy is very easy and can be achieved even by the absorption of low energy radiations of visible region.

  As a result of the absorption of such selected wavelengths of visible light, the complexes appeared coloured.

  Relationship between the λ of light absorbed and the colour observed can be examplified as,

Wavelength Associated with Different Colours

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

Limitations of CFT

The crystal field theory can explain the spectra of the metal ions and complexes on the assumption that these arise from the transition of electrons from lower energy d-orbitals to higher energy d-orbitals. However, the position and intensities of spectral bands calculated on the basis of crystal field theory do not always coincide with those determined experimentally.

Apart from this, a pure electrostatic interaction between central metal ion and ligand fails to explain the relative positions of ligands in spectrochemical series. Along with this there is clear evidence that covalent bonding too makes a significant contribution towards the metal ligand bonding.

As ligands are considered as point charges the anionic ligands should exert greater splitting effect. But in actual practice anionic ligands are present at low end of spectrochemistry series.

The above written facts about the crystal field theory was modified so as to include the contribution of covalent bonding in the metal ligand bond and is called **ligand field theory,** which assumes that the extent of covalent character in metal ligand bond is generally low as compared to the extent of the ionic character of the bond that means the conclusions arrived by the crystal field theory are still valid to a larger extent.

Stability of Complexes

The stability of a complex in solution is infact the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type

$$M + 4L \rightleftharpoons ML_4$$

then the larger the stability constant K, the higher the proportion of ML_4 that exists in solution. Alternatively $1/K$ values, called the **instability constant,** explain the dissociation of the complex into metal ion and ligands in the solution.

A coordination 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 = coordination number of metal ion) may be supposed to take place by the following n consecutive steps.

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

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

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

$$\ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots$$

$$\ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots$$

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

$K_1, K_2, K_3, \ldots, K_n$ are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n. Alternatively, we can write the **overall stability constant** thus

$$M + 4L \rightleftharpoons ML_4; \beta_4 = \frac{[ML_4]}{[M][L]^4}$$

The stepwise and overall stability constant are therefore related as follows

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally,

$\beta_i = K_1 \times K_2 \ldots \times K_i$

Factors Affecting Stability of Complexes

The strength of a complex ion depends upon the following factors

(i) **Higher charge** of the central metal ion, i.e. greater ionic potential $\left(\frac{\text{ionic charge}}{\text{ionic radius}}\right)$ and greater is the stability.

(ii) **Greater base strength** of the ligand, greater will be the stability.

(iii) **Ring formation** (chelation) in structure of the complexes is the chief factor, which **increases** the stability of the complexes in solution.

(iv) If a multidentate ligand happens to be cyclic without any steric effects, a further increase in stability occurs. This is called **macrocyclic effect.**

Importance of Coordination Compounds

Some important applications of coordination compounds are as follows

1. **In qualitative and quantitative analysis** Nickel is detected and estimated as its red dimethyl glyoxime complex which is a chelate complex.
   - Mg and Al are estimated as complexes of 8-hydro-oxyquinoline (oxime).
   - The separation of Ag^+ from Hg_2^{2+} in the first group of analysis is based on the fact that while, silver chloride is soluble in aqueous ammonia, Hg_2Cl_2 forms a black insoluble material.

     $$AgCl + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

     $$Hg_2Cl_2 + NH_4OH \longrightarrow \underset{\substack{\text{(Black}\\ \text{insoluble)}}}{Hg(NH_2)Cl} + Hg + HCl + H_2O$$

   - The separation of IIB group sulphides from IIA group sulphides is based on the fact that sulphides of IIB group form, complex sulphides with yellow ammonium sulphide which are soluble while, sulphides of IIA group do not react.

     $$As_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3[AsS_4]$$

     $$Sb_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3[SbS_4]$$

     $$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2[SnS_3]$$

   - The detection of Cu^{2+} is based on the formation of a blue tetra-ammine copper sulphate complex, which gives a deep blue coloured solution upon addition of NH_3 to Cu^{2+} ions.

     $$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

     It also forms a chocolate coloured precipitate with potassium ferrocyanide.

     $$2CuSO_4 + K_4Fe(CN)_6 \longrightarrow \underset{\text{Chocolate ppt.}}{Cu[Fe(CN)_6]} + 2K_2SO_4$$

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

     $$Fe^{3+} + KSCN \longrightarrow \underset{\substack{\text{Blood red}\\ \text{colour}}}{[Fe(SCN)]^{2+}} + K^+$$

   - S^{2-} is detected by the formation of a violet-coloured complex with sodium nitroprusside.

     $$Na_2S + \underset{\substack{\text{Sodium}\\ \text{nitroprusside}}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Violet colour}}{Na_4[Fe(CN)_5NOS]}$$

   - EDTA is used in the complexometric determination of several metal ions such as Ca^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, etc.

2. **In the extraction of metals** The formation of complex compounds is used in the extraction of some metals e.g. Ag and Au are extracted as follows

   $$2K[Ag(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + \underset{\text{Silver}}{2Ag}$$

   It is due to more electropositive nature of Zn as compared to Ag and Au. **Nickel tetracarbonyl** complex is used for the extraction and purification of nickel.

   $$\underset{\substack{\text{(Associated with}\\ \text{other elements)}}}{Ni} + 4CO \longrightarrow [Ni(CO)_4] \xrightarrow{\text{Heating}} Ni + 4CO$$

3. **In biological world** Cyclic ligands impart extra stability to coordinate compounds. Thus, Mg in chlorophyll and iron in haemoglobin are stable towards dissociation due to the formation of coordination compounds. Haemoglobin of the blood gets oxygenated through the binding of dioxygen, O_2 to the ferrous ions in haemoglobin.

4. **Role of coordination compounds in medicinal chemistry** The platinum complex *cis*-$[Pt(NH_3)_2Cl_2]$ (*cis*-platin) is used in the treatment of cancer.
   - EDTA complex of calcium is used in the treatment of lead poisoning. Ca-EDTA is a weak complex, when it is administered, calcium in the complex is replaced by the lead present in the body and is eliminated in the urine.
   - The excess of copper and iron present in animal system are removed by the chelating ligands *D*-penicillamine and desferroxime *B via* the formation of complexes.

5. **In estimation of hardness of water** EDTA is a hexadentate ligand and forms complex with various metal ions. This is used in the estimation of hardness of water by a volumetric method. Hardness of water is due to Ca^{2+} and Mg^{2+} ions. Since, stability constant values of EDTA complex with Ca^{2+} and Mg^{2+} are 10^7 and 10^8 respectively, it helps in selective estimation of different ions.

6. **In electroplating of metals** Coordination compounds are used in **electroplating industry**, e.g. gold and silver are electroplated from their coordination compounds, such as $K[Ag(CN)_2]$ or $K[Au(CN)_4]$.

7. **As catalysts** A coordination complex of Ti and Al is used as a catalyst to convert ethylene and propylene into polyethene. Ziegler-Natta catalyst is $TiCl_4 + (C_2H_5)_3Al$ or $(CH_3)_3Al$.

8. **In pigments** Many pigments such as phthalocyanines used in paints are the coordination compounds.

9. **In photography** The developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex.

10. **In agriculture** To prevent the infection of young plants, the seeds are treated with organometallics such as ethyl mercury chloride.

Practice Exercise

ROUND I Topically Divided Problems

General Terms Related to Coordination Compounds

1. Which of the following species is not excepted to be a ligand? *(NCERT Exemplar)*

(a) NO (b) NH_4^+
(c) $NH_2CH_2CH_2NH_2$ (d) CO

2. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? *(NCERT Exemplar)*

(a) Thiosulphato
(b) Oxalato
(c) Glycinato
(d) Ethane-1,2-diamine

3. The coordination number of Pt in $[Pt(NH_3)_4Cl_2]^{2+}$ ion is

(a) 2 (b) 4 (c) 6 (d) 8

4. The effective atomic number of cobalt in the complex $[Co(NH_3)_6]^{3+}$ is

(a) 36 (b) 24 (c) 33 (d) 30

5. The pair of the compounds in which both the metals are in the higher possible oxidation state is

(a) CrO_2Cl_2, MnO_4^-
(b) $[Co(CN)_6]^{3-}$, MnO_3
(c) TiO_3, MnO_2
(d) $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$

6. Given the molecular formula of the hexa coordinated complexes (*A*) $CoCl_3 \cdot 6NH_3$ (*B*) $CoCl_3 \cdot 5NH_3$ (*C*) $CoCl_3 \cdot 4NH_3$. If the number of coordinated NH_3 molecules in *A*, *B*, and *C* respectively are 6, 5 and 4, primary valency in (*A*), (*B*) and (*C*) are

(a) 0, 1, 2 (b) 3, 2, 1
(c) 6, 5, 4 (d) 3, 3, 3

7. Complex salt can be made by the combination of $[Co^{III}(NH_3)_5Cl]^x$ with

(a) Cl^- (b) $2Cl^-$
(c) PO_4^{3-} (d) $2K^+$

8. How many ions are produced, from the complex, $Co(NH_3)_6Cl_2$ in solution? *(NCERT)*

(a) 6 (b) 4 (c) 3 (d) 2

9. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? *(NCERT)*

(a) CuCN (b) $K_3[Cu(CN)_6]$
(c) $K[Cu(CN)_4]$ (d) $K_2[Cu(CN)_4]$

10. When 1 mole of $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 moles of AgCl are obtained. The formula of the complex is *(NCERT Exemplar)*

(a) $[CrCl_3(H_2O)_3] \cdot 3H_2O$
(b) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
(d) $[Cr(H_2O)_6]Cl_3$

11. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solution but not in acidic solution. What is the reason for it?

(a) In acidic solutions, hydration protects copper ions.
(b) In alkaline solution, insoluble $Cu(OH)_2$ is precipitated.
(c) Copper hydroxide is an amphoteric substance
(d) In acidic solutions, protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

12. Amongst the following, the most stable complex is *(NCERT)*

(a) $[Fe(H_2O)_6]^{3+}$ (b) $Fe(NH_3)_6]^{3+}$
(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[FeCl_6]^{3-}$

13. Which of the following complexes do not follow EAN rule?

(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $Ni(CO)_4$ (d) $[PdCl_4]^{2-}$

14. An aqueous solution of titanium chloride, when subjected to magnetic measurement, measured zero magnetic moment. The formula of the complex assuming it to be octahedral in aqueous solution is

(a) $[Ti(H_2O)_6]Cl_4$ (b) $[Ti(H_2O)_6]Cl_3$
(c) $[Ti(H_2O)_5Cl]Cl_2$ (d) $[Ti(H_2O)_6]Cl$

15. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. A reacts with $AgNO_3$ producing a white precipitate which was soluble in dilute ammonia solution. B reacts with $AgNO_3$ producing a pale yellow precipitate soluble in concentrated ammonia solution. The formulae of A and B are respectively

(a) $[Cr(NH_3)_4Br]Cl_2$; $[Cr(NH_3)Cl_2]Br$
(b) $[Cr(NH_3)_4BrCl]Cl$; $[Cr(NH_3)_3Cl_2Br]NH_3$
(c) $[Cr(NH_3)_4Cl_2]Br$; $[Cr(NH_3)_4BrCl]Cl$
(d) $[Cr(NH_3)_4BrCl]Cl$; $[Cr(NH_3)_4Cl_2]Br$

16. The complex ion which has no d-electrons in the central metal atom is

(a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

17. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by

(a) $MnSO_4 \cdot 4H_2O$ (b) $NiSO_4 \cdot 6H_2O$
(c) $FeSO_4 \cdot 6H_2O$ (d) $CuSO_4 \cdot 5H_2O$

18. Which of the following compounds has same oxidation state of the central metal atom in the cationic and anionic part?

(a) $[Pt(NH_3)_4][PtCl_6]$ (b) $[Pt(py)_4][PtCl_4]$
(c) $[Pt(NH_3)_4Cl_2][PtCl_4]$ (d) $K_4[Ni(CN)_6]$

19. A solution made by dissolving 0.875 g of compound $Co(NH_3)_4Cl_3$ in 25 g of water freezes at –0.56°C. The structural formula of the complex, if cryoscopic constant of water is 1.86 K kg mol^{-1}, is

(a) $[Co(NH_3)_4]Cl_3$ (b) $[Co(NH_3)_4Cl]Cl_2$
(c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]NH_3$

Nomenclature of Coordination Compounds

20. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is *(NCERT Exemplar)*

(a) diamminedichloridoplatinum (II)
(b) diamminedichloridoplatinum (IV)
(c) diamminedichloridoplatinum (0)
(d) dichloridodiammineplatinum (IV)

21. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is (NCERT Exemplar)

(a) platinum diaminechloronitrite
(b) chloronitrito-N-ammineplatinum (II)
(c) diamminechloridonitrito-N-platinum (II)
(d) diamminechloronitrito-N-platinate

22. Pick the correct name of $[Co(NH_3)_5Cl]Cl_2$.

(a) chloropentamminecobalt (III) chloride
(b) chloropentamminecobalt (III)
(c) chloropentamminecobalt (II) chloride
(d) pentamminechloridocobalt (III) chloride

23. The IUPAC name of $K_2[Cr(CN)_2O_2(O)_2(NH_3)]$ is

(a) potassium amminedicyanodioxoperoxochromate (VI)
(b) potassium amminecyanoperoxodioxochromatic (IV)
(c) potassium amminecyanoperoxodioxochromium (IV)
(d) potassium amminecyanoperoxodioxochromium (IV)

24. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is

(a) tetrachloridonickel (II) tetraamminenickel (II)
(b) tetraamminenickel (II) tetrachloridonickel (II)
(c) tetraamminenickel (II) tetrachloridonickelate (II)
(d) tetrachloridonickel (II) tetraamminenickel (0)

25. The correct IUPAC name of $Mn_3(CO)_{12}$ is

(a) dodecacarbonylmanganate (0)
(b) dodecacarbonylmanganic (II)
(c) dodecacarbonyltrimanganese (0)
(d) manganicdodecacarbonyl (0)

26. The IUPAC name of $K_3[Ir(C_2O_4)_3]$ is

(a) potassium trioxalatoiridium (III)
(b) potassium trioxalatoiridate (III)
(c) potassium *tris* (oxalato) iridium (III)
(d) potassium *tris* (oxalato) iridate (III)

27. According to IUPAC nomenclature, sodium nitroprusside is named as

(a) sodium nitroferricyanide
(b) sodium nitroferrocyanide
(c) sodium pentacyanonitrosylferrate (II)
(d) sodium pentacyanonitrosoniumferrate (II)

28. The IUPAC name of the compound $[CuCl_2(CH_3NH_2)_2]$ is

(a) dichlorobis(dimethyl amine) copper (II)
(b) dichlorobis (methyl amine) copper (II)
(c) dimethyl amine copper (II) chloride
(d) *bis* (dimethyl amine) copper (II) chloride

29. The correct IUPAC name of potassium cuprochloride is

(a) potassium copper (I) tetrachloride
(b) potassium tetrachlorocuperate (I)
(c) tetrachloropotassium cuprate (I)
(d) tetrachlorocopper (I) potassiate

30. Name the complex $Ni(PF_3)_4$.

(a) Tetrakis(phosphorus(III) fluoride)nickel(0)
(b) Tetra (phosphorus(III) fluoride)nickel
(c) Nickel etrakis phosphorus(III) fluoride
(d) (Phosphorus(III) tetrakis fluoride) nickel(0)

31. The IUPAC name of $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$ is

(a) hexaamminecobalt(III) *tris* (oxalato)chromium
(b) hexaamminecobalt(III) *tris* (oxalato)chromate(III)
(c) hexaamminecobalt *tris* (oxalato)chromium(III)
(d) hexaamminecobalt(III) (oxalato)chromium(III)

Isomerism in Coordination Compounds

32. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent *(NCERT Exemplar)*

(a) linkage isomerism
(b) ionisation isomerism
(c) coordination isomerism
(d) no isomerism

33. The complexes $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$ exhibit

(a) geometrical isomerism
(b) ionisation energy
(c) coordination isomerism
(d) linkage isomerism

34. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are *(NCERT Exemplar)*

(a) linkage isomers
(b) coordination isomers
(c) ionisation isomers
(d) geometrical isomers

35. Which of the following will exhibit optical isomerism?

(a) $[Cr(en)(H_2O)_4]^{3+}$ (b) $[Cr(en)_3]^{3+}$
(c) *trans*-$[Cr(en)_2Cl_2]^+$ (d) $[Cr(NH_3)_6]^{3+}$

36. Which one of the following is expected to exhibit optical isomerism (en = ethylenediamine)?

(a) *trans*-$[Co(en)_2Cl_2]$ (b) *cis*-$[Pt(NH_3)_2Cl_2]$
(c) *cis*-$[Co(en)_2Cl_2]$ (d) *trans*-$[Pt(NH_3)_2Cl_2]$

37. Indicate the complex ion which shows geometrical isomerism. *(NCERT Exemplar)*

(a) $[Cr(H_2O)_4Cl_2]^+$ (b) $[Pt(NH_3)_3Cl]$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(CN)_5(NCl)]^{3-}$

38. The total number of possible isomers for the complex compound $[Cu(NH_3)_4][PtCl_4]$

(a) 6 (b) 5
(c) 4 (d) 3

39. For square planar complex of platinum (II), $[Pt(NH_3)(Br)(Cl)Py)]^{2+}$, how many isomeric forms are possible?

(a) Two (b) Three
(c) Four (d) Six

40. The number of isomers of Co (diethyl triamine) Cl_3 is

(a) 2 (b) 3
(c) 4 (d) 5

41. Which kind of isomerism is exhibited by octahedral complex $Co(NH_3)_4Br_2Cl$?

(a) Geometrical and ionisation
(b) Geometrical and optical
(c) Optical and ionisation
(d) Geometrical only

42. Which can exist both as diastereoisomer and enantiomer?

(a) $[Pt(en)_3]^{4+}$ (b) $[Pt(en)_2ClBr]^{2+}$
(c) $[Ru(NH_3)_4Cl_2]^0$ (d) $[PtCl_2Br_2]^0$

43. Number of isomeric forms (constitutional and stereoisomers) for $[Rh(en)_2(NO_2)(SCN)]^+$ are

(a) three (b) six (c) nine (d) twelve

44. Facial and meridianal isomerism will be exhibited by

(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(NH_3)_4Cl_2]$ Cl
(c) $[Co(en)_3Cl_3]$ (d) $[Co(NH_3)_5Cl]$ Cl_2

45. Which of the following complex will show geometrical as well as optical isomerism? (en = ethylene diamine)

(a) $Pt(NH_3)_2Cl_2$ (b) $[Pt(NH_3)Cl_4]$
(c) $[Pt(en)_3]^{4-}$ (d) $[Pt(en)_2Cl_2]$

46. Which of the following complex does not show geometrical isomerism?

(a) $[Co(NH_3)_4Cl_2]^+$ (b) $[Fe(NH_3)_2(CN)_4]^-$
(c) $[Cr(Ox)_3]^{3-}$ (d) $[Co(NH_3)_3(NO_2)_3]$

Bonding in Coordination Compounds

47. Among the following ions, which one has the highest unpaired electrons?

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Zn(H_2O)_6]^{2+}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

48. $[Pt(NH_3)_4]Cl_2$ is

(a) pyramidal (b) pentagonal
(c) tetrahedral (d) square planar

49. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are

(a) square planar and tetrahedral respectively
(b) Both tetrahedral
(c) tetrahedral and square planar respectively
(d) Both square planar

50. What is the magnetic moment of $K_3[FeF_6]$?

(a) 3.87 BM (b) 4.89 BM (c) 5.91 BM (d) 6.92 BM

51. Why do compounds having similar geometry have different magnetic moment? *(NCERT Exemplar)*

(a) Due to different reactivity
(b) Due to their labile nature
(c) Due to the presence of weak and strong field ligands
(d) None of the above

52. On the basis of VBT, find which is an inner orbital complex with 0 magnetic moment? ***(NCERT Exemplar)***

(a) $[Mn(CN)_6]^{3-}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Cr(H_2O)_6]^{3+}$ (d) $[FeCl_6]^{4-}$

53. The pair in which both species have same magnetic moment (spin only value) is

(a) $[Cr(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$
(b) $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$
(d) $[CoCl_4]^{2-}$, $[Fe(H_2O)_6]^{2+}$

54. Among $[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Fe(Cl)_6]^{3-}$ species, the hybridisation state of the Fe atom are, respectively.

(a) d^2sp^3, d^2sp^3, sp^3d^2
(b) sp^3d^2, d^2sp^3, d^2sp^3
(c) sp^3d^2, d^2sp^3, sp^3d^2
(d) None of the above

55. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$

(a) $Ni(CO)_4$ is diamagnetic, $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic
(b) $Ni(CO)_4$ and $[NiCl_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(Cl)_4]^{2-}$ is paramagnetic
(d) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

56. $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless why? ***(NCERT Exemplar)***

(a) Because H_2O is a strong field ligand than SO_4^{2-}
(b) Because SO_4^{2-} is a strong field ligand
(c) Because $CuSO_4$ is not a complex
(d) Because no *d-d* transition is possible in $CuSO_4$

57. Which of the following compounds is not coloured yellow? ***(JEE Main 2015)***

(a) $Zn_2[Fe(CN)_6]$ (b) $K_3[Co(NO_2)_6]$
(c) $(NH_4)_3[As(Mo_3O_{10})_4]$ (d) $BaCrO_4$

58. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. This is because of ***(NCERT)***

(a) difference in the nature of ligands
(b) the presence of unpaired electrons
(c) the *d-d* transition
(d) All of the above

59. The correct order for the wavelengths of absorption in the visible region for the following is
I. $[Ni(NO_2)_6]^{4-}$ II. $[Ni(NH_3)_6]^{2+}$ III. $[Ni(H_2O)_6]^{2+}$ ***(NCERT)***

(a) I > II > III (b) II > I > III
(c) III > II > I (d) III > I > II

60. Match the following Columns.

Column I (Complex)	Column II (Structure and magnetic moment)
A. $[Ag(NH_3)_2]^+$	1. Square planar and 1.73 BM
B. $[Co(NH_3)_6]^{3+}$	2. Linear and 0
C. $[Fe(CN)_6]^{3-}$	3. Octahedral and 0
D. $[Cu(NH_3)_4]^{2+}$	4. Octahedral and 0
E. $[Fe(CN)_6]^{4-}$	5. Octahedral and 1.73 BM

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	1	2	3	4	5	(b)	1	3	2	5	4
(c)	2	4	5	1	3	(d)	5	4	3	2	1

61. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

62. The crystal field stabilisation energy (CFSE) is the highest for

(a) $[CoF_4]^{2-}$ (b) $[Co(NCS)_4]^{2-}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[CoCl_4]^{2-}$

63. Which of the following complex has minimum magnitude of Δ_o?

(a) $[Cr(CN)_6]^{3-}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[CoCl_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

64. Which of the following configuration of ions has zero CFSE in both strong and weak ligand fields?

(a) d^{10} (b) d^8 (c) d^6 (d) d^4

65. Which of the following coordination entities should be expected to absorb light of lowest frequency?

(a) $(Cr(en)_3]^{3+}$ (b) $[CrCl_6]^{3-}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Cr(CN)_6]^{3-}$

66. The magnitude of crystal field stabilisation energy (CFSE or Δ_t) in tetrahedral complexes is considerably less than in the octahedral field. Because

(a) there are only four ligands instead of six so that ligand field is only 2/3 the size hence the Δ_t is only 2/3 the size
(b) the direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field stabilisation energy (Δ_t) by further 2/3.
(c) both points (a) and (b) are correct.
(d) both points (a) and (b) are wrong.

67. Which of the following pair is not correctly matched?

(a) Absorption peak for $[Cr^{III}(NH_3)_6]^{3+} = 21680\ cm^{-1}$

(b) Effective atomic no. of Pt in $[PtCl_6]^{2-} = 84$

(c) Crystal field stabilisation energy of d^2 in weak ligand field = $(-)0.8\ \Delta_o$

(d) Example of weak ligand field for d^5 configuration $= [Mn^{II}F_6]^{4-}$

68. The most stable ion is

(a) $[Fe(OH)_5]^{3-}$

(b) $[FeCl_6]^{3-}$

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

(d) $[Fe(H_2O)_6]^{3+}$

69. Calculate the overall complex dissociation equilibrium constant for the $Cu(NH_3)_4^{2+}$ ions, given that β_4 for this complex is 2.1×10^{13}.

(a) 8.27×10^{-13}

(b) 4.7×10^{-14}

(c) 2.39×10^{-7}

(d) 1.83×10^{14}

Applications of Coordination Compounds

70. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?

(a) Haemoglobin is the red pigment of blood and contains iron

(b) Cyanocobalamin is B_{12} and contains cobalt

(c) Chlorophyll are green pigments in plants and contains calcium

(d) Carboxypeptidase-A, an enzyme, contains zinc

71. The complex used as an anticancer agent is

(a) *cis*- $[PtCl_2(NH_3)_2]$ (b) Na_2CO_3

(c) *trans*- $[Co(NH_3)_3Cl_3]$ (d) *cis*-$K_2[PtCl_2Br_2]$

72. When EDTA solution is added to Mg^{2+} ion solution, then which of the following statements is not true?

(a) Four coordinate sites of Mg^{2+} are occupied by EDTA and remaining two sites are occupied by water molecules

(b) All six coordinate sites of Mg^{2+} are occupied

(c) pH of the solution is decreased

(d) Colourless $[Mg\text{-}EDTA]^{2-}$ chelate is formed

ROUND II Mixed Bag

1. The coordination number and oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$ are respectively

(a) +6 and +3 (b) 3 and 0

(c) 4 and +2 (d) 3 and +3

2. The oxidation state of Fe in the brown ring complex $[Fe(H_2O)_5NO]SO_4$ is

(a) +3 (b) 0 (c) +2 (d) +1

3. Which of the following statements is correct?

(a) In $K_3[Fe(CN)_6]$, the ligand has satisfied both primary and secondary valencies of ferric ion.

(b) In $[Cu(NH_3)_4]SO_4$, the ligand has satisfied only the secondary valency of copper.

(c) In $K_3[Fe(CN)_6]$, the ligand has satisfied only the secondary valency of ferric ion.

(d) Both (b) and (c)

4. According to IUPAC nomenclature sodium nitroprusside is named as

(a) sodium pentacyanonitrosylferrate (II)

(b) sodium pentacyanonitrosylferrate (III)

(c) sodium nitroferricyanide

(d) sodium nitroferrocyanide

5. I. $K_4[Fe(CN)_6]$ II. $K_3[Cr(CN)_6]$

III. $K_3[Co(CN)_6]$ IV. $K_2[Ni(CN)_4]$

Select the complexes which are diamagnetic.

(a) I, II and III (b) II, III and IV

(c) I, III and IV (d) I, II and IV

6. Mixture $X = 0.02$ mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L of solution

1 L of mixture $X +$ excess $AgNO_3 \longrightarrow Y$

1 L of mixture $X +$ excess $BaCl_2 \longrightarrow Z$

Number of moles of Y and Z are

(a) 0.01, 0.01 (b) 0.01, 0.02

(c) 0.02, 0.01 (d) 0.02, 0.02

7. The hybridisation of central metal ion and shape of Wilkinson's catalyst is

(a) sp^3d, trigonal bipyramidal

(b) sp^3, tetrahedral

(c) dsp^2, square planar

(d) d^2sp^2, octahedral

8. An aqueous solution of $CoCl_2$ on addition of excess of concentrated HCl turns blue due to formation of

(a) $[CoCl_4]^{2-}$

(b) $[Co(H_2O)_2Cl_4]^{2-}$

(c) $[Co(H_2O)_22Cl_4]^{2-}$

(d) $[Co(H_2O)_4Cl_2]$

9. Which one of the following complexes is an outer orbital complex?

(a) $[Fe(CN)_6]^{4-}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Ni(NH_3)_6]^{2+}$ (d) None of these

10. Which one of the following has highest number of isomers?

(a) $[Co(NH_3)_5Cl]^{2+}$
(b) $[Co(en)_2Cl_2]^+$
(c) $[Ru(NH_3)_4Cl^-]$
(d) $[In(Ph_3)_2H(CO)]^{2+}$

11. In which of the following pairs both the complex show optical isomerism?

(a) *Cis*-$[Cr(C_2O_4)_2Cl_2]^{3-}$; *cis*-$[Co(NH_3)_4Cl_2]$
(b) $[PtCl(dien)]Cl$, $[NiCl_2Br_2]^{2-}$
(c) $[Co(NO_3)_3(NH_3)_3]$, *cis*-$[Pt(en)_2Cl_2]$
(d) $[Co(en)_3]Cl_3$, *cis*-$[Co(en)_2Cl_2]Cl$

12. Match the complex ions given in Column I with the colours given in Column II and assign the correct code *(NCERT Exemplar)*

Column I (Complex ion)	**Column II** (Colour)
A. $[Co(NH_3)_6]^{3+}$	1. Violet
B. $[Ti(H_2O)_6]^{3+}$	2. Green
C. $[Ni(H_2O)_6]^{2+}$	3. Pale blue
D. $[Ni(H_2O)_4(en)]^{2+}$ (*aq*)	4. Yellowish orange
	5. Blue

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	5	(b)	4	3	2	1
(c)	3	2	4	1	(d)	4	1	2	3

13. Match the complex species given in Column I with the possible isomerism given in Column II and assign the correct code *(NCERT Exemplar)*

Column I (Complex species)	**Column II** (Isomerism)
A. $[Co(NH_3)_4Cl_2]^+$	1. Optical
B. *cis* - $[Co(en)_2Cl_2]^+$	2. Ionisation
C. $[Co(NH_3)_5(NO_2)]Cl_2$	3. Coordination
D. $[Co(NH_3)_6][Cr(CN)_6]$	4. Geometrical
	5. Linkage

Codes

	A	B	C	D
(a)	1	2	4	5
(b)	4	3	2	1
(c)	4	1	5	3
(d)	4	1	3	2

14. Match the complex ions given in Column I with the hybridisation number of unpaired electrons given in Column II and assign the correct code *(NCERT Exemplar)*

Column I (Complex ion)	**Column II** (Hybridisation and number of unpaired electrons)
A. $[Cr(H_2O)_6]^{3+}$	1. dsp^2, 1
B. $[Co(CN)_4]^{2-}$	2. sp^3d^2, 5
C. $[Ni(NH_3)_6]^{2+}$	3. d^2sp^3, 3
D. $[MnF_6]^{4-}$	4. sp^3, 4
	5. sp^3d^2, 2

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	5	2	(b)	4	3	2	1
(c)	3	2	4	1	(d)	4	1	3	2

15. Match the coordination compounds given in Column I with the central metal atoms given in Column II and assign the correct code *(NCERT Exemplar)*

Column I (Coordination compound)	**Column II** (Central metal atom)
A. Chlorophyll	1. Rhodium
B. Blood pigment	2. Cobalt
C. Wilkinson catalyst	3. Calcium
D. Vitamin B_{12}	4. Iron
	5. Magnesium

Codes

	A	B	C	D		A	B	C	D
(a)	5	4	1	2	(b)	3	4	5	1
(c)	4	3	2	1	(d)	3	4	1	2

16. Which of the following complexes are heteroleptic ?

(a) $[Cr(NH_3)_6]^{3+}$ (b) $[Fe(NH_3)_4Cl_2]^+$
(c) $[Mn(CN)_6]^{4-}$ (d) $[MnF_6]^{4-}$

17. An aqueous pink solution of cobalt (II) chloride changes to deep blue on addition of excess of HCl. This is because *(NCERT Exemplar)*

(a) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_6]^{4-}$
(b) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$
(c) Octahedral complexes have smaller crystal field splitting than octahedral complexes
(d) tetrahedral complexes have larger crystal field splitting than octahedral complex

18. In which of the following, the chemical formula and the name correctly not matched ?

(a) $K_3[Cr(C_2O_4)_3]$ — Potassium trioxalatochromate (III)
(b) $K[Pt(NH_3)Cl_5]$ — Potassium amminepentachlorido platinate (IV)
(c) $Na_2[Ni(EDTA)]$— Sodium ethylenediaminetetra acetatonickel (I)
(d) $[Ag(CN)_2]^-$ — Dicyanoargentate (I) ion

19. Identify the optically active compounds from the following *(NCERT Exemplar)*

(a) $[Co(en)_3]^{3+}$ (b) *trans*- $[Co(en)_2Cl_2]^+$

(c) *cis*- $[Co(en)_2Cl_2]^{2+}$ (d) $[Cr(NH_3)_5Cl]$

20. Among the following pairs of complexes, in which case the Δ_o value is higher for the first one?

(a) $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$

(b) $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$

(c) $[Rh(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{2+}$

(d) $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$

21. Which of the following statements is correct ?

(a) Zinc (II) ion has a zero CFSE for any geometry

(b) A solution of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ appear colourless in dil solutions

(c) A solution of $[Ni(H_2O)_6]^{2+}$ is green as the value of Δ for the H_2O complex is in the visible region

(d) All of the above

22. In which of the following complex ion, the metal ion will have t_{2g}^6, e_g^0 configuration according to CFT?

(a) $[Fe(CN)_6]^{3-}$ (b) $[FeF_6]^{3-}$

(c) $[Fe(CN)_6]^{4-}$ (d) None of these

23. Match Column I with Column II.

Column I	Column II
A. $[Co(NH_3)_6][Cr(CN)_6]$	1. Linkage isomerism
B. $[Co(NH_3)_3(NO_2)_3]$	2. Solvate isomerism
C. $[Cr(H_2O)_6]Cl_3$	3. Coordination isomerism
D. *cis*-$[CrCl_2(ox)_2]^{3-}$	4. Optical isomerism

Choose the correct answer from the options given below *(JEE Main 2021)*

	A	B	C	D		A	B	C	D
(a)	3	1	2	4	(b)	4	2	3	1
(c)	2	1	3	4	(d)	1	2	3	4

24. Arrange the following metal complex/compounds in the increasing order of spin only magnetic moment. Presume all the three, high spin system. (Atomic numbers Ce = 58, Gd = 64 and Eu = 63.)

(i) $(NH_4)_2[Ce(NO_3)_6]$ (ii) $Gd(NO_3)_3$ and

(iii) $Eu(NO_3)_3$ *(JEE Main 2021)*

Answer is

(a) (ii) < (i) < (iii) (b) (iii) < (i) < (ii)

(c) (i) < (ii) < (iii) (d) (i) < (iii) < (ii)

25. Which among the following will be named as dibromidobis (ethylenediamine) chromium (III) bromide? *(AIEEE 2012)*

(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$

(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

26. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? *(AIEEE 2011)*

(a) The complex involves d^2sp^3-hybridisation and is octahedral in shape

(b) The complex is paramagnetic

(c) The complex is an outer orbital complex

(d) The complex gives white precipitate with silver nitrate solution

27. Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength, is *(AIEEE 2011)*

(a) $CO < NH_3 < en < CN^-$ (b) $NH_3 < en < CN^- < CO$

(c) $CN^- < NH_3 < CO < en$ (d) $en < CN^- < NH_3 < CO$

28. Which one of the following complex ions has geometrical isomers? *(AIEEE 2011)*

(a) $[Co(en)_3]^{3+}$ (b) $[Ni(NH_3)_5Br]^+$

(c) $[Co(NH_3)_2(en)_2]^{3+}$ (d) $[Cr(NH_3)_4(en)]^{3+}$

29. Which of the following has an optical isomer? *(AIEEE 2009)*

(a) $[Co(NH_3)_3Cl]^+$ (b) $[Co(en)(NH_3)_2]^{2+}$

(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Co(en)_2(NH_3)_2]^{3+}$

30. Which of the following pairs represents linkage isomers? *(AIEEE 2009)*

(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(b) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

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

(d) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

31. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is *[JEE Main 2014]*

(a) $L_4 < L_3 < L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$

(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

Numeric Value Questions

32. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is …… . *(AIEEE 2011)*

33. The sum of coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylenediamine) is …… . *(AIEEE 2008)*

34. The sum values of m and n in the anionic species $[V(CO)_m]^{n-}$, if it is following Sidgwick EAN rule and having octahedral shape?

35. Consider the following carbonyl complex compounds

(I) $H_xCr(CO)_5$ (II) $CO_2(CO)_y$ (III) $Mo(CO)_z$ then the value of $\left(\frac{x+y+z}{5}\right)$ is ……

Answers

Round I

1. (b)	**2.** (a)	**3.** (c)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (b)	**8.** (c)	**9.** (d)	**10.** (d)
11. (d)	**12.** (c)	**13.** (b)	**14.** (a)	**15.** (d)	**16.** (a)	**17.** (d)	**18.** (b)	**19.** (c)	**20.** (a)
21. (c)	**22.** (d)	**23.** (a)	**24.** (c)	**25.** (c)	**26.** (b)	**27.** (d)	**28.** (b)	**29.** (c)	**30.** (a)
31. (b)	**32.** (d)	**33.** (c)	**34.** (a)	**35.** (b)	**36.** (c)	**37.** (a)	**38.** (c)	**39.** (b)	**40.** (a)
41. (a)	**42.** (b)	**43.** (d)	**44.** (a)	**45.** (d)	**46.** (c)	**47.** (d)	**48.** (d)	**49.** (c)	**50.** (c)
51. (c)	**52.** (b)	**53.** (b)	**54.** (c)	**55.** (c)	**56.** (d)	**57.** (a)	**58.** (a)	**59.** (c)	**60.** (c)
61. (c)	**62.** (c)	**63.** (c)	**64.** (b)	**65.** (b)	**66.** (c)	**67.** (b)	**68.** (c)	**69.** (b)	**70.** (c)
71. (a)	**72.** (a)								

Round II

1. (a)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (a)	**9.** (c)	**10.** (b)
11. (d)	**12.** (b)	**13.** (c)	**14.** (a)	**15.** (a)	**16.** (b)	**17.** (b)	**18.** (c)	**19.** (a)	**20.** (c)
21. (b)	**22.** (c)	**23.** (a)	**24.** (d)	**25.** (b)	**26.** (c)	**27.** (b)	**28.** (c)	**29.** (d)	**30.** (b)
31. (b)	**32.** (2.82)	**33.** (9)	**34.** (7)	**35.** (2.4)					

Solutions

Round I

1. Ligands have tendency to donate its lone pair. NH_4^+ ion have no lone pair so it is unable to behave like a ligand.

2. Chelating agent coordinates through more than one coordinating sites. Thiosulphate ($S_2O_3^{2-}$) although coordinate through only one coordinating site, so it is not referred as chelating agent.

6. The complexes can be written as follows

$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_4]Cl$

Hence, number of primary valencies are 3, 2 and 1 respectively.

7. $[Co(NH_3)_5Cl]^{2+} + 2Cl^- \longrightarrow [Co(NH_3)_5Cl]Cl_2$

8. The complex will dissociate in aqueous solution to produce 3 ions.

$$Co(NH_3)_6Cl_2 \xrightarrow{Aq.} [Co(NH_3)_6]^{2+} + 2Cl^{-\prime}$$

9. When excess of KCN(*aq*) is mixed with $CuSO_4(aq)$, a complex named potassium tetracyanocuprate (II) is formed. Since, CN^- ions are strong ligands, the complex is quite stable. It is evident from the stability constant value ($K = 2.0 \times 10^{27}$).

$$\underset{\text{(Excess)}}{4KCN(aq)} + CuSO_4(aq) \longrightarrow \underset{\text{(Soluble)}}{K_2[Cu(CN)_4](aq)} + K_2SO_4(aq)$$

$$\big\downarrow + H_2S$$

No cleavage and no production of Cu^{2+} ions

10. Formation of 3 moles AgCl from 1 mole complex suggests the presence of all the three Cl^- outside the coordination sphere. Thus, the formula of the complex should be $[Cr(H_2O)_6]Cl_3$.

11. In acidic solution, proton coordinates with ammonia to form NH_4^+. NH_4^+ does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.

12. In all these complexes, Fe is in +3 oxidation state. However, the complex (c) form a chelate because three $C_2O_4^{2-}$ ions act as the chelating ligands. Thus, the most stable complex is $[Fe(C_2O_4)_3]^{3-}$.

13. According to Sidgwick,

EAN = atomic number of nearest noble gas

In case of $[Fe(CN)_6]^{3-}$, $EAN = 26 - 3 + 2 \times 6 = 35$

While, the atomic number of nearest noble gas is 36. Thus, it does not follow EAN rule.

14. $Ti_{22} = [Ar]\,3d^2 4s^2$

Since, its magnetic moment is zero, it is present in the form of Ti^{4+}. Thus, the formula of the complex is $[Ti(H_2O)_6]Cl_4$ as only in it the oxidation state of Ti is +4.

15. Since, the compound *A* gives white precipitate with $AgNO_3$, which is soluble in dilute ammonia solution, it contains at least one Cl-atom outside the coordination sphere.

Thus, its formula is $[Cr(NH_3)_4BrCl]Cl$.

$$[Cr(NH_3)_4BrCl]Cl \longrightarrow [Cr(NH_3)_4BrCl]^+ + Cl^-$$

$$AgNO_3 + Cl^- \longrightarrow \underset{\text{White ppt.}}{AgCl} + NO_3^-$$

Similarly, compound B gives a yellow precipitate which is soluble in concentrated ammonia solution, it contains a Br atom outside the sphere. Thus, its formula must be $[Cr(NH_3)_4Cl_2]Br$.

$$[Cr(NH_3)_4Cl_2]Br \longrightarrow [Cr(NH_3)_4Cl_2]^+ + Br^-$$
$$Br^- + AgNO_3 \longrightarrow \underset{\substack{\text{Pale yellow}\\ \text{ppt.}}}{AgBr} + NO_3^-$$

16. In $[MnO_4]^-$, the oxidation state of Mn is +7.

$$Mn\,(25) = [Ar]\,3d^5 4s^2$$
$$Mn^{7+} = [Ar]$$

Thus, in $[MnO_4]^-$ no d-electron is present.

17. In $MnSO_4 \cdot 4H_2O$, Mn is present as Mn^{2+}.

$$Mn^{2+} = \overset{3d^5}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}} \quad \overset{4s^0}{\boxed{}} \quad \text{(unpaired electrons = 5)}$$

In $CuSO_4 \cdot 5H_2O$, Cu is present as Cu^{2+}.

$$Cu^{2+} = \overset{3d^9}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}} \quad \overset{4s^0}{\boxed{}} \quad \text{(unpaired electron = 1)}$$

In $FeSO_4 \cdot 6H_2O$, Fe is present as Fe^{2+}

$$Fe^{2+} = \overset{3d^6}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}} \quad \overset{4s^0}{\boxed{}} \quad \text{(unpaired electrons = 4)}$$

In $NiSO_4 \cdot 6H_2O$, Ni is present as Ni^{2+}

$$Ni^{2+} = \overset{3d^8}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}} \quad \overset{4s^0}{\boxed{}} \quad \text{(unpaired electrons = 2)}$$

Since, paramagnetic character $\propto$ unpaired electrons. Thus, $CuSO_4 \cdot 5H_2O$ has the lowest degree of paramagnetism among the given at 298 K.

18. $[Pt(py)_4][PtCl_4]$

Let the oxidation state of Pt be x.

$$x + 0 \times 4 + x + (-1) \times 4 = 0$$
$$2x = 4 \;\Rightarrow\; x = +2$$

Thus, it is the complex in which the central metals atom in cationic and anionic parts have same oxidation state.

19. $$-\Delta T_f = 0.56 = i \times 1.86 \times \frac{0.875}{233.5} \times \frac{1000}{25} \quad [\because\ \Delta T_f = i\, k_f \cdot m]$$

$$\therefore \qquad i = 2$$

Hence, the formula of the complex ion is $[Co(NH_3)_4Cl_2]Cl$.

[For details see chapter 2 'solutions']

20. IUPAC name of $[Pt(NH_3)_2Cl_2]$ is diamminedichloridoplatinum (II).

21. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is diamminechloridonitrito-N-platinum (II).

25. dodecacarbonyltrimanganese (0)

26. potassium trioxalatoiridate (III)

27. According to IUPAC sodium nitrosoprusside is named as sodium pentacyanonitrosoniumferrate (II).

28. dichlorobis (methyl amine) copper (II)

29. potassium tetrachlorocuperate (I)

30. *Ttetrakis* (phosphorus(III) fluoride) nickel (0)

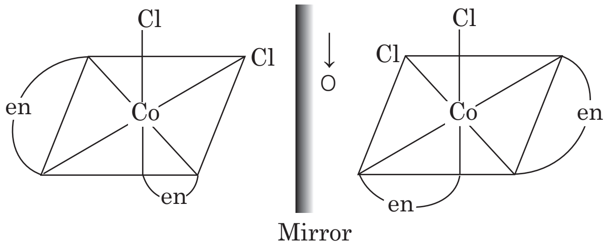
31. hexaamminecobalt(III) *tris* (oxalato) chromate(III)

32. The given complexes are not isomers as their composition is not same. (Isomers have same composition but different arrangement and properties.)

33. $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$ exhibit coordination isomerism. Coordination isomerism is possible when both positive and negative ions of a salt are complex ions and the two isomers differ in distribution of ligands in the cation and the anion.

34. Complexes having ambidentate ligands like SCN exhibit linkage isomerism.

36. *cis* $[Co(en)_2Cl_2]$ will exhibit optical isomerism as shown below.



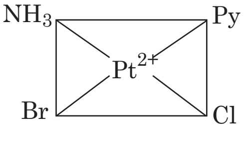
cis $[Co(en)_2Cl_2]$

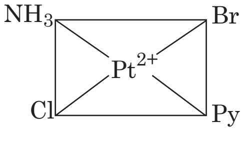
37. Octahedral complexes of the type $[MA_4B_2]^+$ (where, A and B are two different monodentate ligands) exhibit geometrical isomerism. Hence, among the given only $[Cr(H_2O)_4Cl_2]^+$ exhibit geometrical isomerism.

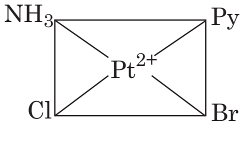
38. Total 4 isomers are possible which are as follows

$[Cu(NH_3)_3Cl]\,[Pt\,Cl_3NH_3]$,
$[Cu(NH_3)_2Cl_2][PtCl_2(NH_3)_2]$,
$[Cu\,NH_3Cl_2]\,[Pt\,Cl(NH_3)_3]$, $[CuCl_4]\,[Pt(NH_3)_4]$

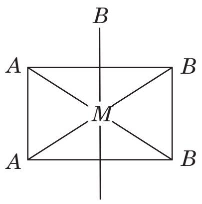
39. (*Mabcd*) type complexes exist in three isomeric forms.



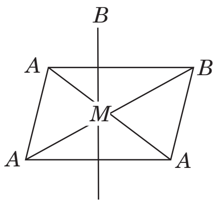




40. The given compound is of MA_3B_3 type where diethylene triammine is $H_2NCH_2CH_2NH$, $CH_2CH_2NH_2$ a tridentate ligand. It shows two geometrical isomers *fac* and *mer*.



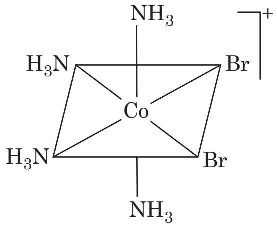
(*fac*)



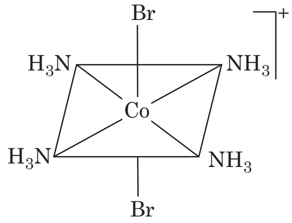
(*mer*)

41. The complex shows geometrical as well as ionisation isomerism.

$[Co(NH_3)_4Br_2]Cl \rightleftharpoons [Co(NH_3)_4Br_2]^+ + Cl^-$

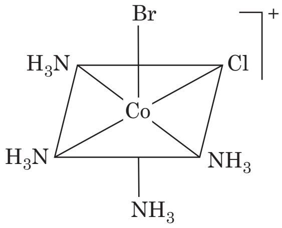


cis

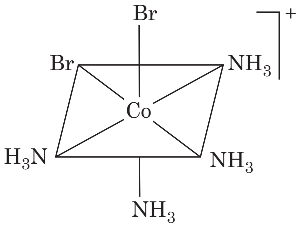


trans

$[Co(NH_3)_4BrCl]Br \rightleftharpoons [Co(NH_3)_4BrCl]^+ + Br^-$

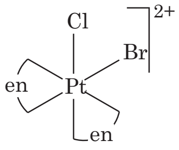


cis

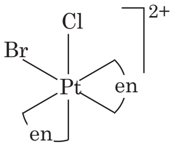


trans

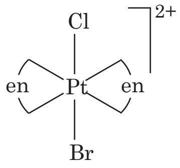
42. $[Pt(en)_2ClBr]^{2+}$ can exit both as diastereoisomer (geometrical) and enantiomer (optical).



cis
(+)
d-isomer

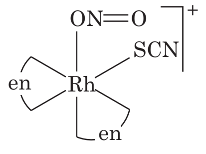


(–)
i-isomer

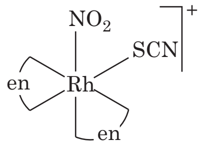


trans

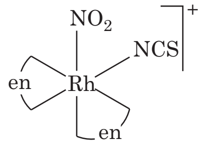
43. Ambidentate ligands NO_2^- and SCN^- will give two different isomers.



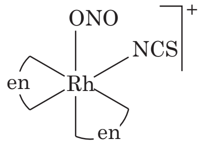
cis, d–



cis, d–

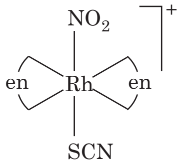


cis, d–

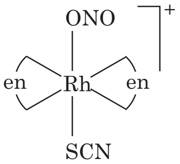


cis, d–

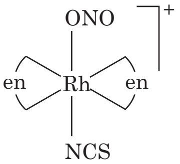
I to IV each will have further two more isomers *cis*, *l* and *trans* (shown below),



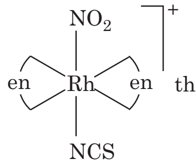
trans–



trans–



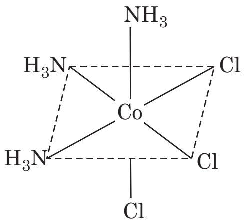
trans–



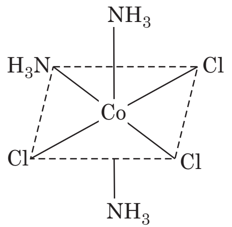
thus, giving total isomeric forms = 12

trans–

44. Facial (*fac*) and meridianal (*mer*) isomerism, a type of geometrical isomerism, is shown by octahedral complexes having Ma_3b_3 general formula, where, M is central metal and a and b are monodentate ligands. Hence, $[Co(NH_3)_3Cl_3]$ exhibits *fac-mer* isomerism as,

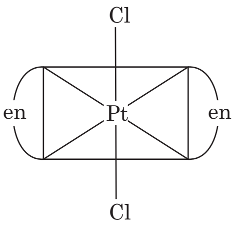


fac-form

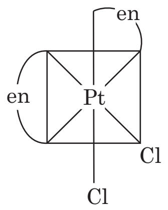


mer-form

45. $[Pt(en)_2Cl_2]$ exhibit both geometrical as well as optical isomerism.

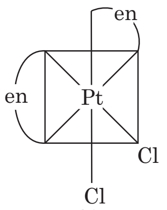


trans-isomer

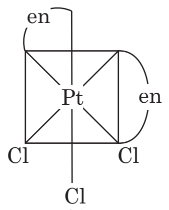


cis-isomer

Geometrical isomers



cis-*d*-isomer



cis-*d*-isomer

Optical isomers

46. Octahedral complexes of the type MA_4X_2, MA_3X_3, MA_2X_4, $M(AA)_2X_2$, $M(AA)_2XY$ exist are *cis* and *trans* isomers (show geometrical isomerism). Thus, $[Cr(ox)_3]^{3-}$ will not show geometrical isomerism.

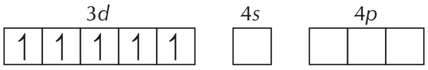
47. $[Fe(H_2O)_6]^{3+}$ has five unpaired electrons.

48. Since, hybridisation of $[Pt(NH_3)_4]Cl_2$ is dsp^2 so, it is square planar.

49. $Ni(CO)_4$ has sp^3 hibridisation so it geometry would be tetrahedral whereas $Ni(PPh_3)_2Cl_2$ has dsp^2 hybridisation so its ... would be square planar.

50. $K_3[FeF_6]$

$Fe^{3+} = [Ar]3d^5 4s^0$



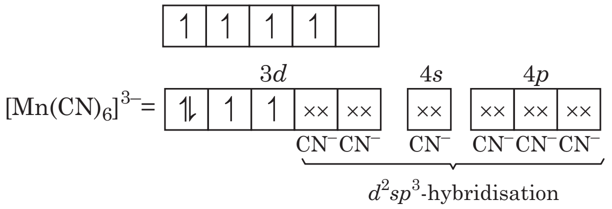
Number of unpaired electrons = 5

Magnetic moment $= \sqrt{5(5+2)} = \sqrt{s(s+2)}$

$= \sqrt{35} = 5.91$ BM

51. It is due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and *vice-versa*, e.g. $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic, and the latter is diamagnetic because F^- is a weak field ligand and NH_3 is a strong field ligand.

52. (a) **$[Mn(CN)_6]^{3-}$** $Mn^{3+} = 3d^4$



(i) d^2sp^3-hybridisation

(ii) Inner orbital complex because $(n-1)$ d-orbitals are used.

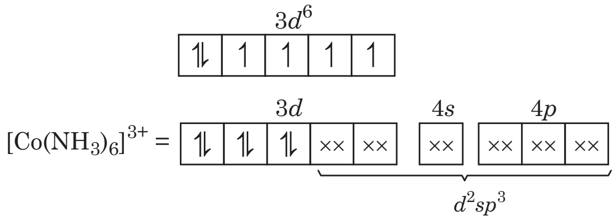
(iii) Paramagnetic, as two unpaired electrons are present.

(iv) Spin only magnetic moment

$(\mu) = \sqrt{2(2+2)} = \sqrt{8} = 2.82$ BM

(b) **$[Co(NH_3)_6]^{3+}$**

$Co^{3+} = 3d^6 4s^0$



(NH_3 pair up the unpaired $3d$ electrons.)

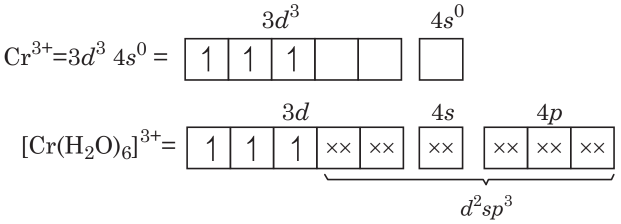
(i) d^2sp^3-hybridisation

(ii) Inner orbital complex because of the involvement of $(n-1)$ d-orbital in bonding.

(iii) Diamagnetic, as no unpaired electron is present.

(iv) $\mu = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$ (zero)

(c) **$[Cr(H_2O)_6]^{3+}$**



(i) d^2sp^3-hybridisation

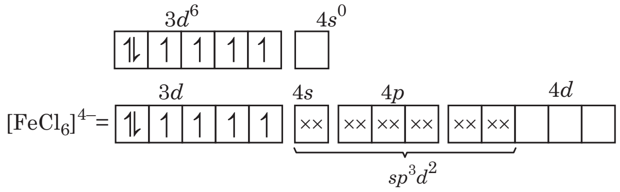
(ii) Inner orbital complex (as $(n-1)$ d-orbitals take part.)

(iii) Paramagnetic (as three unpaired electrons are present.)

(iv) $\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

(d) **$[Fe(Cl)_6]^{4-}$**

$Fe^{2+} = 3d^6$



(i) sp^3d^2-hybridisation

(ii) Outer orbital complex because nd-orbitals are involved in hybridisation.

(iii) Paramagnetic (because of the presence of four unpaired electrons).

(iv) $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)}$

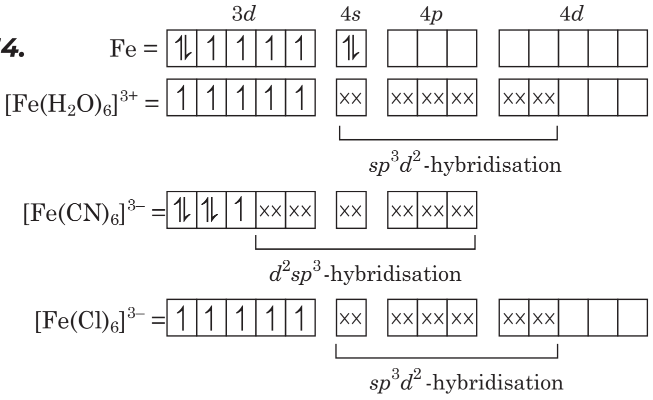
$= \sqrt{24} = 4.9$ BM

53. Species having the same number of unpaired electrons, have same magnetic moment because magnetic moment is related with number of unpaired electrons (n) as, $\mu = \sqrt{n(n+2)}$

$Cr^{2+} = [Ar]3d^4$ (4 unpaired electrons)
$Co^{2+} = [Ar]3d^7$ (3 unpaired electrons)
$Mn^{2+} = [Ar]3d^5$ (5 unpaired electrons)
$Fe^{2+} = [Ar]3d^6$ (4 unpaired electrons)

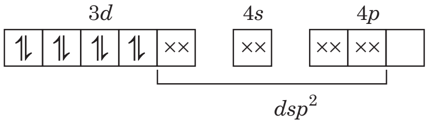
Thus, $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ have same magnetic moment.

54.

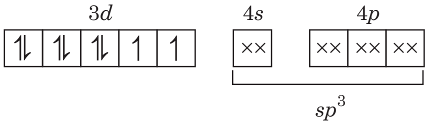


55. The electronic configuration of Ni in $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are as follows

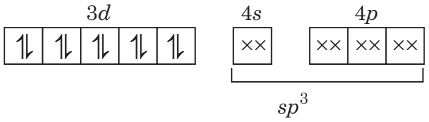
Ni^{2+} in $[Ni(CN)_4]^{2-}$,



Ni^{2+} in $[NiCl_4]^{2-}$,



Ni in $[Ni(CO)_4]$,



CO and CN^- are strong ligands so, they induces pairing of electrons so, their complexes are diamagnetic while, Cl^- is a weak field ligand so, it does not induce the pairing of electrons so, its complex is paramagnetic.

56. In $CuSO_4 \cdot 5H_2O$ water acts as ligand as a result it causes crystal field splitting. Hence, *d-d* transition is possible thus $CuSO_4 \cdot 5H_2O$ is coloured. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence, it is colourless.

57. $Zn_2[Fe(CN)_6]$, $K_3[Co(NO_2)_6]$ and $[(NH_4)_3As(Mo_3O_{10})_4]$ show colour due to *d-d* transition while $BaCrO_4$ is coloured due to charge transfer phenomenon.

Further, according to spectrochemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO_2, NH_4^+, O^{2-} etc., ligands show yellow colour while CN^- forces the complex to impart white colour.

Spectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^-$
$< C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN < py < NH_3$
$< en < bipy < Phen < NO_2^- < PPh_3 < CN^- \approx CO$

58. In both the complex compounds, Fe is in +2 oxidation state with configuration $3d^6$, i.e. it has four unpaired electrons. In the presence of weak H_2O ligands, the unpaired electrons do not pair up. But in the presence of strong ligand CN^-, they get paired up. Then, no unpaired electron is left. Due to this difference in the number of unpaired electrons, both complex ions have different colours.

59. We know that, CFSE is higher for the complex having strong field ligand and varies inversely with wavelength. In all the given complexes, the metal ion is Ni^{2+}. The increasing field strengths of the ligands present as per electrochemical series are in the order

$$H_2O < NH_3 < NO_2^-$$

The energies absorbed for excitation will be in the order

$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

As $E = \frac{hc}{\lambda}$, i.e. $E \propto \frac{1}{\lambda}$; the wavelengths will be in the opposite order, that is as follows

$[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

60. (a) $[Ag(NH_3)_2]^+$ has coordination number 2. It has linear structure and because of no unpaired electron, its dipole moment is zero.

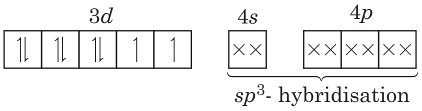
(b) $[Co(NH_3)_6]^{3+}$ has d^2sp^3-hybridisation and octahedral structure. Because of no unpaired electron, it is diamagnetic, i.e. magnetic moment = zero.

(c) $[Fe(CN)_6]^{3-}$ has d^2sp^3-hybridisation and octahedral structure. It has one unpaired electron. So, it is paramagnetic and has magnetic moment.

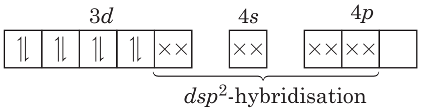
(d) $[Cu(NH_3)_4]^{2+}$ has dsp^2-hybridisation and is square planar in structure and has unpaired electron. So, it is paramagnetic and has magnetic moment.

(e) $[Fe(CN)_6]^{4-}$ has d^2sp^3-hybridisation and octahedral structural. It has no unpaired electron, hence magnetic moment is zero.

61. $[NiCl_2\{PEt_2Ph\}_2]$ contains Ni^{2+} with electronic configuration, $Ni^{2+} = [Ar]\,3d^8 4s^0$



In high spin state, it is paramagnetic, sp^3-hybridisation at tetrahedral. In low spin state, it is diamagnetic, dsp^2-hybridised an square planar.



62. In octahedral strong ligand field complex is $[Co(NH_3)_6]^{3+}$, the CFSE value is higher as all $3d^6$ electrons occupy lower energy t_{2g}-orbitals.

63. Magnitude of Δ_o depends upon the strength of the ligand to cause crystal field splitting. The strength can be compared from the position of the ligand in the spectrochemical series. The order of increasing strength is $Cl^- < H_2O < NH_3 < CN^-$. As Cl^- is the weakest ligand, the complex $[CoCl_6]^{3-}$ has minimum magnitude of Δ_o.

64. For d^8 to d^{10} configurations we have only one possible arrangement.

$d^{10} = t_{2g}^6 e_g^4$ CFSE $= (-.4 \times 6 + .6 \times 4) = 0$

65. The coordination entity for which crystal field splitting is smaller, absorbs light of lowest frequency. Weaker the ligand field strength, smaller will be the crystal field splitting. The order or field strength of various ligands is $CN^- > en > NH_3 > Cl^-$.

Hence, $[CrCl_6]^{3-}$ due to presence of weak field ligand Cl^-, absorbs light of lowest frequency.

66. CFSE in case of tetrahedral complexes is less than the octahedral field due to the points (a) and (b).

67. EAN of Pt in $[PtCl_6]^{2-} = 86$

68. Stability of complex increases with increase in charge on the central metal ion and with increase in basic strength of ligand.

In $[Fe(CN)_6]^{3-}$, oxidation state of Fe is +3 and basicity of CN^- is higher than that of OH^-, Cl^- and H_2O. Thus, $[Fe(CN)_6]^{3-}$ is the most stable ion among the given.

69. Dissociation constant is the reciprocal of β_4, the stability constant.

Overall complex dissociation equilibrium constant

$$= \frac{1}{\beta_4}$$

$$= \frac{1}{2.1 \times 10^{13}} = 4.7 \times 10^{-14}$$

70. Chlorophyll are green pigment in plant and contain magnesium instead of calcium.

71. *cis*-isomer of $[Pt(NH_3)_2Cl_2]$ is used as an anticancer drug for treating several type of malignant tumours. When it is injected into the blood stream, the more reactive Cl groups are lost so, the Pt atom bonds to a N-atom in guanosine (a part of DNA). This molecule can bond to two different guanosine units and by bridging between them it upsets the normal reproduction of DNA.

72. $[H_2EDTA]^{2-} + Mg^{2+} \longrightarrow [MgEDTA]^{2-} + 2H^+$

(a) In this complex, four donor sites are occupied by oxygen and two donor sites are occupied by nitrogen.
(b) This complex is six coordinated.
(c) Complex $[MgEDTA]^{2-}$ is colourless.
(d) Increase in $[H^+]$ decreases pH of the solution.

Round II

1. Its coordination number will be 6 because it is bonded with three bidentate ligands.

Let x be the oxidation state of Cr.

$$\therefore \quad x + 3(-2) + 3(+1) = 0 \Rightarrow x = +3$$

2. Let the oxidation state of Fe in $[Fe(H_2O)_5NO]SO_4$ is x.

$[Fe(H_2O)_5NO]^{2+}$

$$\Rightarrow \quad x + 0 + 1 = 2$$

$$\therefore \quad x = +1$$

Hence, NO exists as nitrosyl ion (NO^+).

3. In $K_3[Fe(CN)_6]$, the ligands are negatively charged which is present in coordination spheres shows a dual behaviour. It may satisfied both primary and secondary valencies while neutral ligand satisfied only secondary valencies.

4. IUPAC name of sodium nitroprusside $Na_2[Fe(CN)_5NO]$ is sodium pentacyanonitrosoyl ferrate (III) because in it NO is neutral ligand and the oxidation number of Fe is III, which is calculated as

$$2 \times \text{O.N. of Na} + \text{O.N. of Fe} + 5 \times \text{O.N. of CN} + 1 \times \text{O.N. of NO} = 0$$

$$2 \times (+1) + \text{O.N. of Fe} + 5 \times (-1) + 1 \times 0 = 0$$

$$\therefore \quad \text{O.N. of Fe} = 5 - 2 = +3$$

5. Structure $K_4[Fe(CN)_6]$, $K_3[Co(CN)_6]$, $K_2[Ni(CN)_4]$ are diamagnetic.

6. $$\underset{}{[Co(NH_3)_5SO_4]Br} + \underset{\text{Excess}}{AgNO_3} \longrightarrow \underset{\substack{0.02 \text{ mol} \\ (Y)}}{[Co(NH_3)_5SO_4]} + AgBr$$

$$\underset{\frac{0.02}{2} \text{ mol L}^{-1}}{[Co(NH_3)_5Br]SO_4} + \underset{\text{Excess}}{BaCl_2} \longrightarrow \underset{\substack{(Z) \\ 0.01 \text{ mol L}^{-1}}}{[Co(NH)_5Br]Cl_2} + BaSO_4$$

7. Wilkinson's catalyst, $(Ph_3P)_3RhCl$

$$Rh^+ = [Kr]\,4d^8s^0$$

i.e. dsp^2-hybridisation.

Rh atom in Wilkinson's catalyst is dsp^2-hybridised giving a square planar shape to the molecule.

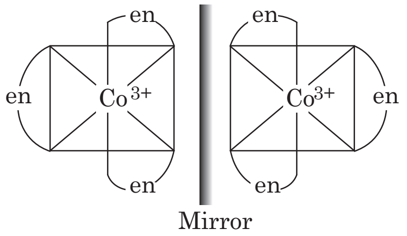
8. $CoCl_2$ is a weak Lewis acid, It reacts with chloride ions to produce salt containing the tetrahedral $[CoCl_4]^{2-}$ ion. $CoCl_2$ is blue when anhydrous, and a deep magenta colour when hydrated, for this reason it is widely used as an indicator for water.

9.

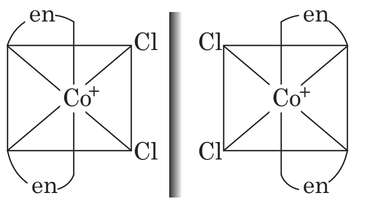
Complex ion	**Hybridisation of central atom**
$[Fe(CN)_6]^{4-}$	d^2sp^3 (inner)
$[Co(NH_3)_6]^{3+}$	d^2sp^3 (inner)
$[Ni(NH_3)_6]^{2+}$	sp^3d^2 (outer)

10. $[Co(en)_2Cl_2]^+$ shows highest number of isomers as it exhibits geometrical as well as optical isomerism.

11. $[Co(en)_3]Cl_3$, i.e. $[Co(en)_3]^{3+}$



cis- $[Co(en)_2Cl_2]Cl$, i.e. *cis* $[Co(en)_2Cl_2]^+$



Mirror

12. In $[Co(NH_3)_6]^{3+}$, Co is present as $Co^{3+}(d^6)$ and NH_3 is a strong field ligand, so unpaired electrons = 0.

So, it is yellowish orange.

In $[Ti(H_2O)_6]^{3+}$, Ti is present as $Ti^{3+}(d^1)$ so it contains one unpaired electron. It is pale blue in colour.

In $[Ni(H_2O)_6]^{2+}$, Ni is present as Ni^{2+} (d^8) so it have two unpaired electrons. It is of green colour.

$[Ni(H_2O)_4(en)]^{2+}$ is violet as en is a strong field ligand.

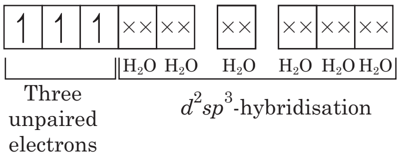
13. $[Co(NH_3)_4Cl_2]^+$ exhibits geometrical isomerism.

cis $[Co(en)_2Cl_2]^+$ because of the absence of symmetry elements exhibits optical isomerism.

$[Co(NH_3)_5(NO_2)]Cl_2$ because of the presence of ambidentate (NO_2) ligand exhibit linkage isomerism. $[Co(NH_3)_6][Cr(CN)_6]$ exhibits coordination isomerism because here cation and anion both are complex.

14. In $[Cr(H_2O)_6]^{3+}$, Cr is present as Cr^{3+}.

$Cr^{3+} = 3d^3, \quad 4s^0, \quad 4p^0$

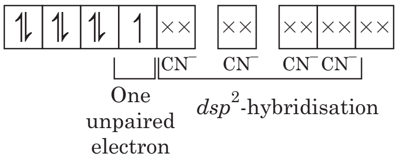


In $[Co(CN)_4]^{2-}$, Co is present as Co^{2+}

$Co^{2+} = 3d^7, 4s^0, 4p^0$

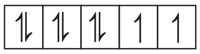
(CN⁻ being strong field ligand pair up the unpaired *d* electrons.)

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

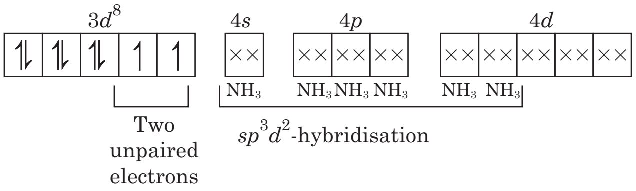


(c) In $[Ni(NH_3)_6]^{2+}$, Ni is present as Ni^{2+}.

$Ni^{2+} = [Ar]\,3d^8, 4s^0$



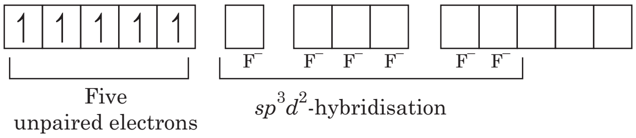
$[Ni(NH_3)_6]^{2+} =$



(d) In $[MnF_6]^{4-}$, Mn is present as Mn^{2+}.

$Mn^{2+} = 3d^5\ 4s^0$

$[MnF_6]^{4-} =$



15. Chlorophyll contains Mg, blood pigment, i.e. haemoglobin contains iron (Fe), Wilkinson catalyst contains Rh (rhodium) and vitamin B_{12} have cobalt metal.

16. Heteroleptic complexes are those in which more than one kind of ligands are present. e.g. $[Fe(NH_3)_4Cl_2]^{4+}$, $[Co(NH_3)_4Cl_2]$ etc.

17. $$\underset{\substack{\text{Pink}\\\text{(octahedral)}}}{[Co(H_2O)_6]^{2+}} \xrightarrow{HCl} \underset{\substack{\text{Deep blue}\\\text{(tetrahedral)}}}{[CoCl_4]^{2-}}$$

The colour changes because crystal field splitting is more in case of octahedral complexes as compared to tetrahedral complexes.

18. Three names and formulas are correctly matched.

$K_3[Cr(C_2O_4)_3]$ — Potassium trioxalatochridomate (III)

$K[Pt(NH_3)Cl_5]$ — Potassium amminepentachloroplatinate (IV)

$[Ag(CN)_2]^-$ — Dicyanoargentate (I) ion

19. $[Co(en)_3]^{3+}$ is optically active compounds because of the absence of symmetry elements.

20. In complexes $[Rh(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$, central metal cations have same oxidation state as well as same ligands and they fall in same group, but Δ_o of $[Rh(H_2O)_6]^{3+} > \Delta_o$ of $[Co(H_2O)_6]^{3+}$ because Rh^{3+} has high Z_{eff} value than Co^{3+}.

21. Δ_o is so large for $[Fe(CN)_6]^{4-}$ that its absorption peak is in ultraviolet region. Δ_o for $[Fe(H_2O)_6]^{2+}$ is so small that its absorption peak is in infrared region.

22. In case of $[Fe(CN)_6]^{4-}$ the metal atom will have $t_{2g}^6\, e_g^{60}$ configuration. In $[Fe(CN)]^{4-}$, the oxidation state of Fe is +2 $(3d^6 4s^0)$. As CN⁻ is a strong ligand it would pair up the electrons and thus configuration would be $t_{2g}^6\, e_g^0$.

24. (i) ${}_{58}Ce \rightarrow [Xe]4f^2 5d^0 6s^2$

In complex $Ce^{4+} \rightarrow [Xe]4f^0 5d^0 6s^0$

These is no unpaired electron so $\mu_m = 0$

(ii) ${}_{64}Gd^{3+} \rightarrow [Xe]4f^7 5d^0 6s^0$

contain seven unpaired electrons so,

$\mu_m = \sqrt{7\,(7+2)} = \sqrt{63}$ BM

(iii) $_{63}Eu^{3+} \rightarrow [Xe]4f^6 5d^0 6s^0$
contain six unpaired electron
so, $\mu_m = \sqrt{6(6+2)} = \sqrt{48}$ BM
Hence, order of spin only magnetic movement

$$\boxed{(ii) > (iii) > (i)}$$

25. Two Br, two (en) and one Cr are parts of complex. Charge on the complex is

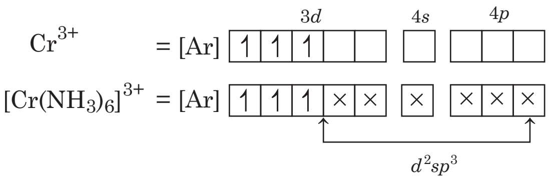
$$\left.\begin{aligned} 2\ (\text{Br}) &= -2 \\ 2\ (\text{en}) &= 0 \\ 1\ (\text{Cr}) &= +3 \end{aligned}\right\} = +1$$

Thus, complex ion is $[Cr(en)_2Br_2]^+$. Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]Br$.

26. $\underbrace{[Cr(NH_3)_6]}_{\text{Coordinate sphere}} \underbrace{Cl_3}_{\text{Ionisable}} \rightleftharpoons [Cr(NH_3)_6]^{3+} + 3Cl^-$

$$[Cr(NH_3)_6]^{3+} + 3Cl^- \xrightarrow{AgNO_3} \underset{\text{White precipitate}}{AgCl\downarrow}$$

$Cr(24) = [Ar]3d^5 4s^1$
$Cr^{3+} = [Ar]3d^3 4s^0$



☒ Indicates lone-pair of NH_3 donated to Cr

(a) d^2sp^3-hybridisation, octahedral.
(b) There are three unpaired electrons, hence paramagnetic.
(c) It is inner orbital complex.
(d) Due to ionisable Cl^- ions, white precipitate with $AgNO_3$.

28.

	Complex	Isomerism shown
(a)	$[Co(en)_3]^{3+}$	Optical only
(b)	$[Ni(NH_3)_5Br]^+$	No geometrical isomer
(c)	$[Co(NH_3)_2(en)_2]^{3+}$	*cis* and *trans*
(d)	$[Cr(NH_3)_4(en)]^{3+}$	No geometrical isomer

30. Linkage isomerism are caused due to presence of ambidentate ligands. $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers due to SCN, ambidentate ligands.

31.

Ligand	L_1	L_2	L_3	L_4
Coloured region of absorbed wavelength	Red	Green	Yellow	Blue

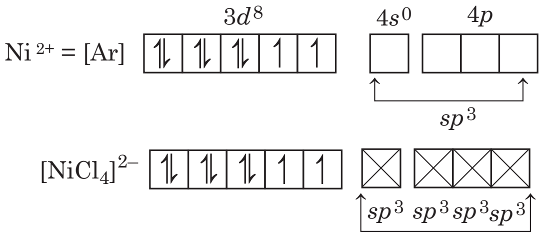
Coloured regions of visible light (VIBGYOR) are arranged in the increasing order of wavelength or decreasing order of energy [$\because E \propto 1/\lambda$]. Therefore,

$$\underset{(L_1)}{E_{\text{Red}}} < \underset{(L_2)}{E_{\text{yellow}}} < \underset{(L_3)}{E_{\text{green}}} < \underset{(L_4)}{E_{\text{blue}}}$$

This suggests that L_4 will absorbs higher energy wavelength followed by L_2, L_3 and L_1. Since, higher absorbed energy corresponds to greater extent of crystal field splitting and thus, higher field strength of the ligand. Hence, the increasing order of ligand strength of the four ligands is $L_1 < L_3 < L_2 < L_4$.

32. $[NiCl_4]^{2-}$; oxidation number of Ni, $x - 4 = -2$

$\therefore \quad x = +2,\ Ni_{(28)}\ [Ar]\ 3d^8, 4s^2$



Four sp^3-hybrid orbitals

sp^3-hybrid orbitals, tetrahedral
Cl^- is a weak field ligand and thus, unpaired electrons are not paired. Lone pairs from 4 Cl^- are accomodated in four sp^3-hybrid orbitats.
N = unpaired electrons = 2, paramagnetic
Magnetic moment (spin only) = $\sqrt{N(N+2)}$ BM
$= \sqrt{8} = 2.828$ BM

33. en, $\begin{array}{l} CH_2—NH_2 \\ | \\ CH_2—NH_2 \end{array}$ is a bidentate ligand.

$C_2O_4^{2-}$ is also a bidentate ligand.
Hence, coordinating head are six
(en : 2 × 2 = 4 + (ox) 2)
Coordination number 6
Complex can be ionised as
$[E(en)_2(C_2O_4)]NO_2 \longrightarrow [E(en)_2(C_2O_4)]^+ NO_2^-$
Oxidation number $x + 0 + (-2) = +1$
$\Rightarrow$ Oxidation number, $x = 3$
$\therefore$ Their sum would be $(6 + 3) = 9$

34. $[V(CO)_m]^{n-}$; $V(Z = 22) = 3d^3 4s^2$
For octahedral shape of complex, $m = 6$
EAN of $V = Z + (-\text{ve charge}) + 2r\ m = 36)$
$= (22 + n + 2 \times 6) = 36 \Rightarrow n = 1$
Hence $m = 6$, $n = 1$
$m + n = 6 + 1 = 7$

35. The carbonyls in general obey EAN rule and their A.
EAN = Atomic number of next noble gas.
(I) $H_xCr(CO)_5$; EAN = 36
$\therefore \quad x + 24 + 2 \times 5 = 36 \qquad \therefore \quad x = 2$
(II) $Co_2(CO)_y$; EAN = 36
$\therefore$ 27 + 1 (from other Co atom) + $2y = 36$
$\therefore \quad y = 4$
(III) $Mo(Co)_z$; EAN = 54
$\therefore \quad 42 + 2z = 54 \quad \Rightarrow \quad z = 6$

$$\therefore \quad \left(\frac{x + y + z}{5}\right) = \left(\frac{2 + 4 + 6}{5}\right) = 2.4$$