

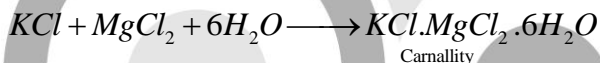
# LESSON 21

## CO-ORDINATION COMPOUNDS & ORGANOMETALLICS

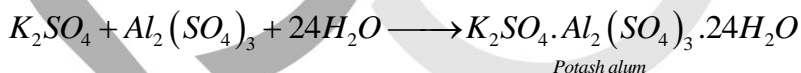
### DOUBLE SALTS AND COORDINATION COMPOUNDS

It is well known that when solutions containing two or more salts in stoichiometric (i.e., simple molecular) proportions are evaporated or simply mixed, new compounds, called **molecular** or **addition compounds** are formed. For example,

- (i) When saturated solution of potassium chloride and magnesium chloride is evaporated, we get a new substance called *carnallite*.



- (ii) When saturated solutions of potassium sulphate and aluminum sulphate are mixed and the solution is evaporated, we get the well known compound, *potash alum*.

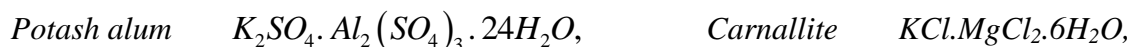


- (iii) If we add a solution of potassium cyanide to a white precipitate of nickel cyanide,  $Ni(CN)_2$ , the precipitate immediately dissolves and a red orange solution of a new compound is obtained.



Broadly, such addition or molecular compounds can be grouped into two categories.

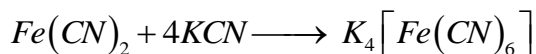
- Double salts :** Double salts are those molecular compounds which exist only in crystal lattices and lose their identity when dissolved in water. These are formed by mixing two apparently saturated compounds. Some well known double salts are



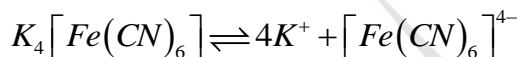
Shape and size of the crystals of a double salt are different from that of its component salts. As mentioned above, these compounds exist (are stable) in the solid state and as soon as the lattice is disrupted on dissolution in water or any other solvent or on melting, they decompose into their

individual constituents. Thus their solutions will show the same physical and chemical properties as a mixture of solutions of their components. Thus, for example, aqueous solution of potash alum will give the tests of  $K^+$ ,  $Al^{3+}$  and  $SO_4^{2-}$  ions.

- Coordination or Complex compounds :** *Coordination compounds are those molecular compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituents.* For example, potassium ferrocyanide is a complex compound. It is formed by adding KCN to a saturated solution of ferrous cyanide.



When potassium ferrocyanide is dissolved in water, it does not give the usual tests for  $Fe^{2+}$  and  $CN^-$  ions indicating that these ions which were originally present are not formed when potassium ferrocyanide is dissolved in water. Actually these ions are present in the form of a new ion, called ferrocyanide ion which is a **complex ion** and does not ionize into constituent ions.



Compounds containing complex ions are called **complex compounds**. Since the complex ions have coordinate bonds in their structures, these are also known as coordinate ions and hence the corresponding compound as coordinate compound.

Other common complex ions are nickel cyanide,  $[Ni(CN)_4]^{2-}$ , copper ammonium,  $[Cu(NH_3)_4]^{2+}$ , argentocyanide,  $[Ag(CN)_2]^+$

Thus **complex ion** may be defined as an electrically charged (cationic or anionic) or even a neutral species and is formed by the combination of a simple cation with more than one neutral molecule or negative ion. For example, ferrocyanide ion is formed by the union of six cyanide ions with ferrous ion;  $[Ag(NH_3)_2]^+$  is formed by the combination of two moles of ammonia and one mole of  $Ag^+$  ion. The anions or neutral molecules attached to the central metal atom are called **ligands**. The central metal cation is generally a transition metal and has a positive oxidation state. Coordination compounds in which the metal is in zero oxidation state (e.g., carbonyls) are also known.

The complex compounds may roughly be classified into two types, namely **penetrating** and **normal complexes**. *The penetrating complexes are those which possess sufficient stabilities to retain their identities in solution, examples are  $[Fe(CN)_6]^{4-}$  and  $[Co(NH_3)_6]^{3+}$ . The normal complexes are those which are reversibly dissociated in solution into their components; examples are  $Cd(CN)_4]^{2-}$  and  $[Co(NH_3)_6]^{3+}$ .* However, it should be remembered that this classification is more in convenience than of fundamental importance.

## TERMS USED IN COORDINATE COMPOUNDS

- Central ion, Centre of coordination :** *The cation to which one or more neutral molecules or anions are attached is called the centre of coordination.* Since the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atom of the ligand, it must have empty orbitals. This explains why the transition metals having empty *d*-orbitals form coordination compounds very readily.

Thus in the complexes  $[Ni(NH_3)_6]^{2+}$  and  $[Fe(CN)_6]^{3-}$ ,  $Ni^{2+}$  and  $Fe^{3+}$  respectively are the central ions.

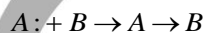
2. **Ligand** : Any atom, ion or molecule which is capable of donating a pair of electrons to the central atom is called a **coordinating group or ligand**. Further in a ligand, the particular atom which actually donates the electron pair is called the donor atom. The common donor atoms are N, O, S and halogens. The ligand containing one, two or more donor atoms are known as unidentate, bidentate and multidentate respectively. Examples of unidentate ligands are  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $CN^-$ ,  $SCN^-$ ,  $NO_2^-$ ,  $NH_3$ ,  $H_2O$  pyridine,  $(C_2H_5)_3N$  acetone, etc. Generally, a monodentate ligand is capable of forming only one coordinate bond to the metal atom.

The common examples of bidentate ligand are ethylenediamine and dimethyl glyoxime. These have two donor atoms which can simultaneously coordinate to the metal atom.

3. **Coordination number (CN)** : The total number of ligands attached to the central ion is known as the coordination number of that ion. Thus the coordination numbers of silver and copper ion in the complexes  $[Ag(NH_3)_2]^+$  and  $[Cu(H_2O)_4]^{2+}$  are 2 and 4 respectively.

Some common coordination numbers are 2, 3, 4 and 6. The lighter transition elements generally exhibit the coordination numbers of 4 and 6 while the heavier transition elements generally prefer to attain a coordination number greater than six, i.e. 7, 8 or 9.

1. Recall that a coordinate bond is formed when both the bonding electrons are donated by one atom.



Thus the two necessary factors for the formation of a coordinate bond are :

- The presence of a species having atoms which can donate a pair of electrons, such species or atom is called donor.
- The presence of an atom (in second compounds) having a vacant orbital that can accept a pair of electrons. Such atom is known as acceptor as it accepts a pair of electrons from the donor atom. This point explains why transition elements having empty d-orbitals form coordinate compounds very easily.

4. **Coordination sphere** : The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere. Coordination sphere is written inside square bracket, for example  $[Co(NH_3)_6]^{3+}$ . Remember that the central metal atom and the ligands inside the square bracket behave as a single entity.
5. **Oxidation number** : It is a number (numerical value) which represents the electric charge on the central metal atom of a complex ion. For example, the oxidation number of Fe, Co and Ni in  $[Fe(CN)_6]^{4-}$ ,  $[Co(NH_3)_6]^{3+}$  and  $Ni(CO)_4$  is +2, +3 and zero respectively.

*Determination of oxidation number and coordination number of a metal atom or ion in a complex.*  
Let us take few examples to illustrate this.

- (i) **Potassium ferrocyanide,  $K_4[Fe(CN)_6]$**  : Since the complex has four monovalent cations outside the coordination sphere, the complex ion must carry four negative charge, i.e., it is  $[Fe(CN)_6]^{4-}$

The number of  $CN^-$  ions (univalent ion), i.e., 6 represents the coordination number of the iron ion.

The oxidation state of iron can be easily determined as below, knowing that cyanide ion is unidentate and the complex on the whole carries -4 charges

$$[Fe(CN)_6]^{4-} \quad x + (-6) = -4 \quad \therefore x = +2$$

Thus here iron is present as  $Fe^{2+}$  or  $Fe(II)$

- (ii)  **$[Co(NH_3)_3(NO_2)_3]$**  : Note that the complex does not carry any charge, i.e., it is neutral. Here the central atom is attached to three ammonia molecules and three  $NO_2^-$  radicals, both are unidentate. Thus here the CN of cobalt is 6.

Oxidation state of cobalt can be established as usual and given below

$$[Co(NH_3)_3(NO_2)_3] \quad x + (0)_3 + (-3) = 0 \quad x - 3 = 0 \quad \therefore x = +3$$

Thus the oxidation state of Co is + 3.

- (iii)  **$[Cr(C_2O_4)_3]^{3-}$**  : Note that here the oxalate ligand is dinegative ion, i.e. it is bidentate, therefore three oxalate ligands carry a total charge of -6. Hence CN of Cr is 6. Now since the complex carries -3 charge, therefore the oxidation state of Cr must be + 3.
- (iv)  **$Ni(CO)_4$**  : Here the CN of Ni is 4 since carbonyl group is unidentate. Further since the complex as well as the ligand has no charge, nickel atom must also be neutral i.e., it is in zero oxidation state.

**6. Complex ion :** As described earlier, a complex (coordinate) ion is an electrically charged or a neutral species formed by the combination of a central cation with more than one ligand species. The charge carried by a complex ion is the algebraic sum of charges carried by the central ion and the ligands coordinated to it. Charges of some complex compounds are given below :

Complex compound (ion)	Charge on complex (ion)
(i) $[Cu(NH_3)_4]^{2+}$	+ 2 of Cu + 0 of $NH_3$ ; $\therefore$ Net charge = +2
(ii) $[Fe(CN)_6]^{4-}$	+ 2 of Fe + (-6) of 6 CN; $\therefore$ Net charge = -4
(iii) $[Co(NH_3)_5Cl]^{2+}$	+ 3 of Co + 0 of $NH_3$ + (-1) of Cl; $\therefore$ Net charge = +2
(iv) $[^1Co(NH_3)_3Cl_3]$	+ 3 of Co + 0 of $NH_3$ - 3 of 3 Cl; $\therefore$ Net charge = 0

Complex compounds as (iv) in the above case which do not carry any charge is a non-electrolyte as it is not capable of forming any ion.

Ions present outside the square bracket are ionisable.

## WERNER'S THEORY OF COORDINATION COMPOUNDS

The coordination compounds were known since 18<sup>th</sup> century but no satisfactory theory was available to explain the observed properties of these compounds. Alfred Werner in 1893 put forward his concept of auxillary (secondary) valency for advancing a correct explanation for the characteristics of the coordination compounds. The *fundamental postulates of Werner's theory* which was actually a result of dream and made Werner a noble prize winner in chemistry may be summarized as below.

1. Metals possess two types of valencies, namely *primary (principal) or ionizable valency and secondary (auxillary) or nonionizable valency*.

**Primary valencies** are those which a metal normally exhibit in the formation of its simple salts. Thus in the formation of  $PtCl_4$ ,  $CuSO_4$  and  $AgCl$  the primary valencies of Pt, Cu and Ag are 4, 2 and 1 respectively, *Primary valencies are satisfied by negative ions*.

**Secondary valencies** are those which a metal cation exercises towards a neutral molecule or negative group in the formation of its complex ions. Thus secondary valencies may be satisfied by negative ions, neutral molecules having lone electron pair (e.g.  $H_2O$ ,  $NH_3$ , etc.) or even sometimes by some positive groups. In every case, the coordination number of the metal must be fulfilled.

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

2. Every metal has a fixed number of secondary valencies, e.g. cobalt<sup>3+</sup> and platinum<sup>4+</sup> were recognized to have six secondary valencies and copper<sup>2+</sup> four. The total number of secondary valencies required by a metal is more commonly known as coordination number (C.N.)
3. The secondary valencies are always directed towards fixed positions in space about the central metal ion. Thus the number and arrangement of ligands<sup>2</sup> in space determines the stereochemistry of a complex. Thus in case of *six secondary valencies* the arrangement of secondary valencies was as directed to the apices of a *regular octahedral* while in case of four *secondary valencies* arrangement might be either in *a planar or a tetrahedral manner* and thus this postulate predicted the possibilities of a variety of type of isomerism in coordination compounds. Remember that primary valencies are non-directional.

To distinguish between the two types of valencies, Werner introduced the square brackets [ ] to enclose atoms making up the coordination complex and which are therefore not ionized. The portion enclosed in the bracket is known as *coordination sphere* and the portion present outside the bracket as *ionizing sphere*.



The important aspect of structure of five different complexes of  $PtCl_4$  with ammonia prepared by Werner are given in **Table. 1**

**Table 1. Coordination Compounds of  $PtCl_4$  with  $NH_3$**

Complex	Modern formula	No. of $Cl^-$ ions precipitated	Total number of ions
$PtCl_4.6NH_3$	$[Pt(NH_3)_6]Cl_4$	4	5
$PtCl_4.5NH_3$	$[Pt(NH_3)_5Cl]Cl_3$	3	4
$PtCl_4.4NH_3$	$[Pt(NH_3)_4Cl_2]*Cl_2$	2	3
$PtCl_4.3NH_3$	$[Pt(NH_3)_3Cl_3]Cl$	1	2
$PtCl_4.2NH_3$	$[Pt(NH_3)_2Cl_4]$	0	0 (non-electrolyte)

In all these compounds, platinum exhibits a primary valency (oxidation number) of four and secondary valency (coordination number) of six.

1. Complexes in which some of the ligands are neutral (e.g.  $NH_3$  molecules) and others are anions (e.g. ( $Cl^-$ )) are called mixed complexes.
2. As described earlier, the groups attached to the metal ion by means of secondary valencies are known as ligands.

## SIDWICK THEORY AND EAN RULE

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

Atomic number of Cobalt = 27

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

$$\therefore \text{Total number of electrons in } Co^{3+} = 27 - 3 = 24$$

Since each  $NH_3$  ligand contributes two electrons to the cobalt ion.

$$\text{Electrons contributed by 6 } NH_3 \text{ ligands} = 6 \times 2 = 12$$

$$\therefore \text{The EAN of } Co^{3+} \text{ in the complex} = 24 + 12 = 36$$

In general, EAN of metal = At. No. – Oxi. State +  $CN \times 2$

In the said example since the number (36) corresponds to the atomic number of krypton, according to Sidwick the complex will be stable. Though EAN rule (i.e., those complexes are stable or those metal ions form complexes whose EAN is the same as the atomic number of the next noble gas) is applicable in many cases, there are several examples in which EAN rule is not obeyed.

**Example 1** Apply the concept of EAN rule on the complexes  $[Fe(CN)_6]^{4-}$  and  $[Fe(CN)_6]^{3-}$ . What conclusion you draw about the validity of the EAN rule from these two well-known complexes? [Atomic number of Fe = 26].

**Solution** (a) Let us take the case of  $[Fe(CN)_6]^{4-}$

Oxidation state\* of Fe in  $[Fe(CN)_6]^{4-} = +2$

No. of electrons in iron = 26

$\therefore$  No. of electrons in Fe(II) of the complex =  $26 - 2 = 24$

Number of electrons donated by six  $CN^-$  ligands =  $6 \times 2 = 12$

$\therefore$  EAN of Fe (II) in  $[Fe(CN)_6]^{4-} = 24 + 12 = 36$

Since this number (36) = number of electrons in the atom of the nearest noble gas (Kr.) the complex  $[Fe(CN)_6]^{4-}$  follows the **EAN rule** or the **EAN rule is valid on this complex**.

(b) Now let us take the case of  $[Fe(CN)_6]^{3-}$

Oxidation state of iron = +3

$\therefore$  Number of electrons in Fe (III) of the complex =  $26 - 3 = 23$

Number of electrons donated by six  $CN^-$  ligands = 12

$\therefore$  EAN of Fe (III) in  $[Fe(CN)_6]^{3-} = 23 + 12 = 35$

Since this number (35) is different from the electrons present in the next noble gas (Kr = 36), we can say that the **EAN rule is not valid** on this complex.

**Example 2** Using the EAN rule, predict the molecular formulae of simple carbonyls of Fe. (at. number 26) and Cr (at. number 24). The metals have zero oxidation state in the carbonyls.

*Note :- As mentioned earlier, Oxidation state of the metal in a complex can be determined by taking it x, e.g. in  $[Fe(CN)_6]^{4-}$   $x - 6 = -4$ ;  $\therefore x = 2$ . Thus the oxidation state of Fe in  $[Fe(CN)_6]^{4-}$  is +2*

**Solution** Molecular formula of iron carbonyl

At number of iron = 26; At. No. of the next noble gas, Kr (I.e. EAN) = 36

$\therefore$  No. of electrons to be provided by CO =  $36 - 26 = 10$

Since each CO provides 2 electrons, total number of carbonyl (CO) group =  $\frac{10}{2} = 5$

$\therefore$  Molecular formula of simple iron carbonyl =  $Fe(CO)_5$

Molecular formula of chromium carbonyl

At No. of chromium = 24 ; EAN = 36

$\therefore$  No. of electrons to be provided by CO =  $36 - 34 = 12$

$\therefore$  No. of CO group  $12/2 = 6$

Hence the molecular formula of chromium carbonyl will be  $\text{Cr}(\text{CO})_6$

## NOMENCLATURE OF CO-ORDINATION COMPOUNDS

*The International Union of pure and Applied chemistry (IUPAC) publication Nomenclature of inorganic chemistry (1989), Blackwell scientific publishers, contains the rules for the systematic naming of coordination compounds. The basic rules are summarized here :*

- The positive ion is named first followed by the negative ion.*
- When writing the name of a complex, the ligands are quoted in alphabetical order, regardless of their charge (followed by the metal).*
- When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is named first, and then the coordinated groups are listed in the order: negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group)*
  - The names of negative ligands end in -O, for example:*

$\text{F}^-$	<b>Fluoro</b>	$\text{H}^-$	<b>Hydrido</b>	$\text{HS}^-$	<b>Mercapto</b>
$\text{Cl}^-$	<b>chloro</b>	$\text{OH}^-$	<b>hydroxo</b>	$\text{S}^{2-}$	<b>Thio</b>
$\text{Br}^-$	<b>Bromo</b>	$\text{O}^{2-}$	<b>OXO</b>	$\text{CN}^-$	<b>Cyano</b>
$\text{I}^-$	<b>Iodo</b>	$\text{O}_2^{2-}$	<b>Peroxo</b>	$\text{NO}_2^-$	<b>Nitro</b>
  - Neutral groups have no special endings. Examples include  $\text{NH}_3$  ammine,  $\text{H}_2\text{O}$  aqua, CO carbonyl and NO nitrosyl. The ligands  $\text{N}_2$  and  $\text{O}_2$  are called dinitrogen and dioxygen. Organic ligands are usually given their common names, for example phenyl, methyl, ethylenediamine, pyridine, triphenylphosphine.*
  - Positive group end in -ium, e.g.  $\text{NH}_2$  hydrazinium.*
- Where there are several ligands of the same kind, we normally use the prefixes di, tri, tetra penta and hexa to show the number of ligand of that type. An exception occurs when the name of the ligand includes a number, e.g. dipyridyl or ethylenediamine. To avoid confusion in such cases, bis, tris and tetrakis are used instead of di, tri and tetra and the name of the ligand is placed in brackets.*
- The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following its name (i.e. no space, e.g. titanium (III)).*



6. Complex positive ions and neutral molecules have no special ending but complex negative ions end in—ate.
7. If the complex contains two or more metal atoms, it is termed polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix-  $\mu$ . If there are two or more bridging groups of the same kind, this is indicated by di  $\mu$  -, Tri  $\mu$  - etc. Bridging groups are listed alphabetically with the other groups unless the symmetry of the molecule allows a simpler name. If a bridging group bridges more than two metals atoms it is shown as  $\mu_3, \mu_4, \mu_5$  or  $\mu_6$  to indicate how many atoms it is bonded to.
8. Sometimes a ligand may be attached through different atoms. Thus M-NO<sub>2</sub> is called nitro and M-ONO is called nitrito. Similarly the SCN group may bond M-SCN thiocyanato or M-NCS isothiocyanato. These may be named systematically thiocyanato -S or thiocyanato -N to indicate which atom is bonded to the metal. This convention may be extended to other cases where the mode of linkage is ambiguous.
9. If any lattice components such as water or solvent of crystallization are present, these follow the name, and are preceded by the number of these groups in Arabic numerals. These rules are illustrated by the following examples :

## IUPAC NOMENCLATURE OR COMPLEXES

### Name of negative ligands

Ligand	Name	Ligand	Name
H <sup>-</sup>	hydrido	HS <sup>-</sup>	mercapto
O <sup>2-</sup>	oxo	NH <sub>2</sub> <sup>-</sup>	amido
O <sub>2</sub> <sup>2-</sup>	peroxo	NH <sup>2-</sup>	imido
O <sub>2</sub> H <sup>-</sup>	perhydroxo	NO <sub>3</sub> <sup>-</sup>	nitrato
OH <sup>-</sup>	hydroxo	ONO <sup>-</sup>	nitrito
F <sup>-</sup>	fluoro	NO <sub>2</sub> <sup>-</sup>	nitro
Cl <sup>-</sup>	chloro	N <sup>3-</sup>	nitrido
Br <sup>-</sup>	bromo	P <sup>3-</sup>	phosphido
I <sup>-</sup>	iodo	N <sub>3</sub> <sup>-</sup>	azido
CO <sub>3</sub> <sup>2-</sup>	carbonato	CNO <sup>-</sup>	cyanato
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	oxalato	NCO <sup>-</sup>	isocyanato
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	acetato	SCN <sup>-</sup>	thiocyanato or thiocyanato-S
CN <sup>-</sup>	cyano	NCS <sup>-</sup>	isothiocyanato or thiocyanato-N
SO <sub>4</sub> <sup>2-</sup>	sulphato	HCO <sub>3</sub> <sup>-</sup>	hydrogencarbonato

$\text{SO}_3^{2-}$	sulphito	$\text{S}_4\text{O}_6^{2-}$	tetrathionato
$\text{S}^{2-}$	sulphido	EDTA $(^-\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}$ $(\text{CH}_2\text{CO}_2^-)_2$	ethylenediaminetetraacetato
$\text{HSO}_3^-$	hydrogensulphito	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	glycinato
$\text{S}_2\text{O}_3^{2-}$	thiosulphato	$\text{C}_5\text{H}_5^-$	cyclopentadienyl

Ligands whose names end in “-ite” or “-ate” become “-ito” or “-ato”, i.e., by replacing the ending -e with -o.

### Name of Neutral ligands

Ligand	Name	Abbreviation	Ligand	Name	Abbreviation
$\text{H}_2\text{O}$	aqua/aquo	—	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	ethylenediamine	(en)
$\text{NH}_3$	ammine	—	$\text{CH}_3\text{NH}_2$	methylamine	—
$\text{CO}$	carbonyl	—	$\text{C}_6\text{H}_6$	benzene	—
$\text{NO}$	nitrosyl	—	$\text{N}_2$	dinitrogen	—
$\text{CS}$	thiocarbonyl	—	$\text{O}_2$	dioxygen	—
$\text{NS}$	thionitrosyl	—	$\text{Ph}_3\text{P}$	triphenylphosphine	—
$\text{C}_5\text{H}_5\text{N}$	pyridine	(py)	$\text{CH}_3\text{COCH}_3$	acetone	—

### Name of Positive ligands

Ligand	Name
$\text{NO}^+$	nitrosonium
$\text{NO}_2^+$	nitronium
$\text{NH}_2\text{NH}_3^+$	hydrazinium

### Coordination compounds containing complex cationic ion

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	Hexaammineplatinum (IV) chloride
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}$	Tetraammineaquochlorocobalt (II) chloride
$[\text{Cu}(\text{en})_2]\text{SO}_4$	Bis(ethylenediamine)copper(II) sulphate
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$	Tetraaquodichlorochromium(III) ion
$[\text{Fe}(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)]_2\text{SO}_4$	Tetraaquooxalatoiron(III) sulphate

$[\text{Cr}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{NO}_3$	Tetraamminechloronitritochromium(III) nitrate
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Diamminesilver(I) chloride
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$	Pentaammineisothiocyanatocobalt(III) chloride
$[\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Rh}]\text{Cl}$	Tris(triphenylphosphine)rhodium(I) chloride

**Coordination compounds containing complex anionic ion**

$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatochromate(III)
$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$	Potassium dichlorodioxalatocobaltate(III)
$\text{K}_2\text{HgI}_4$	Potassium tetraiodomercurate(II)
$\text{K}_2[\text{PtCl}_6]$	Potassium hexachloroplatinate(IV)
$\text{Na}[\text{Ag}(\text{CN})_2]$	Sodium dicyanoargentate(I)
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II) ion
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrocobaltate(III)
$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Potassium pentacyanonitrosylferrate(II)

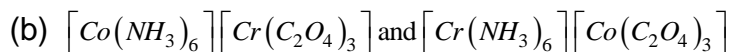
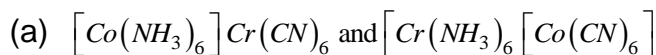
**Coordination compounds containing complex cationic and anionic ions :**

$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	Hexaamminechromium(III) hexacyanocobaltate(III)
$[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$	Tetraammineplatinum(II) tetrachlorocuprate(II)
$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{Cr}_2\text{O}_4)_3]$	Hexaamminechromium(III) trioxalatocobaltate (III)
$[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	Tetrapyridineplatinum(II) tetrachloroplatinate(II)

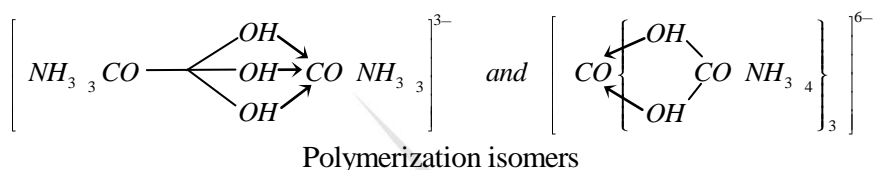
**Non-ionic coordination compounds**

$\text{Fe}(\text{CO})_5$	Pentacarbonyliron(0)
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triamminetrinitrocobalt(III)
$\text{Cu}(\text{Gly})_2$	Diglycinatocopper(II)
$\text{Ni}(\text{DMG})_2$	Bis(dimethylglyoximate) nickel(II)

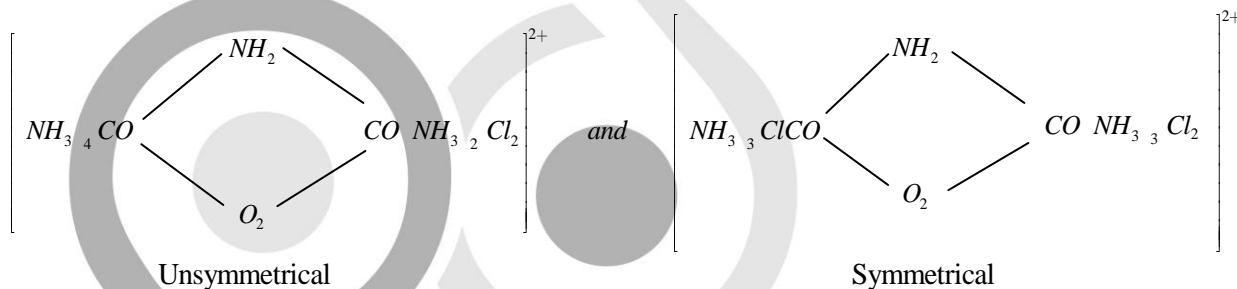




- (v) **Polymerization isomerism** : This type of isomerism is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights. Thus,  $[Pt NH_3_2 Cl_2]$ ,  $[Pt NH_3_4] PtCl_4$ ,  $[Pt NH_3_4][Pt NH_3 Cl_3]_2$  and  $[Pt NH_3_3 Cl]_2 PtCl_4$  all have the same empirical formula. Polymerization isomerism may be due to a different number of nuclei in the complex, as shown in figure.



- (vi) **Coordination position isomerism** : This type of isomerism is exhibited by polynuclear complexes by changing the position of ligands with respect to different metal atoms present in the complex. For example :



Both the chloro ligands are with same cobalt ion (Same ligands are linked with both cobalt ions)

- (2) **STEREoisomerism** :- Stereoisomerism is the type of isomerism in which two substances of the same composition and even constitution differ only in the relative position in space assumed by certain of their constituent atoms or groups. Or

Compounds are stereo-isomers when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space. Stereo-isomerism is of two types :

- (a) Geometrical isomerism and                      (b) Optical isomerism

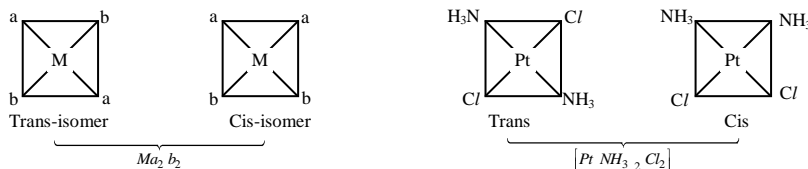
- (a) **Geometrical isomerism** : This isomerism is due to ligands occupying different positions around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as cis-trans isomerism.

Geometrical isomerism is very much common in coordination number 4 and 6 complexes.

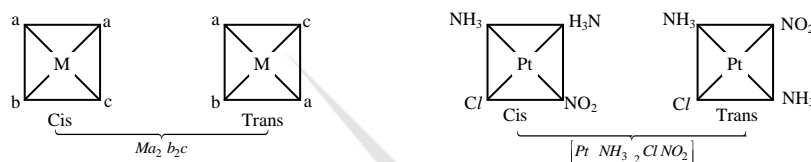


**Square planar complexes** (coordination number four) exhibit geometrical isomerism.

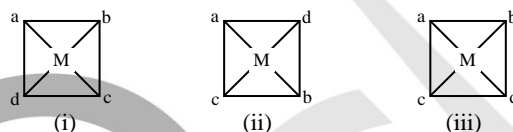
- (i) complexes with general formula,  $Ma_2b_2$  (where both a and b are monodentate) can have cis-and trans-isomers.



- (ii) Complexes with general formula,  $Ma_2b_2c$  can have cis-and trans-isomers.

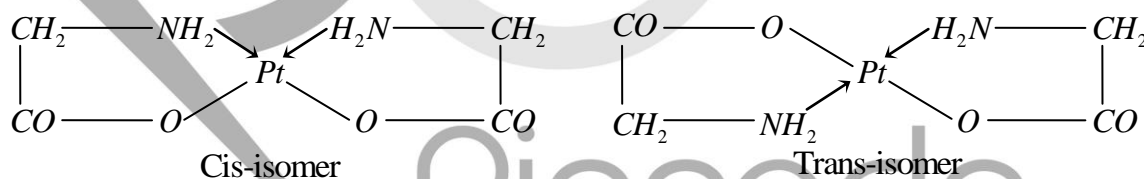


- (iii) Complexes with general formula,  $Ma_2bcd$  can have three isomers

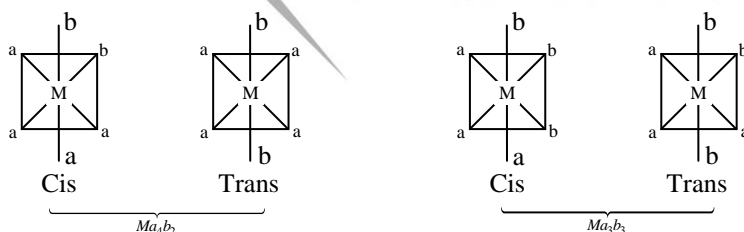


Example :  $[Pt(NH_3)(NH_2OH)(NO_2)(Py)]NO_2$

- (iv) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism. For example, platinum glycinate complex,  $[Pt(Gly)_2]$ , exhibits geometrical isomerism.



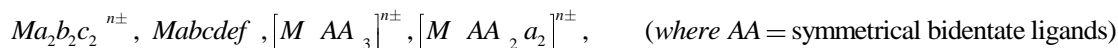
- (v) Octahedral Complexes of the type  $Ma_4b_2$  and  $Ma_3b_3$  exhibit geometrical isomerism.



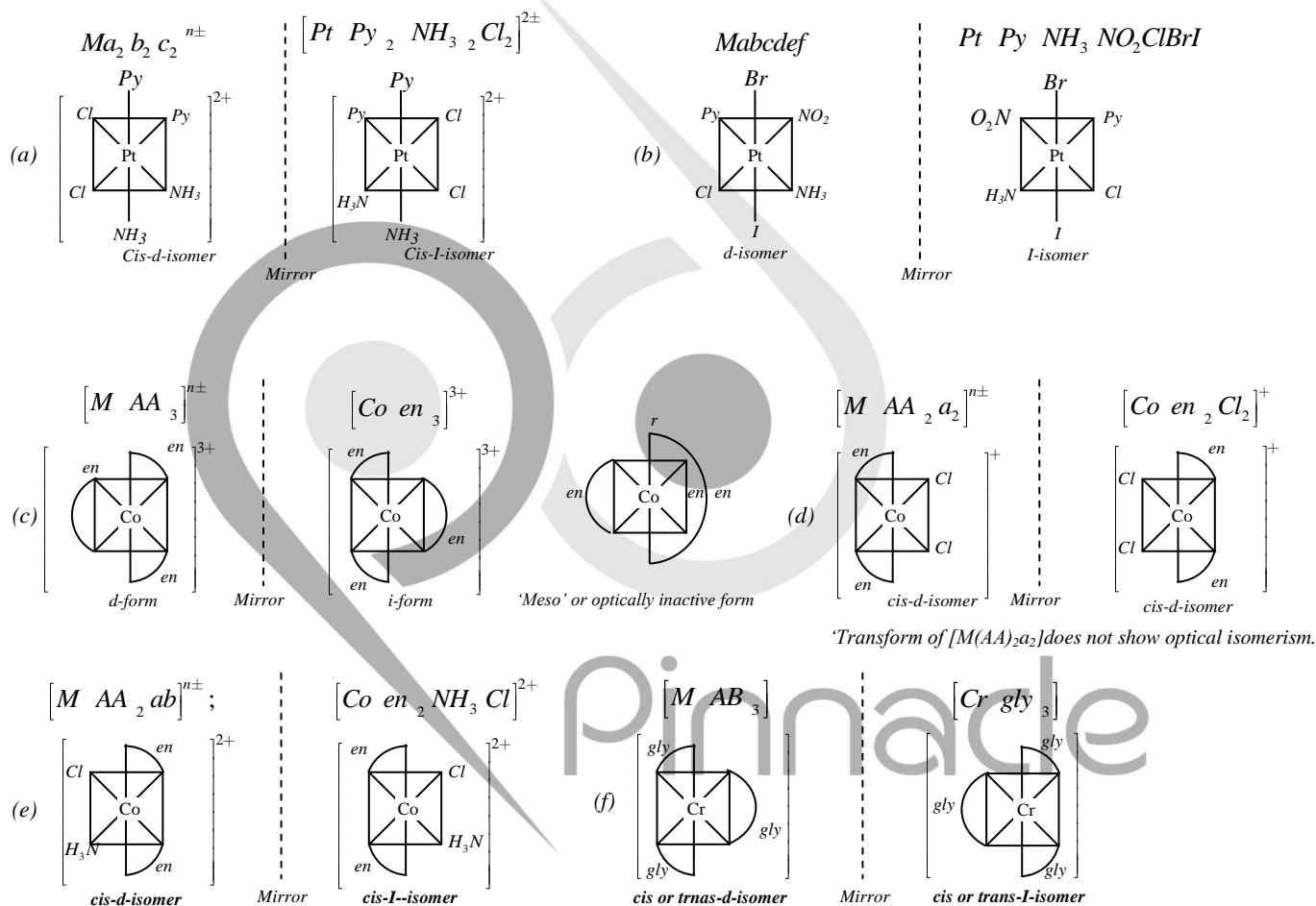
**Example**  $[Co(NH_3)_4Cl_2]Cl$ ,  $[Co(NH_3)_3Cl_3]$  Octahedral complexes of general formula,  $Mabcdef$ , can have fifteen geometrical isomers.

- (b) **Optical isomerism** : A coordination compound which can rotate the plane of polarized light is said to be optically active. When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarized light are said to exhibit optical isomerism and the molecules are optical isomers. The optical isomers are pair of molecules which are non-superimposable-mirror images of each other.

**Key concept** : The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure. octahedral complexes of general formulae are :

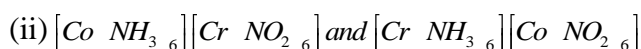
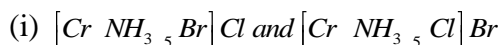


$[M AA_2 ab]^{n\pm}$  and  $[M AB_3]^{n\pm}$  (where  $AB$ =unsymmetrical ligands) show optical isomerism Examples :

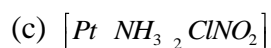


**Example**  $[Cr ox_3]^{3-}; [Fe dipy_3]^{2+}; [Cr ox_2 H_2O_2]; [Pt en_3]^{4+}$

**Illustration** How do you distinguish between the following pairs of isomers?



**Example** *Platinum II forms square planar complexes and platinum IV gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures :*



## HYBRIDIZATION AND GEOMETRY

**Hybridization and geometries of mononuclear coordination compounds (Linear, Tetrahedral, square planar and Octahedral)**

### VALENCY BOND (VB) THEORY

Pauling proposed simple valence bond theory to explain bonding in co-ordination compounds. The main postulates of valence bond theory are :

- The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.
- The atomic orbitals (s, p or d) of the metal ion hybridize to form hybrid orbitals with definite directional properties. These hybrid orbitals now overlap with the ligand orbitals to form strong chemical bonds.
- The d-orbitals involved in the hybridization may be either **inner** ( $n-1$ ) d-orbitals or **outer**  $n$  d-orbitals. The complexes formed in these two ways are referred to as **low spin and high spin complexes**, respectively.
- Each ligand contains a lone pair of electrons.
- A covalent-bond is formed by the overlap of a vacant hybridized metal orbital and a filled orbital of the ligand. The bond is also sometimes called as a coordinate bond.
- If the complex contains unpaired electrons, it is **paramagnetic** in nature, while if it does not contain unpaired electrons, it is **diamagnetic** in nature.
- The number of unpaired electrons in the complex points out the geometry of the complex and vice-versa. In practice, the number of unpaired electrons in a complex is found from magnetic moment measurements as given in **Table -2**

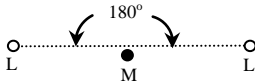
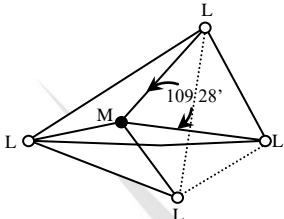
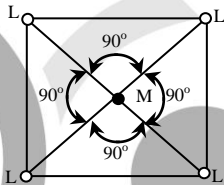
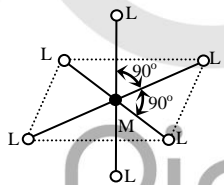
**Table 2. Relation between unpaired electron and magnetic moment.**

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



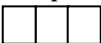
Thus the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.


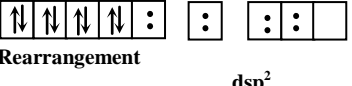
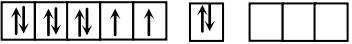

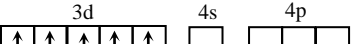

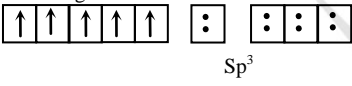


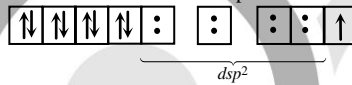

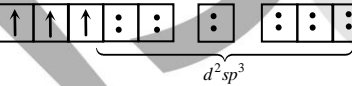
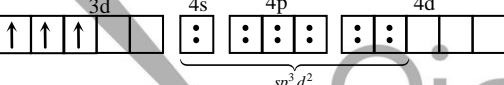

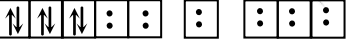
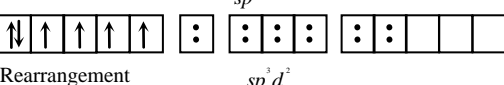

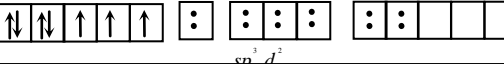
- Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.

**Note :** (i) C.N. = Coordination number of the central metal, M indicated by black circles.  
(ii) L = Ligands indicated by white circles. These may be the same or different.


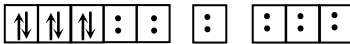
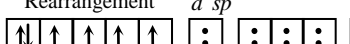


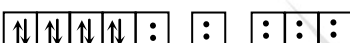


C.N.	Type of hybridization	Geometry of the hybrid orbitals or complex	Examples of complexes
2.	$sp$ ( $4s4p$ )	Linear or diagonal ( $ML_2$ ) 	$[Ag NH_3_2]^+$ , $[Ag CN_2]$
4	$sp^3$ $4s4p^3$	Tetrahedral $ML_4$ 	$[Ni Co_4]$ , $[Zn NH_3_4]^{2+}$ , $ZnCl_4^{2-}$ , $CuX_4^{2-}$ , $MnX_4^{2-}$ , $NiX_4^{2-}$ , $X = Cl^-, Br^-, I^-$
4	$dsp^2$ ( $3d_{x^2-y^2} 4s4p_x 4p_y$ )	Square Planar $ML_4$ 	$[Ni CN_4]^{2-}$ , $[Ni NH_3_4]^{2+}$ , $[Cu NH_3_4]^{2+}$ ,
6	$d^2sp^3$ $3d_{x^2-y^2} 3d_{z^2} 4s4p^3$ $sp^3d^2$ $4s4p^3 4d_{x^2-y^2} 4d_{z^2}$	 Inner-orbital octahedral Outer-orbital octahedral	$[Cr NH_3_6]^{3+}$ $[Mn CN_6]^{3-}$ , $Fe CN_6^{3-}$ etc. $FeF_6^{3-}$ , $[Co H_2O_6]^{2+}$ , $[Ni NH_3_6]^{2+}$ etc.

**Table - Geometry (Shape) and magnetic nature of some of the complexes (Application of valence bond theory)**

Sl. No	Atom/Ion/ Complex	Configuration	Oxidation state of metal	Type of hybridization	Geometry (Shape)	No. of Unpaired Electrons	Magnetic nature
	$Ni^{2+} (d^8)$	<div style="display: flex; align-items: center; gap: 10px;"> <div>3d   </div> <div>4s   </div> <div>4p   </div> </div>	+ 2			2	Paramagnetic

1.	$[NiCl_4]^{2-}$		+ 2	$sp^3$	Tetrahedral	2	Paramagnetic
	$[Ni(CN)_4]^{2-}$	 Rearrangement $dsp^2$	+ 2	$dsp^2$	Square Planar	0	Diamagnetic
2.	$Ni(d^8 s^2)$		0			2	Paramagnetic
	$[Ni(CO)_4]$	 Rearrangement $sp^3$	0	$sp^3$	Tetrahedral	0	Diamagnetic
3.	$Mn^{2+}(d^5)$		+ 2			5	Paramagnetic
	$[Mn(CN)_6]^{4-}$		+ 2	$d^2sp^3$ (Inner)	Octahedral	1	Paramagnetic
	$[MnCl_4]^{2-}$	 Rearrangement $sp^3$	+ 2	$sp^3$	Tetrahedral	5	Paramagnetic
4.	$Cu^{2+}(d^9)$		+ 2			1	Paramagnetic
	$[CuCl_4]^{2-}$		+ 2	$sp^3$	Tetrahedral	1	Paramagnetic
	$[Cu(NH_3)_4]^{2+}$	 $dsp^2$ One electron is shifted from 3d to 4p-orbital	+ 2	$dsp^2$	Square Planar	1	Paramagnetic
5.	$Cr^{3+}(d^3)$		+ 3			3	Paramagnetic
	$[Cr(NH_3)_6]^{3+}$		+ 3	$d^2sp^3$ (Inner)	Octahedral	3	Paramagnetic
	$[Cr(H_2O)_6]^{3+}$		+ 3	$sp^3d^2$ (Outer)	Octahedral	3	Paramagnetic
6.	$Co^{3+}(d^6)$		+ 3			4	Paramagnetic
	$[Co(NH_3)_6]^{3+}$		+ 3	$d^2sp^3$ (Inner)	Octahedral	0	Diamagnetic
	$[CoF_6]^{3-}$	 Rearrangement $sp^3d^2$	+ 3	$sp^3d^2$ (Outer)	Octahedral	4	Paramagnetic
7.	$Co^{2+}(d^7)$		+ 2			3	Paramagnetic
	$[Co(H_2O)_6]^{2+}$		+ 2	$sp^3d^2$ (outer)	Octahedral	3	Paramagnetic



							c
8.	$Fe^{2+} (d^6)$		+ 2				
	$[Fe(CN)_6]^{4-}$		+ 2	$d^2 sp^3 (Inner)$	Octahedral	0	Paramagnetic
	$[Fe(H_2O)_6]^{2+}$		+ 2	$sp^3 d^2 (Outer)$	Octahedral	4	Paramagnetic
	$[Fe(NH_3)_6]^{2+}$		+ 2	$sd^2 d^2 (Outer)$	Octahedral	4	Paramagnetic
		Rearrangement $d^2 sp^3$ $sp^3 d^2$ Same					
9.	$Fe^{3+} (d^5)$		+ 3			5	Paramagnetic
	$[Fe(CN)_6]^{3-}$		+ 3	$d^2 sp^3 (Inner)$	Octahedral	1	Paramagnetic
		$sp^2 d^3$					
10.	$Fe(d^6 s^2)$		0		Trigonal	4	Paramagnetic
	$[Fe(CO)_5]$		0	$dsp^3 (Inner)$	Bipyramidal	0	Diamagnetic
		$dsp^3$					

**Illustration** Diamminesilver (I) chloride  $[Ag(NH_3)_2]Cl$

**Illustration** Tetramminezinc (II) chloride  $[Zn(NH_3)_4]Cl_2$

**Illustration** Tetracyano Nickel (II) sulphate  $[Ni(CN)_4]SO_4$

**Illustration** Hexa – ammine chromium (III) chloride  $[Cr(NH_3)_6]Cl_3$

## LIMITATIONS OF VBT

- Although valence bond theory provides a satisfactory representation of the complex compound based upon the concept of orbital hybridisation, it cannot account for the relative stabilities for different shapes and coordination numbers in metal complexes.
- VBT cannot explain as to why  $Cu(+2)$  forms only distorted octahedral complexes even when all the six ligands are identical.
- The valence bond theory does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
- Sometimes the theory requires the transfer of electron from lower energy to the higher energy level, which is very much unrealistic in absence of any energy supplier (for example, this happens in the case of  $[CuX_4]^{-2}$ ).
- The changes in the properties of the metal ion along with the ligands and the simple metal ions can not be explained. For example, the colour changes associated with electronic transition within d

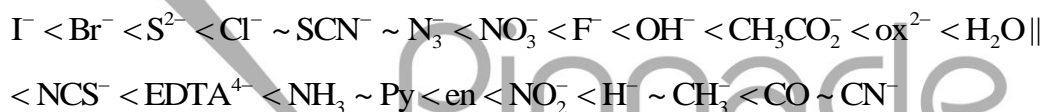
orbitals are affected on formation of complex, but the valence bond theory does not offer any explanation.

6. Sometimes the same metal acquires different geometry when formation of complex takes place with different ligands. The theory does not explain as to why at one time the electrons must be rearranged against the Hund's rule while, at other times the electronic configuration is not disturbed.
7. The energy change of the metal orbitals on formation of complex is difficult to be calculated mathematically.
8. VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments.
9. The VBT does not explain why certain complexes are more labile than the others.
10. It does not give quantitative interpretation of thermodynamic or kinetic stabilities of coordination compounds.
11. It does not make exact predictions regarding the tetrahedral and square planar structure of 4-coordinate complexes.
12. It does not tell about the spectral properties of coordination compounds.

## CRYSTAL FIELD THEORY (CFT)

In crystal field theory, we assume the ligands to be the point charges and there is interaction between the electrons of the ligands and the electrons of the central metal atom or ion. The five d-orbitals in an isolated gaseous metal atom or ion are degenerate. This degeneracy is maintained if an spherically symmetrical negative field surrounds the metal atom/ion. However, when ligands approach the central metal atom/ion, the field created is not exactly spherically symmetrical and the degeneracy of the d-orbitals is lifted. It results in the splitting of d-orbitals and the pattern of splitting depends upon the nature of the crystal field. This splitting of d-orbitals energies and its effects, form the basis of the crystal field treatment of the coordination compounds.

Ligands that cause large degree of crystal field splitting are termed as **strong field ligands**. Ligands that cause only a small degree of crystal field splitting are termed as **weak field ligands**. The common ligands can be arranged in ascending order of crystal field splitting energy. The order remains practically constant for different metals and this series is called the **spectrochemical series**.



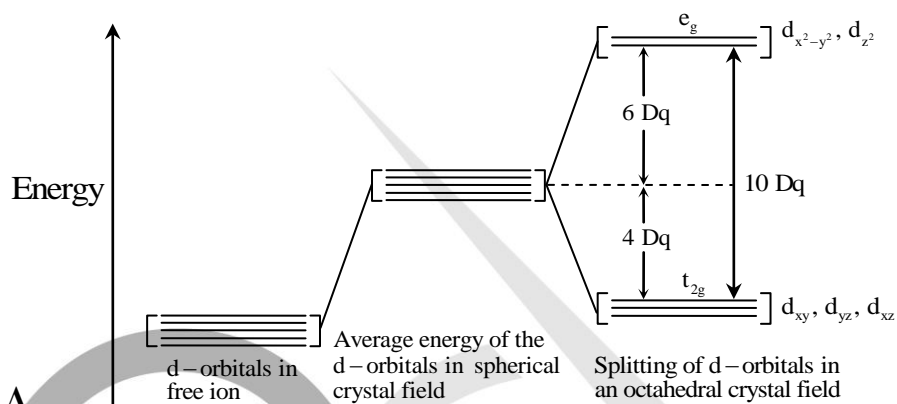
The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of  $\sigma$  and  $\pi$ -bonding. The halides are in the order expected from electrostatic effects. In other cases, we must consider covalent bonding to explain the order. A pattern of increasing  $\sigma$ -donation is as follows :

Halides donors < O donors < N donors < C donors

The crystal field stabilization produced by the strong  $\text{CN}^-$  is almost double that of halide ions. This is attributing  $\pi$ -bonding in which the metal donates electrons from a filled  $t_{2g}$  orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as  $\pi$ -acceptors.

### Crystal field effects in octahedral coordination entities

Let us assume that the six ligands are positioned symmetrically along the Cartesian axis with the metal atom or ion at the origin. As the ligands approach the central metal atom or ion, the energy of the d-orbitals of the central metal atom or ion increases. If the field created by the ligands is spherical, then the increase in the energies of all the d-orbitals is the same. However, under the influence of octahedral field, the energies of the d-orbitals lying along the axis (i.e.  $d_{z^2}$  and  $d_{x^2-y^2}$ ) increases more than the d-orbitals lying between the axis (i.e.  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ). Thus, the degenerate d-orbitals (with no field effect or spherical field effect) splits up into two sets of orbitals (i) the lower energy set,  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ) and (ii) the higher energy set,  $e_g$  ( $d_{x^2-y^2}$  and  $d_{z^2}$ ). The energy separation is denoted by  $\Delta_o$  or  $10 Dq$ . (where  $\Delta_o$  stands for octahedral field), as shown below :



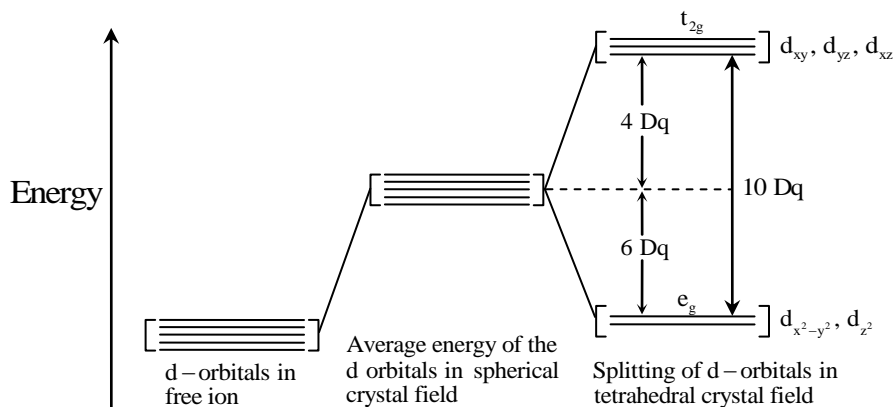
### Significance of $\Delta_o$

A strong field ligand approaches the central metal atom/ion strongly and thus the magnitude of  $\Delta_o$  is high. Hence, in the case of strong field ligand, the magnitude of  $\Delta_o$  is greater than the pairing energy (the energy required to pair up two negatively charged electrons having opposite spin in an orbital). However, under the influence of weak field ligand,  $\Delta_o < P$  (where  $P$  represents the pairing energy).

Now, let us consider the  $d^4$  configuration of the central metal atom/ion. The first three electrons will go into  $t_{2g}$  orbitals using Hund's rule of maximum multiplicity. The fourth electron will go in the  $e_g$  orbital when the ligands are weak as,  $\Delta_o < P$  giving the configuration  $t_{2g}^3 e_g^1$ . But if the ligands are strong then the fourth electron will pair up with any of the singly occupied  $t_{2g}$  orbitals (as  $\Delta_o > P$ ) to give the configuration  $t_{2g}^4 e_g^0$ .

### Crystal field effects in tetrahedral coordination entities

Under the influence of tetrahedral field, the d-orbital splitting is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that  $\Delta_t = \frac{4}{9} \Delta_o$ . Consequently the orbital splitting energies are not sufficiently large for forcing pairing and therefore low spin or spin paired configurations are rarely observed.



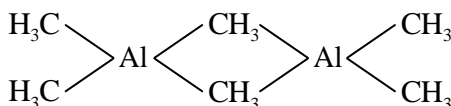
## ORGANOMETALLIC COMPOUNDS

Compounds that contain at least one carbon-metal bond are called organometallic compounds. Zeisse, in 1830, prepared the first organometallic compound by the action of ethylene on a solution of potassium chloroplatinate (II). In the last four decades, enormous work has been done in this field and many fascinating compounds have been synthesised and investigated. Grignard reagent,  $RMgX$  is a familiar example of organometallic compounds where  $R$  is an alkyl group. Diethyl zinc  $[Zn(C_2H_5)_2]$ , lead tetraethyl  $[Pb(C_2H_5)_4]$ , ferrocene  $[Fe(C_5H_5)_2]$ , dibenzene chromium  $[Cr(C_6H_6)_2]$ , metal carbonyls are other examples of organometallic compounds. The compounds of metalloids such as germanium and antimony and non-metallic elements such as boron and silicon are also included under this classification.

Organometallic compounds may be classified in three classes :

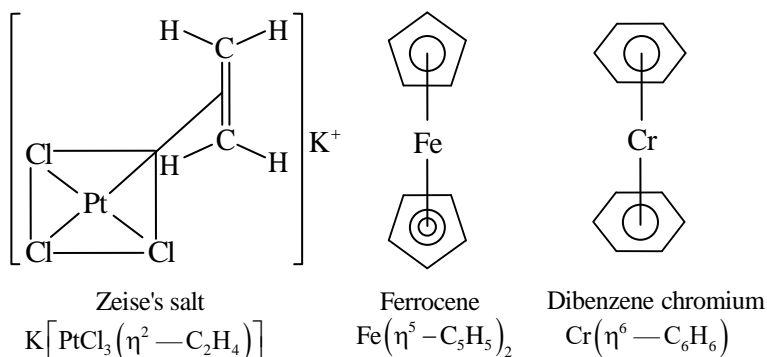
1. Sigma ( $\sigma$ ) bonded complexes,
  2. Pi ( $\pi$ ) bonded complexes,
  3. Complexes containing both  $\sigma$ - and  $\pi$ -bonding characteristics.
- 1. Sigma bonded complexes :** In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, i.e., the ligand contributes one electron and is, therefore, called one electron donor. Examples are :
- (i) Grignard reagent,  $R-Mg-X$  where  $R$  is an alkyl or aryl group and  $X$  is a halogen.
  - (ii) Zinc compounds of the formula  $R_2Zn$  such as  $(C_2H_5)_2Zn$ . This was first isolated by Frankland in 1849. Other similar compounds are  $(CH_3)_4Sn$ ,  $(C_2H_5)_4Pb$ ,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$ ,  $Pb(CH_3)_4$ , etc.

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



2.  **$\pi$ -bonded organometallic compounds :** These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond

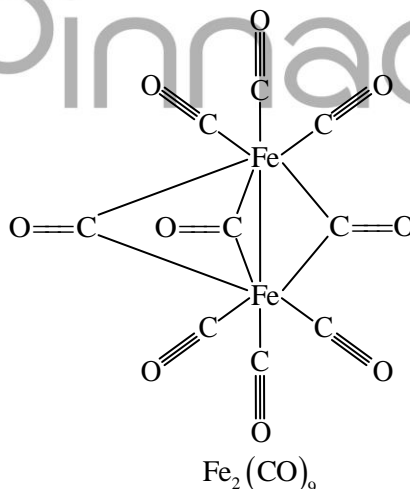
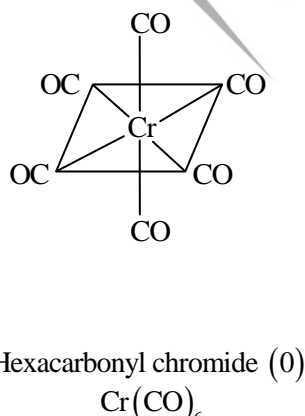
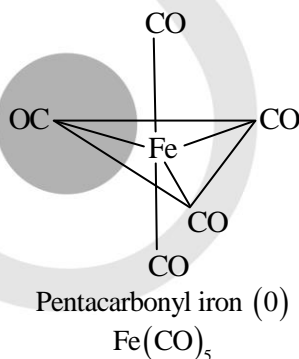
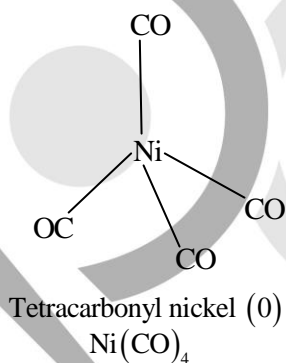
that involves the  $\pi$  electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown here :



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

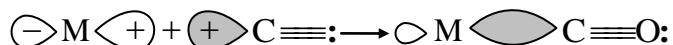
3.  **$\sigma$ - and  $\pi$ -bonded organometallic compounds :** Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. These compounds possess both  $\sigma$ - and  $\pi$ -bonding. The oxidation state of metal atoms in these compounds is zero. Carbonyls may be monomeric, bridged or polynuclear. Carbonyls are mainly formed by the transition metals of VIth, VIIth and VIIIth groups.

Some well known examples are :

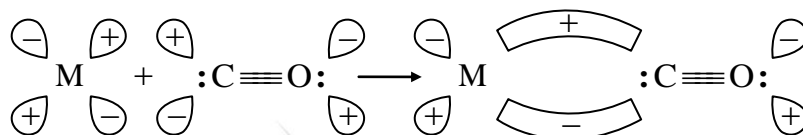




In a metal carbonyl, the metal-carbon bond possesses both the  $\sigma$ - and  $\pi$ -character. A  $\sigma$ -bond between metal and carbon atom is formed when a vacant hybrid bond of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.



Formation of  $\pi$ -bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding  $\pi^*$  orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon. It has been shown below :



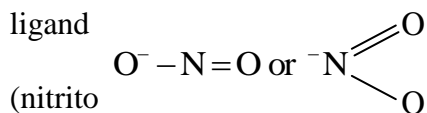
The  $\pi$ -overlap is perpendicular to the nodal plane of  $\sigma$ -bond.

In olefinic complexes, the bonding  $\pi$ -orbital electrons are donated to the empty orbital of the metal atom and at the same time back bonding occurs from filled orbital to the metal atom to the antibonding  $\pi$ -orbital of the olefin.



### Summary

- **Red Alert :** Certain polydentate ligands have flexidentate character e.g., EDTA generally act as a hexadentate ligand but it can also act as a pentadentate or a tetradentate ligand.
- **Red Alert :** Certain ligands like NO can act as a neutral as well as unipositive ( $\text{NO}^+$ ) 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. For example, in the complex  $[\text{Fe}(\text{H}_2\text{O})_5 \text{NO}]^{2+}$  Fe is in + 1 oxidation state with five  $\text{H}_2\text{O}$  neutral ligands and one unipositive  $\text{NO}^+$  ligand. During the formation of this complex, NO gives its unpaired electron to  $\text{Fe}^{2+}$  and change it into  $\text{Fe}^+$ . Another example of this type is the complex nitroprusside ion,  $[\text{Fe}(\text{CN})_5 \text{NO}]^{2-}$ , in which Fe is in + 2 oxidation state with five  $\text{CN}^-$  ligands and one  $\text{NO}^+$  ligand, Similarly,  $\text{NO}_2$  can be a uninegative ligand



(nitrito or a positive ligand ( $\text{NO}_2^+$ )). In such cases, the experimentally

observed magnetic moment of the complex in solid state can decide the oxidation state of the central metal ion. From it, nature of the ligand can be decided.

- **Red Alert :**
1. Square planar complexes of type  $\text{MA}_2\text{B}_2$ ,  $\text{MA}_2\text{BC}$  and  $\text{MABCD}$  show geometrical isomerism. Geometrical isomerism is not possible in square planar complexes of type  $\text{MA}_4$  and  $\text{MA}_3\text{B}$ .
  2. Square planar complex of type  $\text{MABCD}$  having four different ligands give three geometrical isomers.
  3. Complexes of type  $\text{MA}_2\text{B}_4$ ,  $\text{MA}_4\text{BC}$ ,  $\text{MA}_3\text{B}_3$ ,  $\text{MA}_2\text{B}_2\text{C}_2$ , exhibit geometric isomerism.
  4. Complexes of type  $\text{M}(\text{AA})_2\text{B}_2$  where AA is a symmetrical bidentate ligand and B is unidentate ligand show geometric isomersim.
  5. Geometrical isomerism is not possible in tetrahedral complexes of type  $\text{MA}_4$ ,  $\text{MA}_2\text{B}_2$  and  $\text{MABCD}$ ,
  6. Compound of type  $\text{MA}_2\text{X}_2\text{Y}_2$ ,  $\text{MA}_2\text{X}_2\text{YZ}$ ,  $\text{MA}_2\text{XYZL}$ ,  $\text{MABXYZL}$ ,  $\text{M}(\text{AA})_3$ ,  $\text{M}(\text{AA})_2\text{X}_2$  show optical isomerism.
  7.  $\text{MA}_2\text{X}_2\text{Y}_2$  show both optical and geometrical isomerism.
  8. Octahedral complexes of type  $\text{MA}_6$  and  $\text{MA}_5\text{B}$  do not show geometric isomerism
  9. Octahedral complex of type  $\text{MA}_3\text{B}_3$  exist only in two isomeric forms
  10. Octahedral complexes of type  $\text{MABCDXY}$  exist in 15 different geometrical isomeric forms.
  11.  $[\text{M} \text{AA} \text{B}_2\text{C}_2]$  can show geometrical isomerism.

- **Red Alert :** Certain complexes involve special types of electron transfer before hybridization, as explained below.
1.  $[Cu(NH_3)_4]^{2+} \Rightarrow$  Electronic configuration of  $Cu^{2+} : [Ar]^{18} 3d^9$  : In this complex, one electron from 3d-subshell is promoted to 4p-subshell. The remaining eight 3d-electrons pairs up in four 3d-orbitals followed by  $dsp^2$  hybridisation. The resulting complex is square planar with one unpaired electron in 4p-orbital, It is thus paramagnetic.
  2.  $[Co(NH_3)_6]^{2+} \Rightarrow$  Electronic configuration of  $Co^{2+} : [Ar]^{18} 3d^7$  . In this complex, one electron from 3d-subshell is promoted to 4p-subshell and the remaining six 3d-electrons pair up in three 3d-orbitals. This is followed by  $d^2 sp^3$  hybridization. The resulting complex, is octahedral with one unpaired electron in 4p-orbital. It is thus paramagnetic.
  3.  $[Ni(CO)_4] \Rightarrow$  Electronic configuration of  $Ni : [Ar]^{18} 4s^2 3d^8$  . In this complex, the two 4s-electrons jump to 3d-subshell. The ten 3d-electrons pair up in five 3d-orbitals. This is followed by  $sp^3$  – hybridizations giving a tetrahedral complex with no unpaired electrons. The complex is as such diamagnetic.
- **Red Alert :** When  $Fe^{3+}(aq)$  is added to  $K_4[FeCN]_6$  containing Fe (II) the product obtained is called Prussian Blue. When  $Fe^{2+}(aq)$  is added to  $K_3[Fe(CN)_6]$  containing Fe(III) the product obtained is called Turnbull's blue. However, the two are chemically identical. They are mainly a mixtures of ferric potassium ferrocyanide,  $FeK[Fe(CN)_6]$  and ferrous potassium ferricyanide  $FeK[(FeCN)_6]$  with some ferric ferrocyanide,  $Fe_4[Fe(CN)_6]_3$  and ferroferricyanide,  $Fe_3[Fe(CN)_6]_4$ . This is because a mixture of  $Fe^{3+}(aq)$  and potassium ferrocyanide will contain the following four ions.  $Fe^{3+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightleftharpoons Fe^{2+}(aq) + [Fe(CN)_6]^{3-}(aq)$ .

Pinnacle

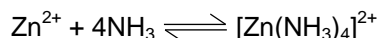
## SOLVED OBJECTIVE EXAMPLES

### Example 1:

What is the ratio of uncomplexed to complexed  $\text{Zn}^{2+}$  ion in a solution that is 10 M in  $\text{NH}_3$ , if the stability constant of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  is  $3 \times 10^9$ ?

- (a)  $3.3 \times 10^{-9}$       (b)  $3.3 \times 10^{-11}$   
(c)  $3.3 \times 10^{-14}$       (d)  $3 \times 10^{-13}$

### Solution:



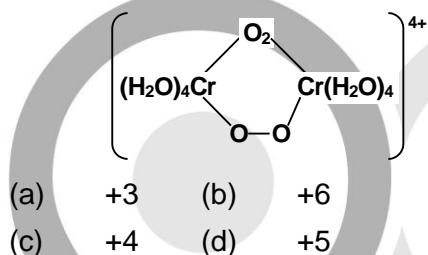
$$K_f = \frac{[\text{Zn}(\text{NH}_3)_4]^{2+}}{[\text{Zn}^{2+}][\text{NH}_3]^4}$$

$$\frac{[\text{Zn}^{2+}]}{[\text{Zn}(\text{NH}_3)_4]^{2+}} = \frac{1}{K_f [\text{NH}_3]^4} = \frac{1}{3 \times 10^9 \times (10)^4} = 3.3 \times 10^{-14}$$

$\therefore$  (c)

### Example 2:

Oxidation state of Cr in the following complex is



### Solution:

Among the bridging ligands,  $\text{O}_2$  is a neutral ligand and  $[\text{O}-\text{O}]^{2-}$  is a bidentate negative ligand. Since the net charge over the complex is  $4+$ , each chromium atom has an oxidation state of  $+3$ .

$\therefore$  (a)

### Example 3:

A compound has an empirical formula  $\text{CoCl}_3 \cdot 5\text{NH}_3$ . When an aqueous solution of this compound is mixed with excess of silver nitrate, 2 moles of  $\text{AgCl}$  precipitates per mole of the compound. On reaction with excess of  $\text{HCl}$ , no  $\text{NH}_4^+$  is detected. Hence the compound is

- (a)  $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]\text{Cl}$       (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
(c)  $[\text{Co}(\text{NH}_3)_5\text{Cl}_3]$       (d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$

### Solution:

As the moles of  $\text{AgCl}$  precipitated is 2 and no  $\text{NH}_4^+$  is detected on reaction with excess of  $\text{HCl}$ , so the compound would be  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .

$\therefore$

(b)

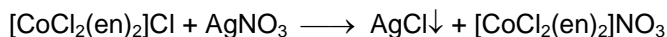
**Example 4:**

If excess of  $\text{AgNO}_3$  solution is added to 100 ml of 0.024 M solution of dichlorobis(ethylene diamine)cobalt(III) chloride, how many moles of  $\text{AgCl}$  will be precipitated?

- (a) 0.0012 (b) 0.0016  
(c) 0.0024 (d) 0.0048

**Solution:**

The formula of the complex is  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ .



Moles of complex = Moles of  $\text{AgCl}$  =  $100 \times 10^{-3} \times 0.024 = 0.0024$

$\therefore$  (c)

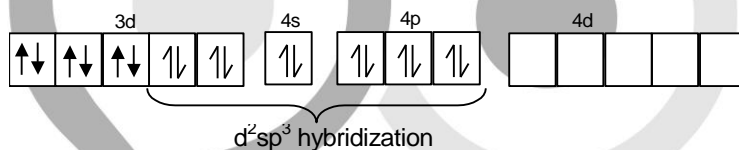
**Example 5:**

In nitroprusside ion, the iron and  $\text{NO}$  exist as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and  $\text{NO}$ . These forms can be distinguished by

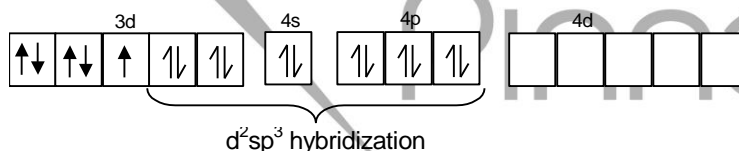
- (a) estimating the concentration of iron  
(b) measuring the concentration of  $\text{CN}^-$   
(c) measuring the solid state magnetic moment  
(d) thermally decomposing the compound

**Solution:**

Nitroprusside ion is  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ . If the central atom iron is present here in  $\text{Fe}^{2+}$  form, its effective atomic number will be  $26 - 2 + (6 \times 2) = 36$  and the distribution of electrons in valence orbitals (hybridised and unhybridized) of the  $\text{Fe}^{2+}$  will be



It has no unpaired electron. So this anionic complex is diamagnetic. If the nitroprusside ion has  $\text{Fe}^{3+}$  and  $\text{NO}$ , the electronic distribution will be such that it will have one unpaired electron i.e. the complex will be paramagnetic.



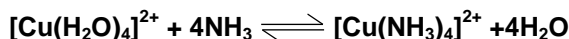
Thus, magnetic moment measurement establishes that in nitroprusside ion, the  $\text{Fe}$  and  $\text{NO}$  exist as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and  $\text{NO}$ .

$\therefore$  (c)



**Example 6:**

Which of the given statements is not true for the following reaction?

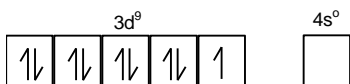


- (a) It is a ligand–substitution reaction.
- (b)  $\text{NH}_3$  is a relatively strong field ligand while  $\text{H}_2\text{O}$  is a weak field ligand.
- (c) During the reaction, there is a change in colour from light blue to dark blue.
- (d)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  has a tetrahedral structure and is paramagnetic.

**Solution:**

For  $_{29}\text{Cu}$ , outermost shell has electronic configuration of  $3d^{10}4s^1$ .

$\therefore$  Electronic configuration of  $\text{Cu}^{2+} = 3d^9 4s^0$



But due to strong field ligand ( $\text{NH}_3$ ), unpaired electron of  $3d^9$  jumps to  $4p$ . Hence,



$\therefore$  Hybridisation of  $\text{Cu}^{2+}$  in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is  $dsp^2$  and it gives the square planar geometry.

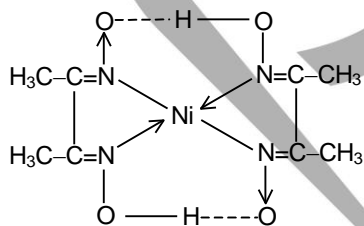
$\therefore$  (d)

**Example 7:**

The IUPAC name of the complex  $[\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2]$  formed from the reaction of  $\text{Ni}^{2+}$  with dimethyl glyoxime is

- (a) Bis(methylglyoxal)nickel(II)
- (b) Bis(dimethyloxime)nickelate(IV)
- (c) Bis(2,3–butanedioldioximato)nickel(II)
- (d) Bis(2,3–butanedionedioximato)nickel(II)

**Solution:**



Bis(dimethylglyoximate)nickel(II) or Bis(2,3–butanedionedioximato)nickel(II)

$\therefore$  (d)

**Example 8:**

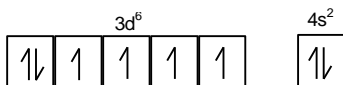
The hybridization states of the central atoms in the complexes  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Co}(\text{NO}_2)_6]^{3-}$  are

- (a)  $d^2sp^3$ ,  $sp^3$  and  $d^4s^2$  respectively
- (b)  $d^2sp^3$ ,  $sp^3d$  and  $sp^3d^2$  respectively
- (c)  $d^2sp^3$ ,  $sp^3d^2$  and  $dsp^2$  respectively
- (d) all  $d^2sp^3$

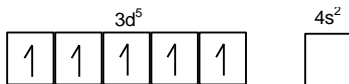
**Solution:**

$[\text{Fe}(\text{CN})_6]^{3-}$  has  $\text{Fe}^{3+}$  ion.

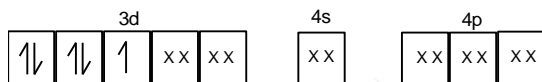
Outermost shell of  $\text{Fe}^{3+}$  ( $Z = 26$ ) has the following configuration,



and outermost shell of  $\text{Fe}^{3+}$  has the configuration:



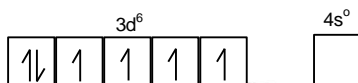
But due to strong field ligand ( $\text{CN}^-$ ), the pairing of electrons takes place.



$\therefore$  Hybridisation is  $d^2sp^3$ .

$[\text{Fe}(\text{CN})_6]^{4-}$  has  $\text{Fe}^{2+}$  ion.

Outermost shell of  $\text{Fe}^{2+}$  has the following configuration:



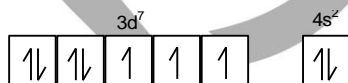
But due to strong field ligand ( $\text{CN}^-$ ), the pairing of electrons takes place.



$\therefore$  Hybridisation is  $d^2sp^3$ .

$[\text{Co}(\text{NO}_2)_6]^{3-}$  has  $\text{Co}^{3+}$  ion.

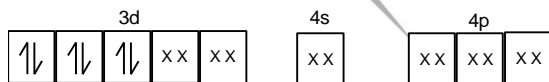
Outermost shell of  $\text{Co}$  ( $Z = 24$ ) has the following configuration,



and outermost shell of  $\text{Co}^{3+}$  has the configuration:



But due to strong field ligand ( $\text{NO}_2^-$ ), pairing of electrons occurs.



$\therefore$  Hybridisation is  $d^2sp^3$ .

$\therefore$  (d)

**Example 9:**

Which of the following statement is incorrect?

- (a) Most four-coordinated complexes of  $\text{Ni}^{2+}$  ions are square planar rather than tetrahedral.
- (b) The  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion is more paramagnetic than the  $[\text{Fe}(\text{CN})_6]^{3-}$  ion.
- (c) Square planar complexes are more stable than octahedral complexes.
- (d) The  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is paramagnetic but  $[\text{Fe}(\text{CN})_6]^{3-}$  ion is diamagnetic.

**Solution:**

$[\text{Fe}(\text{CN})_6]^{4-}$  has  $\text{Fe}^{2+}$  and have no unpaired electron, so it is diamagnetic and  $[\text{Fe}(\text{CN})_6]^{3-}$  has  $\text{Fe}^{3+}$  and having one unpaired electron, so it is paramagnetic.

$\therefore$  (d)

**Example 10:**

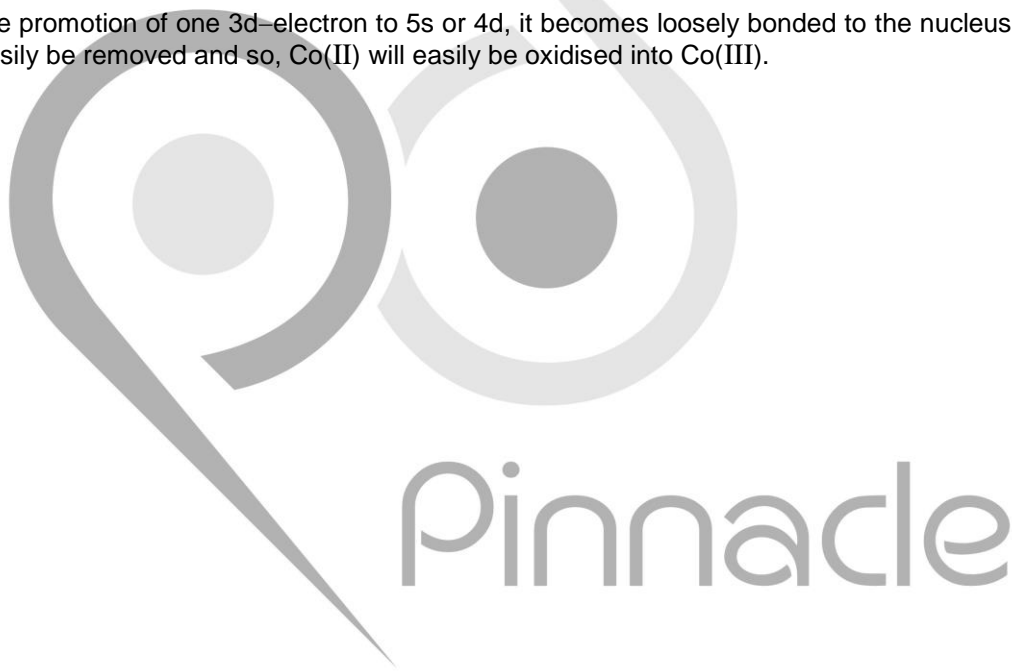
Which of the following statement is correct?

- (a)  $[\text{Co}(\text{NH}_3)_6]^{2+}$  is oxidized to diamagnetic  $[\text{Co}(\text{NH}_3)_6]^{3+}$  by the oxygen in air.
- (b)  $[\text{Fe}(\text{CN})_6]^{3-}$  is stable but  $[\text{FeF}_6]^{3-}$  is unstable.
- (c)  $[\text{NiCl}_4]^{2-}$  is unstable with respect to  $[\text{NiBr}_4]^{2-}$ .
- (d) None of these.

**Solution:**

With the promotion of one 3d-electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so,  $\text{Co(II)}$  will easily be oxidised into  $\text{Co(III)}$ .

$\therefore$  (a)



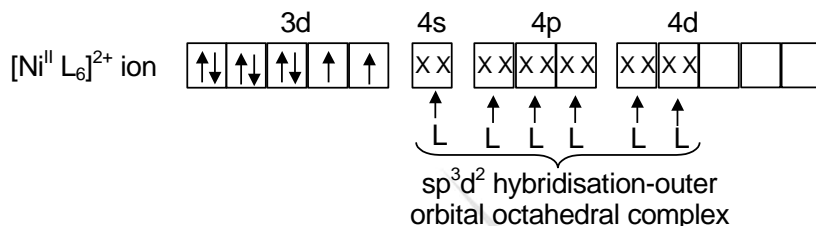
## SOLVED SUBJECTIVE EXAMPLES

### Example 1:

Show that all octahedral complexes of  $\text{Ni}^{2+}$  must be outer-orbital complexes.

#### Solution:

The electronic configuration of  $\text{Ni}^{2+}$  ion ( $3d^8$ ) indicates that two inner d-orbitals (3d-orbitals) cannot be made available to allow  $d^2sp^3$  hybridisation. However, by using two 4d-orbitals,  $sp^3d^2$  hybridisation may be possible.

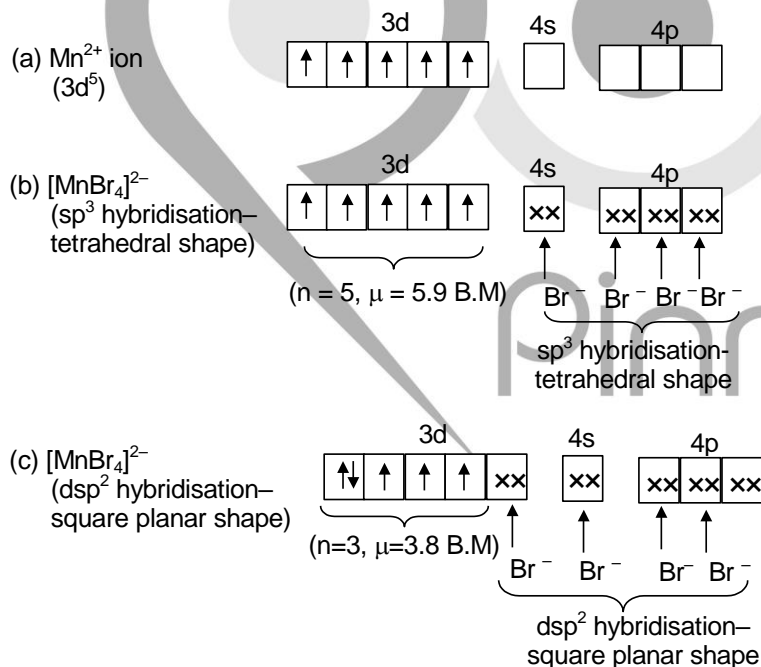


### Example 2:

The magnetic moment of  $[\text{MnBr}_4]^{2-}$  is 5.9 B.M. What is the geometry of this complex ion?

#### Solution:

Since the coordination number of  $\text{Mn}^{2+}$  ion in this complex ion is 4, it may be either tetrahedral ( $sp^3$  hybridisation) or square planar ( $dsp^2$  hybridisation) as shown below at (b) and (c). But the fact that the magnetic moment of the complex ion is 5.9 B.M. shows that it should be tetrahedral in shape rather than square-planar.



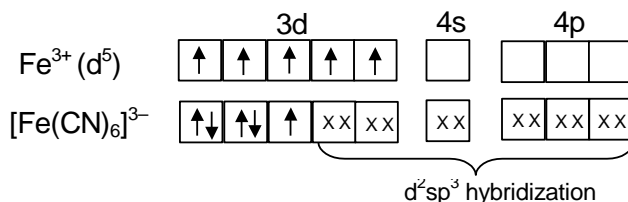
### Example 3:

How would you account for the following?

- (a)  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic.  
 (b)  $\text{Ni}(\text{CO})_4$  possesses tetrahedral geometry while  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar.  
 (c)  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic while  $[\text{NiCl}_4]^{2-}$  is paramagnetic.

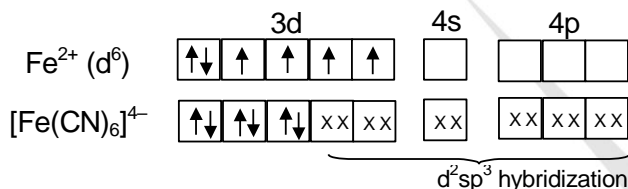
**Solution:**

- (a)  $[\text{Fe}(\text{CN})_6]^{3-}$  involves  $d^2sp^3$  hybridization.



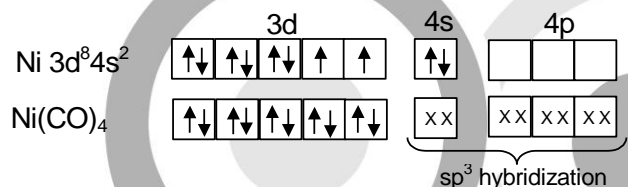
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$  involves also  $d^2sp^3$  hybridization but it has  $\text{Fe}^{2+}$  ion as central ion.

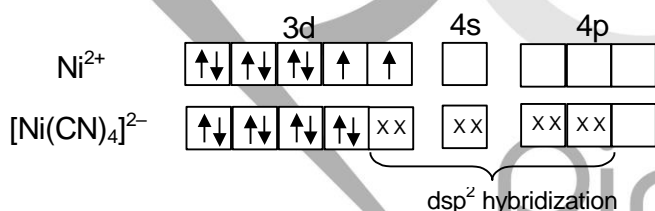


All orbitals are doubly occupied, hence it is diamagnetic in nature.

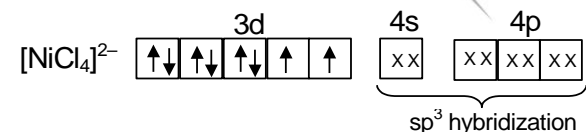
- (b) In the formation of  $\text{Ni}(\text{CO})_4$ , nickel undergoes  $sp^3$  hybridization, hence it is tetrahedral in shape.



- (c) In  $[\text{Ni}(\text{CN})_4]^{2-}$  ion,  $\text{Ni}^{2+}$  undergoes  $dsp^2$  hybridization, hence it is square planar in shape.



In  $[\text{Ni}(\text{CN})_4]^{2-}$ , all orbitals are doubly occupied, hence it is diamagnetic; while in  $[\text{NiCl}_4]^{2-}$ , two orbitals are singly occupied, hence it is paramagnetic in nature.



Strong field ligands like  $\text{CN}^-$ ,  $\text{CO}$ , en,  $\text{NO}_2^-$  have very strong electron donating tendency, hence electrons of central metal ion pair up against Hund's rule and low spin complexes are formed.

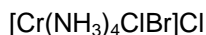
**Example 4:**

A metal complex having composition  $\text{Cr}(\text{NH}_3)_4 \text{Cl}_2 \text{Br}$  has been isolated in two forms (A) and (B). The form (A) reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia,

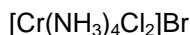
whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridisation of chromium in each. Calculate the magnetic moments (spin-only value).

**Solution:**

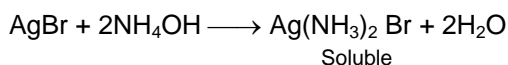
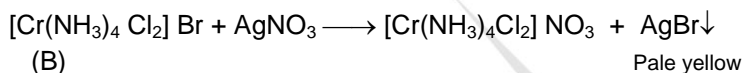
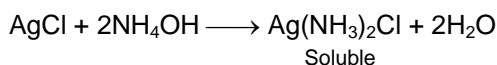
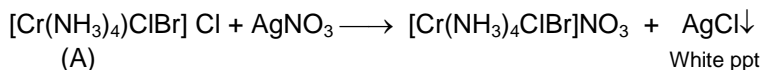
Complex,  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$ , has two isomers. Since, coordination number of Cr is six, the two forms may be represented in the following way



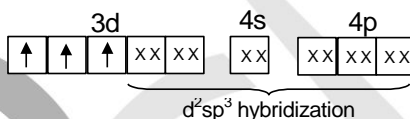
(A)



(B)



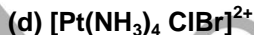
The state of hybridisation of chromium in both the complexes is  $d^2sp^3$ . Chromium is in trivalent state ( $\text{Cr}^{3+}$ ).



As three unpaired electrons are present, the magnetic moment =  $\sqrt{n(n+2)}$  B.M. =  $\sqrt{3 \times 5}$  B.M.  
= 3.87 B.M.

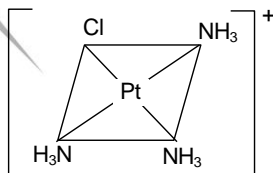
**Example 5:**

Platinum (II) forms square planar complexes and platinum (IV) gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures.



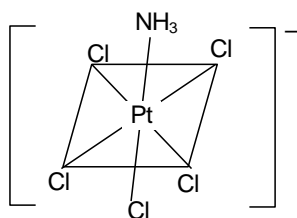
**Solution:**

(a) No isomers are possible for a square planar complex of the type  $\text{MA}_3\text{B}$ .

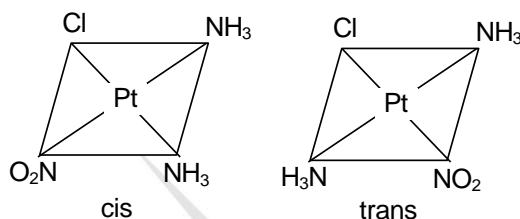




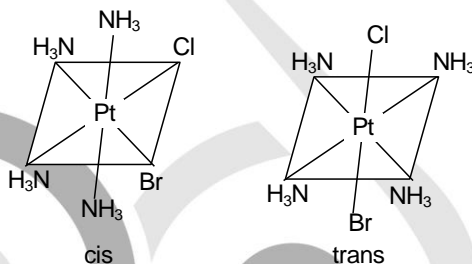
(b) No isomers are possible for an octahedral complex of the type  $\text{MAB}_5$ .



(c) Cis and trans isomers are possible for a square planar complex of the type  $\text{MA}_2\text{BC}$ .

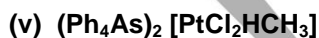
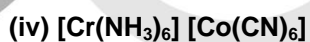


(d) Cis and trans isomers are possible for an octahedral complex of the type  $\text{MA}_4\text{BC}$ .



### Example 6:

Write the IUPAC name of the following complexes:



### Solution:

- Tris(ethylenediamine)cobalt(III) chloride
- Trioxalatocobaltate(III) ion
- Decaammine- $\mu$ -peroxodicobalt(III) ion
- Hexaamminechromium(III) hexacyanocobaltate(III)
- Tetraphenylarsenium dichlorohydridomethylplatinate(II)

**Example 7:**

A solution containing 0.319 g of complex  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was passed through cation exchanger and the solution given out was neutralised by 28.5 ml of 0.125 M NaOH. What is the correct formula of complex?

**Solution:**

The Cl atoms outside the co-ordination sphere will be ionised to produce the acid, HCl.

Thus, milliequivalent of  $\text{Cl}^-$  ions outside = milliequivalent of HCl formed

= milliequivalent of NaOH used

=  $28.5 \times 0.125$

= 3.56

$\frac{0.319}{266.5}$  mole or 1.197 millimole of complex produce 3.56 milliequivalent or millimoles of  $\text{Cl}^-$ . Thus,

1 mole of complex will give 3 mole of  $\text{Cl}^-$ , i.e. all the three Cl atoms are outside the co-ordination sphere. Thus, the complex is  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ .

**Example 8:**

Give the structural formula of these complex compounds:

- (i) Ammonium aquapentafluoroferrate(III)
- (ii) Diaquabis(ethylenediamine)cobalt(III) sulphate
- (iii) Tetraisothiocyanatozincate(II) ion
- (iv) Sodium hexanitrocobaltate(III)
- (v) Tris(ethylenediamine)iron(II) tetracyanoferrate(II)

**Solution:**

- (i)  $(\text{NH}_4)_2[\text{FeF}_5(\text{H}_2\text{O})]$
- (ii)  $[\text{Co}(\text{H}_2\text{O})_2(\text{en})_2]_2(\text{SO}_4)_3$
- (iii)  $[\text{Zn}(\text{NCS})_4]^{2-}$
- (iv)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
- (v)  $[\text{Fe}(\text{en})_3][\text{Fe}(\text{CN})_4]$

**Example 9:**

(A), (B) and (C) are three complexes of chromium (III) with the empirical formula  $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$ . All the three complexes have water and chloride ions as ligands. Complex (A) does not react with concentrated  $\text{H}_2\text{SO}_4$ , whereas complexes (B) and (C) lose 6.75% and 13.5% of their original weight, respectively, on treatment with concentrated  $\text{H}_2\text{SO}_4$ . Identify the octahedral complexes (A), (B) and (C).

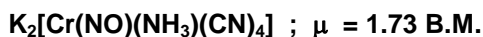
**Solution:**

- (A) :  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (Violet)
- (B) :  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (Green)      Molecular weight = 266.5
- (C) :  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (Dark green)

Compound (A) contains six water molecules as co-ordinated water and thus, does not lose  $\text{H}_2\text{O}$  on treatment with  $\text{H}_2\text{SO}_4$ . Compound (B) contains five water molecules as co-ordinated water and one molecule as lattice water which is lost to  $\text{H}_2\text{SO}_4$  showing a loss of 18 g out of 266.5 g, i.e., 6.75% loss. Similarly, compound (C) contains four co-ordinated water molecules and two molecules of lattice water, which are taken out by  $\text{H}_2\text{SO}_4$  to show a loss of 13.5%.

**Example 10:**

- (a) Write down the IUPAC nomenclature of the given complex along with its hybridisation and structure



- (b) Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$ . Write the hybridisation of atomic orbitals of the transition metal in each case.

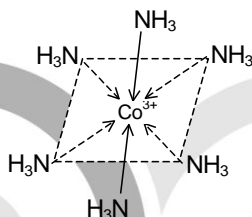
**Solution:**

- (a) Potassium amminetetracyanonitrosoniumchromate(I)

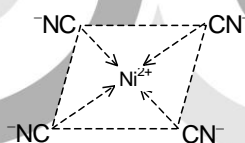
Cr is in +1 oxidation state and possesses  $d^2sp^3$  hybridisation with one unpaired electron.

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM.}$$

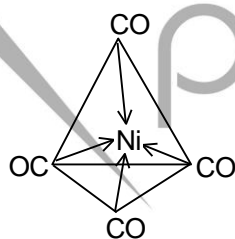
- (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ :  $\text{Co}^{3+}$  is  $d^2sp^3$  hybridised to show octahedral shape.



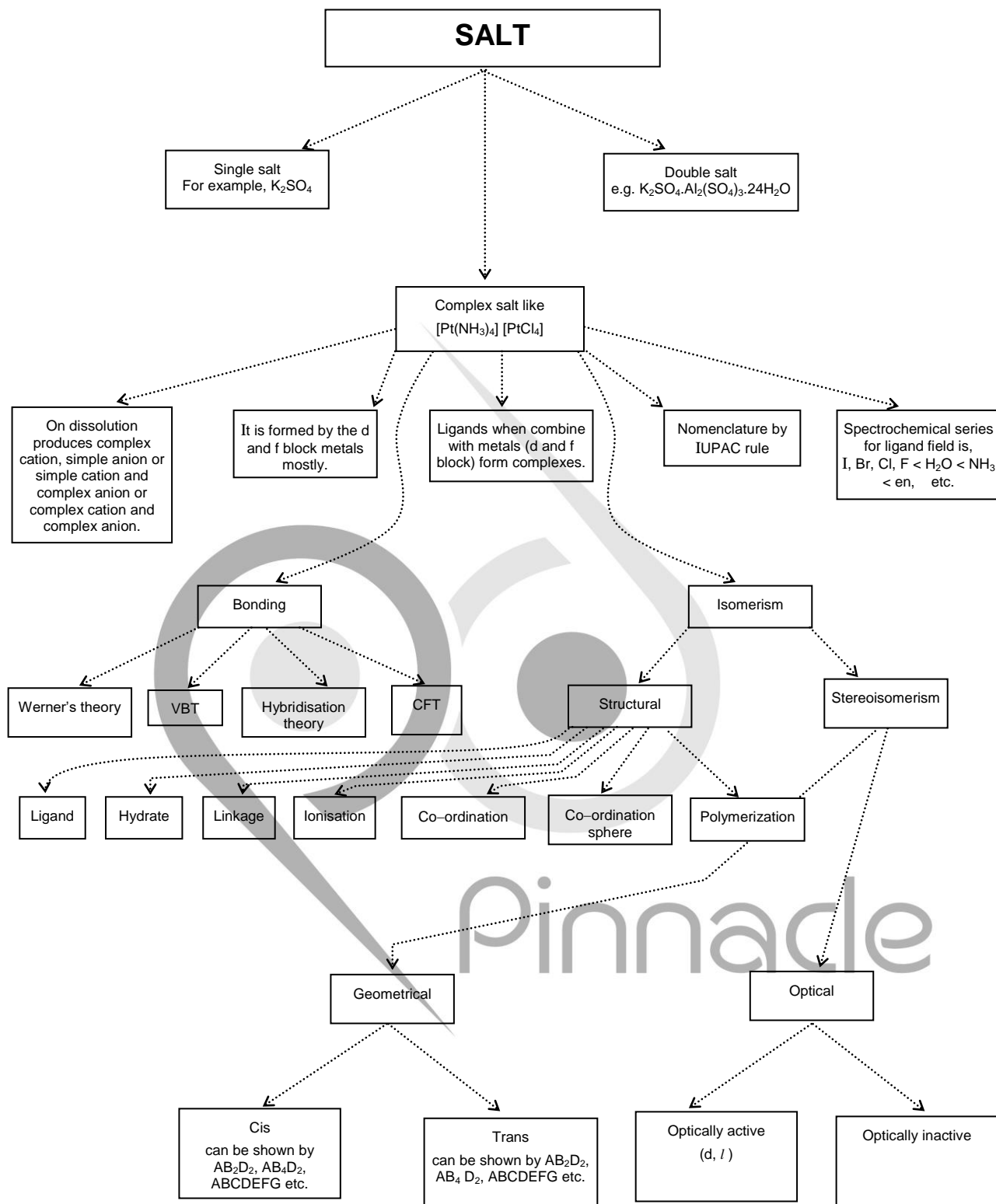
- $[\text{Ni}(\text{CN})_4]^{2-}$ :  $\text{Ni}^{2+}$  is  $dsp^2$  hybridised to show square planar shape.



- $[\text{Ni}(\text{CO})_4]$ : Ni is  $sp^3$  hybridised to show tetrahedral shape.



## MIND MAP



**CBSE Problems**

1.  $\text{Fe}^{3+}$  complexes are more stable than  $\text{Fe}^{2+}$  complexes. Why?
2. Write IUPAC name of linkage isomer of  $[\text{Cr}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ .
3. What is the co-ordination number of Fe in  $[\text{Fe}(\text{EDTA})]$ ?
4. What is the hybridisation of Ni in  $[\text{Ni}(\text{CN})_4]^{2-}$  complex. Also predict the shape of the complex.
5. Explain the following:
  - (i) Ferrocyanide ion is diamagnetic and ferricyanide ion is paramagnetic.
  - (ii) Aqueous solution of potassium ferricyanide does not give test ferric ions.
  - (iii)  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  has a square planar geometry but  $\text{Ni}(\text{CO})_4$  has tetrahedral geometry.
  - (iv)  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colorless while  $[\text{Ti}(\text{H}_2\text{O})_3]^{3+}$  is coloured.
6. What is meant by isomerism? Give example of each of the following in relation to co-ordinate compounds:
  - (i) Ionization isomerism
  - (ii) Linkage isomerism
  - (iii) Geometrical isomerism
  - (iv) Optical isomerism
7. Give a chemical test to distinguish between  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ . What kind of isomerism do they exhibit?
8. What is polymerization isomerism? Discuss with one example.
9. Complete the following statements for the coordination entity (complex ion)  $[\text{CrCl}_2(\text{OX})_2]^{3-}$ 
  - (a) OX is abbreviation for \_\_\_\_\_.
  - (b) The oxidation number of chromium is \_\_\_\_\_.
  - (c) The coordination number of chromium is \_\_\_\_\_.
  - (d) \_\_\_\_\_ is a bidentate ligand.
10. Deduce the magnetic behaviour of each of the following:
  - (i)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$
  - (ii)  $\text{Fe}(\text{CO})_5$

(Atomic numbers of Cr = 24, Fe = 26)

**EXERCISE - I**

- The IUPAC name for  $[\text{Pt}(\text{NH}_3)_3(\text{Br})(\text{NO}_2)(\text{Cl})]\text{Cl}$  is
  - Triamminechlorobromonitroplatinum (IV) chloride
  - Triamminebromochloronitroplatinum (V) chloride
  - Triaminenitrochlorobromoplatinum (IV) chloride
  - Triamminechloronitrobromoplatinum (IV) chloride
- The IUPAC name of the complex  $\text{Ni}[(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2]$ , formed by the reaction between  $\text{Ni}^{2+}$  and dimethylglyoxime, is
  - bis (methylglyoxal) nickel (II)
  - bis (dimethylglyoxime) nickel
  - bis (2,3-butanediol dioximato) nickel (II)
  - bis (2,3 – butanedione dioximato) nickel (II)
- Which of the following complex ions obeys Sidgwick's effective atomic number (EAN) rule?
  - $[\text{Fe}(\text{CN})_6]^{3-}$
  - $[\text{Fe}(\text{CN})_6]^{4-}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{Ni}(\text{en})_3]^{2+}$
- Which one of the following coordination compound exhibits ionization isomerism?
  - $[\text{Cr}(\text{NH}_3)_6]\text{Cl}$
  - $[\text{Cr}(\text{en})_3]\text{Cl}_3$
  - $[\text{Cr}(\text{en})_3]\text{Cl}_3$
  - $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
- The pair  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$  will exhibit
  - Hydrate isomerism
  - Linkage isomerism
  - Ionization isomerism
  - Coordinate isomerism
- Which of the following will have three stereoisomeric forms?
  - $[\text{Cr}(\text{NO}_3)_3(\text{NH}_3)_3]$
  - $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$
  - $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$
  - $[\text{Co}(\text{en})_2\text{ClBr}]$

(where en = ethylene diamine)

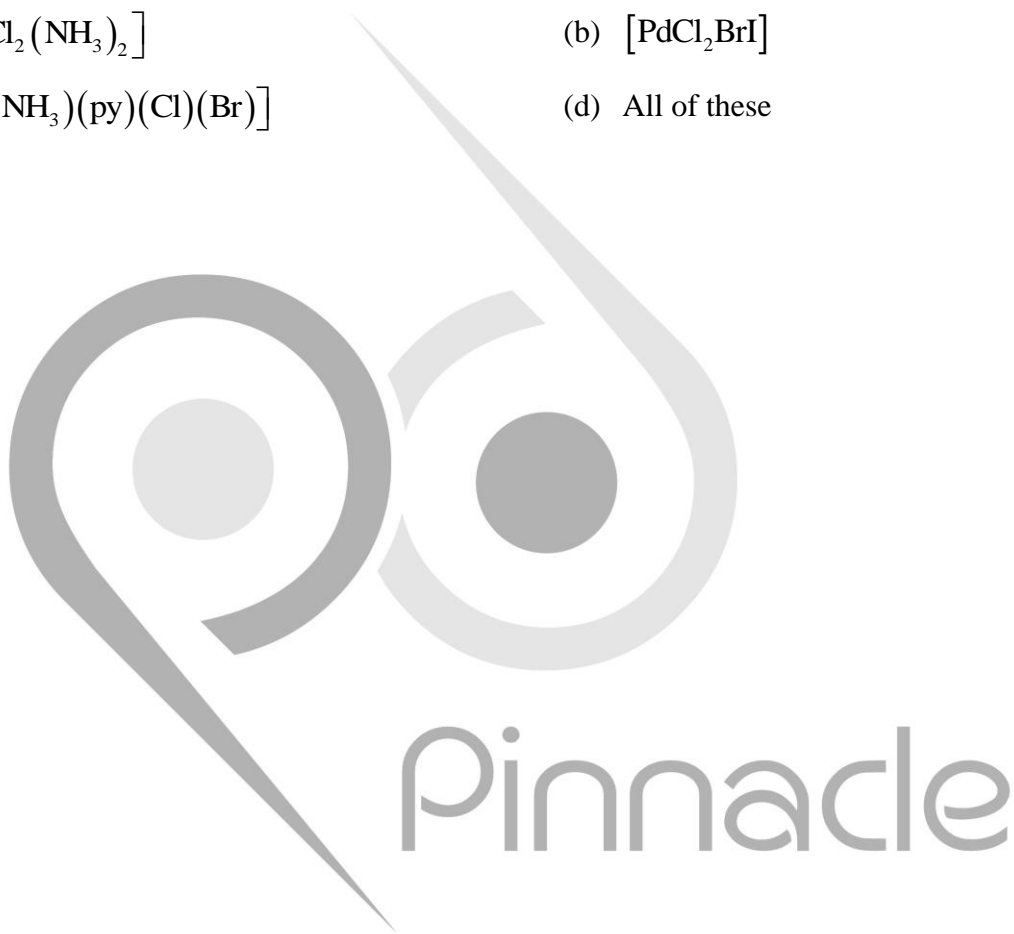
  - (iv) and (iii)
  - (iv) and (i)
  - (iii) and (ii)
  - (i) and (ii)
- A coordination compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One aqueous solution on treatment with an excess of  $\text{AgNO}_3$  gives two moles of  $\text{AgCl}$  as a precipitate. The formula of this complex would be



- (a)  $[\text{Co}(\text{NH}_3)_4 \text{NO}_2 \text{Cl}][\text{NH}_3 \text{Cl}]$  (b)  $[\text{Co}(\text{NH}_3) \text{Cl}][\text{ClNO}_2]$
- (c)  $[\text{Co}(\text{NH}_3)_5 \text{NO}_2] \text{Cl}_2$  (d)  $[\text{Co}(\text{NH}_3)_5][(\text{NO}_2)_2 \text{Cl}_2]$
8. The hybridization states of the central atom in the complex ions  $[\text{FeF}_6]^{3-}$ ,  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  are
- (a)  $\text{sp}^3 \text{d}^2$ ,  $\text{dsp}^2$  and  $\text{d}^4 \text{s}^2$  respectively (b) All  $3\text{d}^2 4\text{s} 4\text{p}^3$
- (c) All  $4\text{s} 4\text{p}^3 4\text{d}^2$  (d)  $\text{sp}^3 \text{d}^2$ ,  $\text{dsp}^3$  and  $\text{p}^4 \text{d}^2$
9. Among  $\text{TiF}_6^{2-}$ ,  $\text{CoF}_6^{3-}$ ,  $\text{CuCl}_2$  and  $\text{NiCl}_4^{2-}$  (atomic numbers of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colorless species are
- (a)  $\text{CoF}_6^{3-}$  and  $\text{NiCl}_4^{2-}$  (b)  $\text{TiF}_6^{2-}$  and  $\text{CoF}_6^{3-}$
- (c)  $\text{Cu}_2 \text{Cl}_2 \text{NiCl}_4^{2-}$  (d)  $\text{TiF}_6^{3-}$  and  $\text{Cu}_2 \text{Cl}_2$
10. Among  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$
- (a)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic.
- (b)  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CO})_4]$  is paramagnetic.
- (c)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{NiCl}_4]^{2-}$  is paramagnetic.
- (d)  $[\text{Ni}(\text{CO})_4]$  is diamagnetic and  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic.
11. Zeise salt, an organometallic compound, has the formula
- (a)  $(\text{C}_6\text{H}_6)_2 \text{Cr}^+ \text{AlCl}_4^-$  (b)  $(\text{CH}_3)_2 \text{AlF}$
- (c)  $\text{Ni}(\text{CO})_4$  (d)  $\text{K}^+ [\text{PtC}_2\text{H}_4 \text{Cl}_3]^- \text{H}_2\text{O}$
12. Which of the following mixture is known as Zeigler – Natta catalyst?
- (a)  $\text{Al}(\text{OCH}_3)_3 + \text{TiCl}_4$  (b)  $(\text{C}_2\text{H}_5)_3 \text{Al} + \text{TiCl}_4$
- (c)  $[(\text{CH}_3)_2 \text{CHO}]_3 \text{Al} + \text{TiCl}_4$  (d)  $\text{LiCH}_3 + \text{TiCl}_4$
13. Which of the following is not an organometallic compound?
- (a) Ferrocene (b) Ruthenocene
- (c) Beryllium acetylacetonate (d) bis (benzene) chromium
14. Which is not a  $\pi$  - bonded complex?
- (a) Zeise salt (b) Ferrocene

- (c) bis (benzene) chromium (d) Tetraethyl lead
15. Which of the following is an organometallic compound?  
 (a) Lithium methoxide (b) Lithium acetate  
 (c) Lithium dimethylamide (d) Methyllithium
16. One mole of the complex compound  $[\text{Co}(\text{NH}_3)_5\text{Cl}_3]$  gives 3 moles of ions of dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  solution to yield two moles of  $\text{AgCl}(\text{S})$ . The structure of the complex is  
 (a)  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2\cdot\text{NH}_3$  (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (c)  $[\text{Co}(\text{NH}_3)_3\text{Cl}]\cdot 2\text{NH}_3$  (d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}\cdot\text{NH}_3$
17. Which of the following aquated metal ions has the highest paramagnetism?  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{3+}$  (d)  $[\text{Zn}(\text{H}_2\text{O})_2]^{2+}$
18. Which of the following species is expected to be colourless?  
 (a)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Ti}(\text{NO}_3)_4]$   
 (c)  $[\text{Cr}(\text{NH}_3)_2]^+$  (d)  $[\text{Fe}(\text{CN})_6]^{4-}$
19. Tollen's reagent contains  
 (a)  $\text{AgNO}_3$  (b)  $\text{AgOH}$   
 (c)  $[\text{Ag}(\text{NH}_3)_2]^+$  (d)  $[\text{Ag}(\text{NO}_3)_2]^+$
20. The ferric ion is detected by the formation of a Prussian blue precipitated on addition of potassium Ferrocyanide solution. The formula of the Prussian blue precipitate is  
 (a)  $\text{Fe}_4^{111}[\text{Fe}^{11}(\text{CN})_6]_3$  (b)  $\text{Fe}_3^{11}[\text{Fe}^{111}(\text{CN})_6]_4$   
 (c)  $\text{KFe}^{111}[\text{Fe}^{11}(\text{CN})_4]$  (d)  $\text{KFe}^{11}[\text{Fe}^{111}(\text{CN})_6]$
21. When a solution of potassium ferricyanide is added to an aqueous solution of ferrous sulphate a deep blue colour, known as Turnbull's is produced. The formula of the compound responsible for this deep blue colour is  
 (a)  $\text{KFe}^{111}[\text{Fe}^{11}(\text{CN})_6]$  (b)  $\text{Fe}_4^{111}[\text{Fe}^{11}(\text{CN})_4]_3$   
 (c)  $\text{KEe}^{11}[\text{Fe}^{111}(\text{CN})_6]$  (d)  $\text{Fe}_3^{111}[\text{Fe}^{111}(\text{CN})_6]_3$
22. The coordination number of Ag in  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  is

- (a) One                      (b) Two                      (c) Three                      (d) Zero
23. The formation of the complex ion  $[\text{Co}(\text{HN}_3)_6]^{3+}$  involves  $\text{sp}^3\text{d}^2$  hybridization of  $\text{Co}^{3+}$ . Hence, the complex ion should possess
- (a) Octahedral geometry                      (b) Tetrahedral geometry  
 (c) Square planar geometry                      (d) Tetragonal geometry
24. The compounds  $[\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3]$ ,  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  exhibit
- (a) Linkage isomerism                      (b) Geometrical isomerism  
 (c) Ionization isomerism                      (d) Hydrate isomerism
25. Which of the following complex compounds exhibits cis – trans isomerism?
- (a)  $[\text{PtCl}_2(\text{NH}_3)_2]$                       (b)  $[\text{PdCl}_2\text{BrI}]$   
 (c)  $[\text{Pt}(\text{NH}_3)(\text{py})(\text{Cl})(\text{Br})]$                       (d) All of these



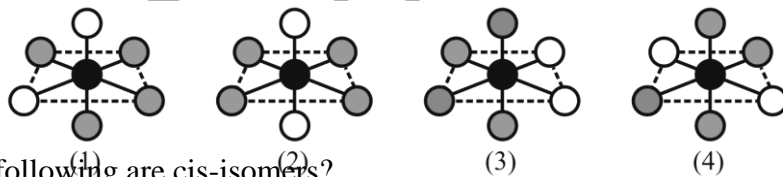
**EXERCISE – II**

- Which of the following species has the electron configuration  $[\text{Ar}] 3d^4$ ?  
 (a) Ti (b)  $\text{V}^{2+}$  (c)  $\text{Cr}^{2+}$  (d)  $\text{Fe}^{2+}$ .
- For transition elements, which of the following occurs as the effective nuclear charge increases?  
 (a) Both the atomic radius and density increases  
 (b) Both the atomic radius and density decreases  
 (c) The atomic radius increases and the density decreases  
 (d) The atomic radius decreases and the density increases.
- What is the name of the complex  $[\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)]\text{SO}_4 \cdot 5\text{H}_2\text{O}$  as per IUPAC rules?  
 (a) Aquaethylenediaminenickel (II) sulfate 1-water  
 (b) Tetraaquaethylenediaminenicke (II) sulfate 5-water  
 (c) Tetraaquabis (ethylenediamine) nickel(II) sulfate 5-water  
 (d) Tetraaquabis (ethylenediamine)nickel(III) sulfate 5-water.
- How many unpaired electrons are present in the high spin form of the  $[\text{CoF}_6]^{3-}$  complex and which metal orbitals are used in bounding?  
 (a) 0 unpaired electrons and 4s, 4p and 4d orbitals to give  $sp^3d^2$  hybridization  
 (b) 4 unpaired electrons and 4s, 4p and 4d orbitals to give  $sp^3d^2$  hybridization  
 (c) 0 unpaired electrons and 3d, 4s and 4p orbitals to give  $d^2sp^3$  hybridization  
 (d) 4 unpaired electrons and 3d, 4s and 4p orbitals to give  $d^2sp^3$  hybridization
- The complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic and the complex  $[\text{NiCl}_4]^{2-}$  is paramagnetic. What can you conclude about their molecular geometries?  
 (a) Both complexes have square planar geometries  
 (b) Both complexes have tetrahedral geometries  
 (c)  $[\text{NiCl}_4]^{2-}$  has a square planar geometry while  $[\text{Ni}(\text{CN})_4]^{2-}$  has a tetrahedral geometry  
 (d)  $[\text{NiCl}_4]^{2-}$  has a tetrahedral geometry while  $[\text{Ni}(\text{CN})_4]^{2-}$  has a square planar geometry.
- What is the expected order for increasing octahedral ( $\Delta_0$ ) crystal field splitting for the ligands?  
 $\text{I}^-, \text{F}^-, \text{H}_2\text{O}, \text{NH}_3, \text{en}$  and  $\text{CO}$ ?  
 (a)  $\text{I}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{CO}$  (b)  $\text{I}^- < \text{F}^- < \text{NH}_3 < \text{en} < \text{CO} < \text{H}_2\text{O}$   
 (c)  $\text{I}^- < \text{F}^- < \text{H}_2\text{O} < \text{CO} < \text{NH}_3 < \text{en}$  (d)  $\text{CO} < \text{en} < \text{NH}_3 < \text{H}_2\text{O} < \text{F}^- < \text{I}^-$ .
- The hybridization states of the central atom in the complexes  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Co}(\text{NO}_2)_6^{3-}$  are:  
 (a)  $d^2sp^3, sp^3d^2$  and  $dsp^2$  respectively (b)  $d^2sp^3, sp^3d^2$  and  $sp^3d^2$  respectively  
 (c)  $d^2sp^3, sp^3$  and  $d^4s^2$  respectively (d) all  $d^2sp^3$ .

8. Tetrahedral complexes of the types of  $[Ma_4]$  and  $[Ma_3b]$  (where M = metal, a, b = achiral ligands) are not able to show optical isomerism because:
- these molecules/ions possess  $C_n$  axis of symmetry
  - these molecules/ions possess a plane of symmetry and hence are achiral
  - these molecules possess a centre of symmetry
  - these molecules/ions have nonsuperimposable mirror images.
9. Which of the following is an organometallic compound?
- Cyclobutadiene
  - Thiotetraamminecopper (II) sulphate
  - Potassium tetrafluoroxochromate (V)
  - Bis(cyclopentadienyl) iron (II).
10. The magnetic moment of a complex ion is 2.83 BM. The complex ion is:
- $[Cr(H_2O)_6]^{3+}$
  - $[Cu(CN)_4]^{2-}$
  - $[V(H_2O)_6]^{3+}$
  - $[MnCl_4]^{2-}$ .
11. The  $E^0$  values for some transition metals are as follows:  
 $Cr^{2+}|Cr = -0.9\text{ V}$ ,  $Mn^{2+}|Mn = -1.2\text{ V}$ ,  $Fe^{2+}|Fe = -0.4\text{ V}$ ,  
 $Cr^{3+}|Cr^{2+} = -0.4\text{ V}$ ,  $Mn^{3+}|Mn^{2+} = +1.5\text{ V}$  and  $Fe^{3+}|Fe^{2+} = 0.8\text{ V}$   
 The correct statement is:
- $Fe^{3+}$  is more reducible than  $Cr^{3+}$  as well as  $Mn^{3+}$
  - Cr is a better reducing agent than Mn but lesser than Fe
  - $Fe^{3+}$  is more reducible than  $Cr^{3+}$  but less than  $Mn^{3+}$
  - $Fe^{2+}$  is a better oxidising agent than  $Mn^{2+}$  but lesser than  $Cr^{2+}$ .
12. What is the least reducing agent of the following set  $MnCl_2$ ,  $Mn(OH)_3$ ,  $MnO_2$  and  $KMnO_4$ ?
- $MnCl_2$
  - $Mn(OH)_3$
  - $MnO_2$
  - $KMnO_4$ .
13. Of the following, which ligand does not possess the name suggested by IUPAC when it acts as a ligand in complex?
- $H_2O$ , aqua
  - $NH_3$ , ammonia
  - CO, carbonyl
  - $F^-$ , fluoro.
14. Which pair of isomers illustrates the concept of ionisation isomers?
- $[Cr(SCN)(NH_3)_5]^{2+}$  and  $[Cr(NCS)(NH_3)_5]^{2+}$
  - $[CoCl(NH_3)_5]SO_4$  and  $[Co(SO_4)(NH_3)_5]Cl$
  - cis- $[PtCl_2(NH_3)_2]$  and trans- $[PtCl_2(NH_3)_2]$
  - (+)  $-[Co(en)_3]^{3+}$  and (-)  $[Co(en)_3]^{3+}$ .
15. Which of the following complex ion is most likely to be colorless?
- $[Co(H_2O)_6]^{2+}$
  - $[Mn(CN)_6]^{3-}$
  - $[CrCl_3(H_2O)_3]$
  - $[Ag(NH_3)_2]^+$ .
16. Which of the following complex has five unpaired electrons?
- $[Mn(H_2O)_6]^{2+}$
  - $[Mn(CN)_6]^{3-}$
  - $[CrCl_3(H_2O)_3]$
  - $[Ag(NH_3)_2]^+$ .
17. Which ion would you expect to have the largest splitting of d-orbitals?

- (a)  $[\text{Fe}(\text{CN})_6]^{4-}$       (b)  $[\text{Fe}(\text{CN})_6]^{3-}$       (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$       (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .
18. Which of the following co-ordination compound is incapable of showing geometrical isomerism?
- (a)  $[\text{PtCl}_2(\text{NH}_3)_2]$       (b)  $[\text{CoCl}_2(\text{NH}_3)_4]^+$   
(c)  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$       (d)  $[\text{Co}(\text{en})]^{3+}$ .
19. A six co-ordinate complex of formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  has green colour. A 0.1 M solution of the complex when treated with excess of  $\text{AgNO}_3$  gave 28.7 g of white precipitate. The formula of the complex would be:
- (a)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$       (b)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$   
(c)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$       (d)  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]3\text{H}_2\text{O}$ .
20. Which of the following statement is incorrect?
- (a) Most of the four-coordinated complexes of  $\text{Ni}^{2+}$  ions are square planar rather than tetrahedral  
(b) The  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion is more paramagnetic than the  $[\text{Fe}(\text{CN})_6]^{3-}$   
(c) Square planar complexes are more stable than octahedral complexes  
(d) The  $[\text{Fe}(\text{CN})_6]^{4-}$  ion is paramagnetic but  $[\text{Fe}(\text{CN})_6]^{3-}$  is diamagnetic.
21. Which of the following is a high-spin (spin-free) complex?
- (a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (b)  $[\text{Fe}(\text{CN})_6]^{4-}$       (c)  $[\text{CoF}_6]^{3-}$       (d)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$ .
22. Which of the following ligands are bidentate or tridentate ligands, capable of forming chelate rings?
- (i)  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$       (ii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$   
(iii)  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CO}_2^-$       (iv)  $\text{NH}_2\text{CH}_2\text{CH}_2$   
(a) (i) and (iii)      (b) (ii) and (iv)  
(c) (i), (ii) and (iii)      (d) (i), (ii), (iii) and (iv).

Consider the following isomers of  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+$ . The black sphere represents Co, gray spheres represent  $\text{NH}_3$  and unshaded spheres represent Br.



23. Which of the following are cis-isomers?
- (a) isomers(1) and (2)      (b) isomers(1) and (3)  
(c) isomers(2) and (4)      (d) isomers(3) and (4).
24. Which of the following are trans-isomers?
- (a) isomers(1) and (2)      (b) isomers(1) and (3)  
(c) isomers(2) and (4)      (d) isomers(3) and (4).
25. Which structures are identical?



- (a) None of the structurea are identical  
 (b) Structure (1) = structure (2) and structure (3) = structure (4)  
 (c) Structure (1) = structure (3) and structure (2) = structure (4)  
 (d) Structure (1) = structure (4) and structure (2) = structure (3).

**MORE THAN ONE CHOICE CORRECT**

- What is/are the co-ordination numbers(s) of Au in the complexes formed by Au?  
 (a) 6 (b) 4 (c) 5 (d) 2.
- If co-ordination number of cabolt in its complex is six then oxidation number of Co may be ....or.....  
 (a) +2 (b) +3 (c) +4 (d) +6.
- $K_4[Fe(CN)_6]$  is:  
 (a) Outer orbital octahedral (b) High spin complex  
 (c) Low spin complex (d) Inner orbital octahedral complex.
- The compounds which dissolve in  $NH_3$  and form the soluble colourless complexes are:  
 (a)  $CuSO_4$  (b)  $AgCl$  (c)  $ZnSO_4$  (d)  $AgI$ .
- The oxides which dissolve in alkali and form the soluble complexes are:  
 (a)  $ZnO$  (b)  $As_2O_3$  (c)  $B_2O_3$  (d) None.
- The sulphides which dissolve in yellow ammonium sulphide and give colourless soluble complexes are:  
 (a)  $SnS$  (b)  $As_2S_3$  (c)  $CuS$  (d) None.
- The d-orbitals involved in  $sp^3d^2$  or  $d^2sp^3$  hybridisation of the central metal ion are:  
 (a)  $d_{x^2-y^2}$  (b)  $d_{xy}$  (c)  $d_{yz}$  (d)  $d_{z^2}$
- $[Cu(NH_3)_4]SO_4$  possesses  
 (a)  $dsp^2$  hybridisation (b) tetrahedral geometry  
 (c)  $sp^3$  hybridisation (d) square planar.
- The complex(es) which is /are blue in colour  
 (a)  $Fe_4[Fe(CN)_6]_3$  (b)  $Zn_2[Fe(CN)_6]$  (c)  $Cu_4[Fe(CN)_6]$  (d)  $Fe_3[Fe(CN)_6]_2$ .
- Which of the following are co-ordination osomers of  $[Co(NH_3)_6][Cr(CN)_6]$ ?  
 (a)  $[Cr(NH_3)_6][Co(CN)_6]$  (b)  $[Cr(NH_3)_2(CN)_4][Co(CN)_4(NH_3)_2]$   
 (c)  $[Cr(NH_3)_3(CN)_3][Co(NH_3)_3(CN)_3]$  (d) None.
- Identify the complexes which are expected to be coloured.

- (a)  $\text{Ti}(\text{NO}_3)_4$                       (b)  $[\text{Cu}(\text{CNCH}_3)]^+\text{BF}_4^-$                       (c)  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$                       (d)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .
12. Bidentate ligands are  
 (a)  $\text{C}_2\text{O}_4^{2-}$                       (b) en                      (c) DMG                      (d) Gly.
13. Which of the following can show co-ordination isomerism?  
 (a)  $[\text{Cu}(\text{NH}_3)_4]\text{PtCl}_4$                       (b)  $[\text{Fe}(\text{NH}_3)_6]_2[\text{Pt}(\text{CN})_6]_3$   
 (c)  $[\text{Co}(\text{NH}_3)_6]_2[\text{Cr}(\text{C}_2\text{O}_4)_3]$                       (d)  $[\text{Pt}(\text{en})_3](\text{SO}_4)_2$ .
14. Which is/ are correct statement(s)?  
 (a)  $[\text{Co}(\text{en})_3]\text{Cr}(\text{CN})_6$  will display co-ordination isomerism  
 (b)  $[\text{Mn}(\text{CO})_5(\text{SCN})]$  will display linkage isomerism  
 (c)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$  will display ionisation isomerism.  
 (d) None
15. Which of the following are paramagnetic?  
 (a)  $[\text{Ni}(\text{CN})_4]^{2+}$                       (b)  $[\text{NiCl}_4]^{2-}$   
 (c)  $[\text{CoF}_6]^{3-}$                       (d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$

### MATCH THE FOLLOWING

**Note:** Each statement in column I has one or more than one match in column II.

1.

#### **Column I (Complex)**

- I.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$   
 II.  $[\text{Ni}(\text{CN})_4]^{2-}$   
 III.  $[\text{Ni}(\text{CO})_4]$   
 IV.  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

#### **Column II (Hybridisation of central atom/ion)**

- A.  $\text{sp}^3$   
 B.  $\text{sp}^3\text{d}^2$   
 C.  $\text{d}^2\text{sp}^3$   
 D.  $\text{dsp}^2$

2.

#### **Column I (ligands)**

- I. (en)  
 II. EDTA  
 III. Trien  
 IV. gly

#### **Column II (Type of ligands)**

- (A) monodentate  
 (B) bidentate  
 (C) tetradentate  
 (D) hexadentate

**Note:** Each statement in column I has only one match in column II.

3.

Column I (complex)	Column II (No. of unpaired electrons)
I. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	(A) 0
II. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	(B) 2
III. $[\text{Fe}(\text{CN})_6]^{4-}$	(C) 3
IV. $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$	(D) 4
	(E) 5

### ASSERTION AND REASON TYPE

**Direction :** Read the following questions and choose :

- (A) If both **Assertion** and **Reason** are true and **Reason** is the correct explanation of the **Assertion**.  
 (B) If both **Assertion** and **Reason** are true but **Reason** is not correct explanation of the **Assertion**.  
 (C) If **Assertion** is true but **Reason** is false.  
 (D) If **Assertion** is false but **Reason** is true.

- Assertion:** Tetrahedral complexes with chiral structure exhibit optical isomerism.  
**Reason:** They lack plane of symmetry.

(a) (A) (b) (B) (c) (C) (d) (D)
- Assertion:** Oxidation state of Fe in  $\text{Fe}(\text{CO})_5$  is zero.  
**Reason:** EAN of Fe in all its complexes is 36

(a) (A) (b) (B) (c) (C) (d) (D)
- Assertion:** Zeise's salt contains  $\text{C}_2\text{H}_4$  molecule as one of the ligands.  
**Reason:** Zeise's salt is an organometallic compound.

(a) (A) (b) (B) (c) (C) (d) (D)
- Assertion:**  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  does not give white precipitate with  $\text{AgNO}_3$  solution.  
**Reason:** Chlorine is not present in the ionisable part of the given complex.

(a) (A) (b) (B) (c) (C) (d) (D)
- Assertion:** Transition metal ion forming octahedral complex undergoes  $\text{sp}^3\text{d}^2$  or  $\text{d}^2\text{sp}^3$  hybridisation.  
**Reason:** Strong field ligands force the unpaired electrons of central metal ion to pair up causing  $\text{d}^2\text{sp}^3$  hybridisation whereas weak field ligands cannot force the pairing and hence the metal ion undergoes  $\text{sp}^3\text{d}^2$  hybridisation.

(a) (A) (b) (B) (c) (C) (d) (D)

### PASSAGE BASED PROBLEMS

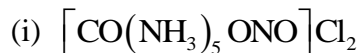
The IUPAC rules of writing names of mononuclear co-ordination compounds are as given below :

- If the compound is ionic, name of the cation is mentioned first followed by the name of the anion.
- For non-ionic compounds the name of the complex is written in one word.
- The sequence of naming co-ordination sphere is to write the names of ligands in the alphabetical order followed by the name of central metal atom/ion and then oxidation number of the metal in Roman numeral.
- For the ligands carrying a negative charge the name of the ligand has a characteristic ending in 'O'.
- For the ligands carrying a positive charge the name of the ligand has a characteristic ending of "ium".
- For organic ligands their names are used as such.
- In case of anionic complexes the suffix 'ate' is attached to the name of central atom/ion.
- Numerical prefixes are used to indicate number of ligands.

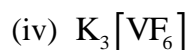
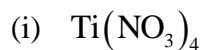
- What is the name of the ligand  $\text{NO}^+$ ?
  - Nitronium
  - Hydrazinium
  - Nitrosonium
  - Nitrosyl.
- The IUPAC name of  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  is:
  - Amine silver chloride
  - Diammine silver chloride
  - Diammine silver(I) chloride
  - Chloroamine silver.
- Iron (III) hexacyanoferrate (II) is:
  - $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
  - $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
  - $\text{Fe}[(\text{CN})_6]$
  - $\text{Fe}[\text{Fe}(\text{CN})_6]$
- The correct structural formula for Aquabromobis(ethylenediamine) chromium (III) chloride is:
  - $[\text{CrBr}(\text{H}_2\text{O})(\text{en})]\text{Cl}$
  - $[\text{CrBr}_2(\text{H}_2\text{O})(\text{en})]\text{Cl}_2$
  - $[\text{CrBr}(\text{H}_2\text{O})(\text{en})_2]\text{Cl}_2$
  - $[\text{CrBr}(\text{H}_2\text{O})(\text{en})_2]\text{Cl}_3$

**EXERCISE - III**
**SUBJECTIVE PROBLEMS**

1. A solution containing 2.665 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of  $\text{AgNO}_3$  to give 2.87 g of  $\text{AgCl}$ . Deduce the structure of compounds.
2. 1 g of the complex  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  was passed through a cation exchanger to produce  $\text{HCl}$ . The acid liberated was diluted to 1 litre. What is normality of this acid solution?
3. A solution containing 0.319 g of complex  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was passed through cation exchanger and the solution given out was neutralized by 28.5 mL of 0.125 M  $\text{NaOH}$ . What is the correct formula of complex?
4. Metal carbonyls having formula  $\text{M}(\text{CO})_x$  where  $x$  is the number of carbonyl units co-ordinated to metal  $\text{M}$  are formed by  $\text{Fe}$ ,  $\text{Cr}$  and  $\text{Ni}$ . If effective atomic number of each metal is 36, what are the formulas of metal carbonyls?
5. How many geometrical isomers with formula  $[\text{M}_{\text{ABCD}}]$  e.g.,  $[\text{Pt}(\text{NH}_3)\text{Py}(\text{NH}_2\text{OH})\text{NO}_2]^+$  are possible?
6. What are facial and, meridional isomers? Explain with examples.
7. Give example of a tetrahedral complex showing optical activity.
8. What do you understand by macrocyclic effect?
9. Explain why  $[\text{Cu}(\text{en})_2]^{2+}$  is less stable than  $[\text{Fe}(\text{EDTA})]^-$ ?
10. The EAN of each  $\text{Mn}$  ( $Z=25$ ) in  $\text{Mn}_2(\text{CO})_{10}$  is 36. What is the structure of this complex?
11. When  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  is treated with conc.  $\text{HCl}$ , two compounds (I) and (II) designated by formula  $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$  are formed. (I) can be converted into (II) by boiling in dil  $\text{HCl}$ . A solution of (I) reacts with oxalic acid to form  $\text{Ni}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2$ . (II) does not react with oxalic acid. Deduce (I) and (II) and decide their geometry.
12. Two compounds have empirical formula corresponding to  $\text{Cr}(\text{NH}_3)_3(\text{NO}_2)_3$ . In aqueous solution, one of these is a non-electrolyte while the other conducts electricity. What is the lowest possible formula weight of the conducting reagent. What is the highest possible formula weight for the non-conducting reagent?
13. The colour of  $\text{Hg}_2\text{Cl}_2$  changes from white to black when treated with  $\text{NH}_3$ . Why?
14. Write the IUPAC name for  $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ .
15. Write the formulas of the following complexes.
  - (i) Pentamminechloro cobalt (III) ion
  - (ii) Lithium tetrahydridoaluminate (III)
16. Write the IUPAC name of this compound  $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$ . Is this compound coloured?
17. Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $\text{Ni}(\text{Cn})_4^{2-}$  and  $\text{Ni}(\text{CO})_4$  and write the hybridization of each.
18. Write IUPAC names of the following compounds:



19. Identify the complexes which are expected to be coloured and explain.



20. (A), (B) and (C) are three complexes of chromium (III) with the empirical formula  $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$ . All the three complexes have water and chloride ion as ligands. Complex (A) does not react with concentrated  $\text{H}_2\text{SO}_4$ , whereas complexes (B) and (C) lose 6.75% and 13.5% of their original weight, respectively, on treatment with concentrated  $\text{H}_2\text{SO}_4$ . Identify (A), (B) and (C)
21. A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms A and B. The form A reacts with  $\text{AgNO}_3$  to give white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of A and B and state the hybridization of chromium in each. Calculate their magnetic moments (spin-only value).
22. Deduce the structure of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species.
23. Write the IUPAC name of given complex along with its hybridization and structure.  $\text{K}_2[\text{Cr}(\text{NO})(\text{NH}_3)(\text{CN})_4]$ ;  $\mu = 1.73\text{BM}$
24.  $\text{AlF}_3$  is not soluble in anhydrous  $\text{HF}$  but soluble in  $\text{KF}$
- (i) Explain this observation.
- (ii) When  $\text{BF}_3$  is added to the above solution,  $\text{AlF}_3$  is precipitated. Write balanced chemical equation.
25. Identify (A) and (B) in the given sequence of reaction. Also write their IUPAC names and calculate only spin magnetic moment of (B).

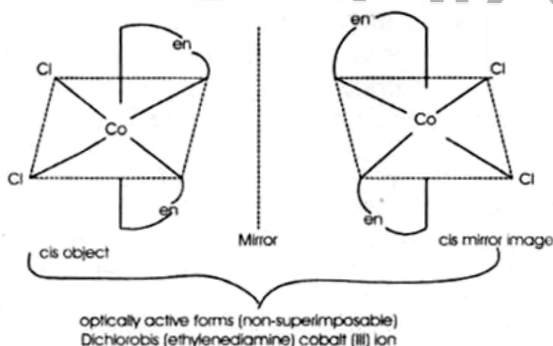
Pinnacle



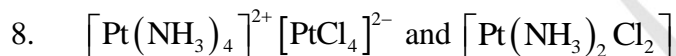
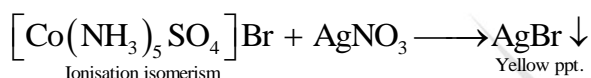
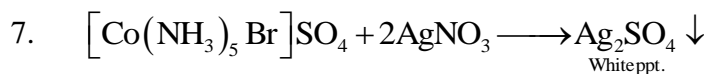
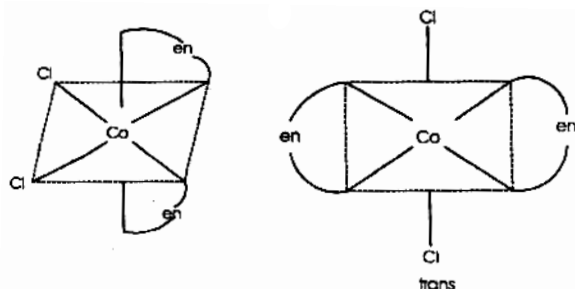
## ANSWERS

### CBSE PROBLEMS

1. Size of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are nearly same but the charge of  $\text{Fe}^{3+}$  is greater than the charge on  $\text{Fe}^{2+}$  hence charge density. If the metal ions have more charge density the complex is more stable.
2. Linkage isomer of  $[\text{Cr}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$  is  $[\text{Cr}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$  The IUPAC name of its is Pentaquaaisothiocyanatochromium (III) ion
3. Co – ordination number is 6.
4.  $\text{dsp}^2$ . Square planar.
5. (i) In  $\text{K}_4[\text{Fe}(\text{CN})_6]$   $\longrightarrow$  no unpaired electrons (Fe in  $\text{d}^2\text{sp}^3$  hybridisation)  
 In  $\text{K}_3[\text{Fe}(\text{CN})_6]$   $\longrightarrow$  one unpaired electron (Fe in  $\text{d}^2\text{sp}^3$  hybridisation)  
 (ii)  $\text{K}_3[\text{Fe}(\text{CN})_6] \xrightleftharpoons{\text{aqueous}} 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$   
 (iii)  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2 \longrightarrow \text{dsp}^2$  Hybridisation  
 $\text{Ni}(\text{CO})_4 \longrightarrow \text{sp}^3$  Hybridisation  
 (iv)  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+} \longrightarrow$  no unpaired electron.  
 $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} \longrightarrow$  one unpaired electron
6. (i) Ionization isomerism  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
 (ii) Linkage isomerism  $[\text{Co}(\text{NH}_3)_4\text{SCN}]^{2+}$   
 $[\text{Co}(\text{NH}_3)_4\text{NCS}]^{2+}$   
 (iii) Optical isomerism



(iv) Geometrical isomerism



$\therefore$  Paramagnetic behaviour.

$$r = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} \text{ B.M.}$$

Number of unpaired electron in Fe in the complex  $\text{Fe}(\text{Co})_5$  are 0.

$\therefore$  Diamagnetic behaviour.

Pinnacle

**EXERCISE - I**

1. (b)	2. (d)	3. (d)	4. (d)	5. (c)
6. (b)	7. (c)	8. (c)	9. (d)	10. (c)
11. (d)	12. (b)	13. (c)	14. (d)	15. (d)
16. (b)	17. (b)	18. (b)	19. (c)	20. (c)
21. (c)	22. (b)	23. (a)	24. (d)	25. (d)

**EXERCISE - II**

1. (c)	2. (d)	3. (b)	4. (b)	5. (d)
6. (a)	7. (d)	8. (b)	9. (d)	10. (c)
11. (c)	12. (d)	13. (b)	14. (b)	15. (d)
16. (a)	17. (b)	18. (d)	19. (b)	20. (d)
21. (c)	22. (a)	23. (b)	24. (c)	25. (c)

**MORE THAN ONE CHOICE CORRECT**

1. (b, d)	2. (a, b)	3. (c, d)	4. (B, C)	5. (a, b, c)
6. (a, b)	7. (a, d)	8. (a, d)	9. (a, d)	10. (a, b)
11. (c, d)	12. (a, b, c, d)	13. (a, b)	14. (a, b, d)	15. (b, c)

**MATCH THE FOLLOWING**

- I-(B); II-(D); III-(A); IV-(D)
- I-(B); II-(D); III-(C); IV-(B)
- I-(D); II-(E); III-(A); IV-(B)

**ASSERTION AND REASON TYPE**

1. (a)	2. (c)	3. (b)	4. (a)	5. (a)
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**PASSAGE BASED PROBLEMS**

1. (c)	2. (c)	3. (a)	4. (c)	
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