Module - 23.1

d - block Elements

Introduction:

The elements that lie in between s-block and P-block are the d-block elements. These elements are called transition elements as they show transitional properties between s and p-block elements. These elements contain partially filled d-orbitals and hence they are called as d-block elements. The general electronic configuration of d-block elements is (n-1) $d^{1-10}ns^{1-2}$.The d-block comprises of 3d, 4d, 5d and 6d series of elements.

First transition series

This is also called as 3d series which corresponds the filling of 3d orbital. It starts from scandium whose atomic number is 21 and includes 10 elements till zinc whose atomic number is 30.

Second transition series

This is also called as 4d series which corresponds the filling of 4d orbital. It starts from yttrium whose atomic number is 39 and includes 10 elements till cadmium whose atomic number is 48.

Third transition series

This is also called as 5d series which corresponds the filling of 5d orbital. The first element of this series is lanthanum whose atomic number is 57 and includes 9 elements from hafnium whose atomic number is 72 to mercury whose atomic number is 80

Fourth transition series

This is also called as 6d series which corresponds the filling of 6d orbitals.

General trends in properties of first row of transition metals:

Electronic configuration of the elements of first transition series:

Element	Atomic number	Electronic configuration:
Scandium	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
Titanium	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$
Vanadium	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$
Chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$
Manganese	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$
Iron	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
Cobalt	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
Nickel	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$
Copper	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
Zinc	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

Chromium and copper exhibit anomalous electronic configurations due to the following reasons.

Electronic configuration of chromium (Z = 24) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

Electronic configuration of copper (Z = 29) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

In case of half filled sub shells there is a maximum number of unpaired electrons in different orbitals. In such cases, the inter electronic repulsions are minimum and there is a maximum possibility of exchange or delocalization of electrons, which further decreases the energy and increases the stability.

Metallic character:

Most of the transition elements of the first row form metallic bonds due to the presence of incomplete outermost energy level. So, all the transition elements exhibit metallic characters. The strength of the metallic bond depends upon the number of unpaired d-electrons. As the number increases the strength also increases. Due to the absence of unpaired electrons 'Zn' is not a hard metal.

Ionization energy:

The ionization energies of first row elements gradually increases with increase in atomic number. The ionization energy of Zn is very high than all the other metals which is due to its fully filled d-orbital. The third ionization energy of Mn is very high than the others.

Ionic radii:

In the first row transition elements the ionic radii decrease with increase in atomic number. The value of ionic radii also depends on the oxidation state of metals. As the oxidation state increases the ionic radius decreases and as the oxidation state decreases the ionic radius increases.

Oxidation states:

d – block elements shows more than one oxidation states due to availability both ns and (n – 1)d electrons in the compound formation. The lowest oxidation state is exhibited by using the s – electrons in the outermost orbit and the maximum oxidation state is given by the sum of the outer s – electrons and unpaired d – electrons.

The maximum oxidation state in first series is +7 exhibited by manganese. In second and third transition series, the maximum oxidation sate is +8 in Ruthenium and osmium shown in their oxides.

In a given series of d – block elements the oxidation state increases upto nearly middle element and then decreases. The most stable oxidation state in all the elements of 3d – series is +2.

Variable oxidation states of 3d series

I series	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
3d	**$4s^2 3d^1$**	**$4s^2 3d^2$**	**$4s^2 3d^3$**	**$4s^1 3d^5$**	**$4s^2 3d^5$**	**$4s^2 3d^6$**	**$4s^2 3d^7$**	**$4s^2 3d^8$**	**$4s^1 3d^{10}$**	**$4s^2 3d^{10}$**
									I	
	II	II	II	II	II	II	II	II	II	II
	III	III	III	III		III	III	III		
		IV			IV					
				VI	VI					
					VII					

Colour:

Transition metal ions are generally coloured due to the presence of unpaired d – electrons. Which absorb light from the visible region and thus move to higher energy level. Therefore, one of the colours of the visible spectrum is absorbed and the transition metal ion gets the complementary colour. The transition metal ion with completely filled d – orbitals are colourless. For example Zn^{+2}, Cd^{+2} and Hg^{+2} are colourless. The colour of transition metal ions is due to excitation of d – orbitals of lower energy to the d – orbitals of higher energy. Since they are completely filled d – orbitals in Zn^{+2} ($3d^{10}$), Cd^{+2} ($4d^{10}$) and Hg^{+2} ($5d^{10}$)

ions, these are colourless. The energy required to excite a d – electron of transition metal ion is small. Hydrated copper (+2) ion i.e. $Cu(H_2O)_6^{+2}$ absorbs red colour from the visible light appears blue, the complementary colour of red. Thus $Cu(H_2O)_6^{+2}$ appear blue.

Example:

Ion	Colour
Cu^{+2}	Blue
Fe^{+2}	Pale green
Fe^{+3}	Yellow
Cr^{+3}	Green
Mn^{+2}	Pink
Zn^{+2}	Colourless

Cu^{+2} ions are coloured and are paramagnetic:

Electronic configuration of Cu^{+2} ion = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

Cu^{+2} ion contains one unpaired d – electron. So it is coloured and paramagnetic.

Magnetic properties:

Those substances which are weakly attracted by the magnetic field are called paramagnetic substances. This magnetic character arises due to the presence of unpaired electrons. Most of the transition elements and their ions contain unpaired d – electrons. So they are paramagnetic substances.

Example:

Ti^{+3}, Cu^{+2}, Sc^{+2} they have unpaired electrons

Those substances which are repelled by the magnetic field are called diamagnetic substances. This magnetic character arises due to the presence of paired electrons. Transition metal ions which contain paired electrons show diamagnetic substances.

Example:

Ti^{+4}, Cu^{+}, Zn^{+2} have all the electrons completely paired.

Those substances which are strongly attracted by the magnetic field are ferromagnetic substances. These also contain unpaired electrons. Iron, cobalt and nickel are ferromagnetic substances.

Catalytic property:

Many d – block elements and their compounds act as catalysts in chemical reactions. This property may be either due to their variable valency which enables them to form unstable intermediate compounds or due to providing suitable reaction surfaces.

Some catalysts used in the industries.

Process	Catalyst
Hydrogenation of oils	Ni
Synthesis of ammonia by Haber's process	Fe
Synthesis of nitric acid by Ostwald's process	Pt
Synthesis of sulphuric acid by contact process	V_2O_5

Complex formation:

d – block metal ions having a great tendency to form complexes due to their small sizes, high charges and due to the presence of vacant d – orbitals.

The bonds involved in the formation of complexes are co – ordinate bonds. So complexes are called co – ordinate compounds. In complexes the groups which donate the electron pairs are called ligands and the metal ions which accept the electron pairs are called central metal ions. The central metal ions and the ligands are represented by a square bracket and other ions are represented outside the bracket. The square bracket part is a complex ion and it involves as a single unit in chemical reactions.

Example:

1. $K_3[Fe(CN)_6]$ potassium ferricyanide.
2. $[Cr(NH_3)_6]Cl_3$ hexamminechromium (III) chloride.

In a series the stability of complexes increases with an increase in the atomic number of the elements and in a particular oxidation state with decrease in the size of its atoms. When the d – block metal atom exhibits more than one oxidation state, the highest valent ion forms more stable complex.

Redox potential of d – block elements:

Standard reduction potentials of 3d series obtained by the reduction of M^{+2} ions to M are given below.

$$M^{+2} + 2e^- \rightarrow M$$

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Reduction potential (Volts)	– 2.1	– 1.6	– 1.2	– 0.91	– 1.18	– 0.44	– 0.28	– 0.25	+ 0.34	+ 0.76

When we observe the values in the table, except copper the remaining elements have higher negative values than standard hydrogen potential (zero).Hence these elements are easily oxidized to give ions.

$$M \rightarrow M^{+2} + 2e^-.$$

Review questions:

Example set:

1. Transition elements are _______ block elements.
   a. s
   b. p

   c. d
   d. f

Solution: c)

2. The first transition element in the 3d series is:
   a. scandium
   b. chromium
   c. nickel
   d. copper

Solution: a)

3. The property, which is not characteristic of transition metals, is:
   a. Variable oxidation states
   b. Tendency to form complexes
   c. Formation of colored compounds
   d. Electro negative behaviour

Solution: d)

4. Which of the following elements exhibits largest number of oxidation states?
   a. Zn
   b. V
   c. Mn
   d. Ni

Solution: c)

5. Transition metals show paramagnetism due to
   a. characteristic configuration
   b. high lattice energy
   c. variable oxidation states
   d. unpaired electrons

Solution: d)

6. How do the following properties very in the first transition series?

a. Atomic size
b. Stability of various oxidation states
c. Ionization energy

Solution:

7. What are d – block elements?

Solution:

The elements in which differentiating electron is accommodated in the d – subshell are called d – block elements.

8. Name three characteristic properties of d – block elements.

Solution:

a. Formation of coloured compounds
b. Formation of complex compounds
c. Paramagnetic in nature

9. Name two elements of 3d – series which show anomalous electronic configuration.

Solution:

Chromium, copper

Problem set:

1. The general electronic configuration of transition elements is
   a. $(n-1)\ d^{1-5}$
   b. $(n-1)\ d^{1-10}\ ns^1$
   c. $(n-1)\ d^{1-10}\ ns^{1 \text{ or } 2}$
   d. None

Solution: c)

2. Chromium has the electronic configuration
   a. $3s^2\ 3p^6\ 3d^4\ 4s^2$

b. $3s^2\ 3p^6\ 3d^5\ 4s^1$
c. $3s^2\ 3p^6\ 3d^6$
d. None of these

Solution: b)

3. Which of the following has the maximum number of unpaired d – electrons?
   a. Zn
   b. Fe^{2+}
   c. Ni^{3+}
   d. Cu^+

Solution: b)

4. Why $CuSO_4$ is blue while $ZnSO_4$ is white?

Solution:

Cu^{2+} in $CuSO_4$ has [Ar] $3d^9\ 4s^0$ configuration. It can undergo d – d transition. It absorbs red light of the visible region and hence $CuSO_4$ appears blue. Blue is complimentary colour of red. In $ZnSO_4$, Zn^{2+} has $3d^{10}\ 4s^0$ configuration. It cannot undergo d – d transition, hence, they are soft in nature.

5. Transition elements form alloys easily. What is the reason?

Solution:

Nearly same atomic radii.

6. Which ions of first transition series show highest paramagnetism?

Solution:

Fe^{3+} and Mn^{2+}.

Exercise questions:

1. What is the magnetic moment of $K_3[FeF_6]$?
   a. 5.91 B.M
   b. 4.89 B.M

   c. 3.87 B.M
   d. 6.92 B.M
2. Why Fe^{+3} compounds are more stable?
3. Why transition metals and their compounds act as catalysts.
4. Why Hg^{2+} and Hg_2^{2+} salts are colourless.
5. Cu^{2+} are paramagnetic while Cu^+ salts are diamagnetic in nature.
6. Predict the spin only magnetic moment for
   a. Fe^{2+}
   b. Mn^{2+}
   c. Cr^{6+}
   d. Cu^+

Solutions:

1. a)
2. $3d^5$ configuration, i.e., all the five orbitals are singly occupied.
3. Because of the availability of d – orbitals they can easily form intermediate products which are activated. The sizes of transition metal atoms and ions are also favourable for transitory complex formation with the reactants.
4. Hg^{2+} and Hg_2^{2+} salts have $5d^{10}$ configuration, i.e. there is no d – d transition, hence colourless.
5. Cu^{+2} configuration is $3d^9$ (one orbital is singly occupied) – paramagnetic; Cu^+ configuration is $3d^{10}$ (all orbitals are doubly occupied) – diamagnetic.
6.

Ion	**Electronic configuration**	**No. of unpaired electrons**	**Magnetic moment**
a. Fe^{2+}	$[Ar]3d^6\ 4s^0$	4	4.90 BM
b. Mn^{2+}	$[Ar]3d^5\ 4s^0$	5	5.96 BM
c. Cr^{6+}	$[Ar]3d^0\ 4s^0$	0	0 BM
d. Cu^+	$[Ar]3d^{10}\ 4s^0$	0	0 BM

Co-ordination Compounds

Module 24.1: Introduction, ligands, co-ordination number, IUPAC nomenclature

Double salts or lattice compounds:

The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called double salts or lattice compounds. Their solutions have the same properties as the mixture of individual components. For example, when Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, is dissolved in water, it exhibits the properties of $FeSO_4$ and $(NH_4)_2SO_4$, *i.e.,* they produce Fe^{2+}, NH_4^+, and SO_4^{2-} ions in the solution. Thus, each ion has its identity in the double salt.

$$FeSO_4.\ (NH_4)_2SO_4.6H_2O \longrightarrow Fe^{2+}_{(aq)} + 2NH^{+}_{4(aq)} + 2SO^{2-}_{4(aq)} + 6H_2O$$

Carnallite: $KCl.MgCl_2.6H_2O$;

Potash alum: $K_2SO_4.\ Al_2(SO_4)_3.24H_2O$ etc. are the examples of double salts.

Co-ordination or complex compounds:

The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions, are called **co-ordination compounds or complex compounds**. The properties of their solutions are different from those of their constituents. When crystals of $CuSO_4.4NH_3$ are dissolved in water there is hardly any evidence for the presence of Cu^{2+} ions or ammonia molecules. A new ion $[Cu(NH_3)_4]^{2+}$ is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of $Fe(CN)_2.4KCN$ does not give tests of Fe^{2+} and CN^- ions but gives the test for a new ion $[Fe(CN)_6]^{4-}$. The ions $[Cu(NH_3)_4]^{2+}$ and $[Fe(CN)_6]^{4-}$ are called **complex ions**.

$$CuSO_4 . 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

$$Fe(CN)_2 . 4KCN \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Thus, a co-ordination or complex compound may be defined as a molecular compound that results from the combination of two or more simple, stable, molecular compounds and retains its identity in the solid as well as in dissolved state.

Definition of the terms used in coordinate compounds:

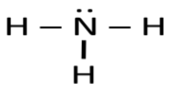
1. Central ion or centre of coordination:

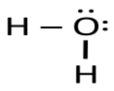
The cation to which one or more neutral molecules or anions are attached is called the central metal ion of coordination. Since, the central ion acts as an acceptor and thus, has to accommodate electron pairs donated by the donor atom of ligand, it must have empty orbitals. This explains why the transition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

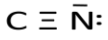
Thus, in the complexes $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$, Ni^{2+} and Fe^{3+} ions respectively are the central metal ions.

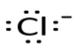
2. Ligands:

The neutral molecules; anions or cations which are directly linked with central metal atom or ion in a complex ion are called ligands. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkages. Free ligands have at least one electron pair that is not engaged in bonding. Some examples are:









The ligands act as a donor as it donates one or more electron pairs to the central metal atom or ion which acts as an acceptor. The ligands are thus Lewis bases and central metal ions are Lewis acids and their union involves following two things.

a. Ligands should have lone pairs of electros which can be donated to the central metal ion or atom.

b. The central atom or ion should have vacant orbital's of nearly equivalent energy to accommodate the electrons donated by ligands. This condition is easily fulfilled by atoms or ions of transition metals.

Types of ligands:

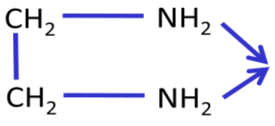
Ligands can be of following types depending on the number of donor atoms present in them.

i. Mono or unidentate ligands:

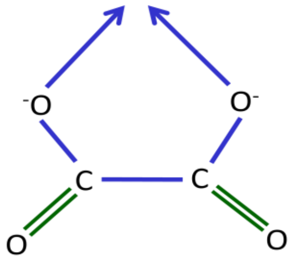
They have one donor atom, *i.e.,* they supply only one electron pair to central metal atom or ion. F^-, Cl^-, Br^-, H_2O, NH_3, CN^-,NO_2^-, OH^-, CO etc. are examples of monodentate ligands.

ii. Bidentate ligands:

Ligands, which have two donor atoms and have the ability to link with the central metal ion at two positions, are called bidentate ligands. Some examples are:



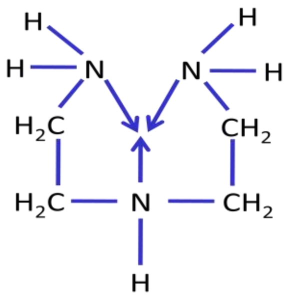
Ethylenediamine (en)



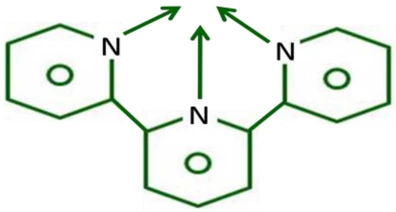
Oxalate (ox)

iii. Tridentate ligands:

The ligands having three donor atoms are called tridentate ligands. Examples are:



Diethylenetriamine (dien)

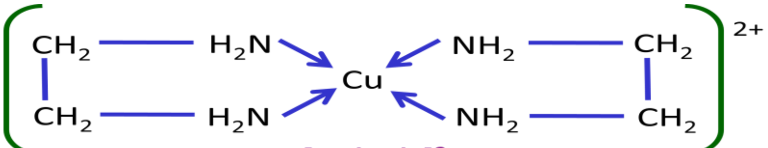


2, 2′, 2 – Tripyridine (terpy)

Similarly polydentate ligands are ligands having more than two donor atoms.

iv. Chelating ligands:

A bidentate or a polydentate ligands is known as a chelating ligands if, on coordination, it results in the formation of a closed or cyclic ring structure. The complexes, thus formed are called chelates. The word chelate has been derived from the *Greek word* chelate *meaning claw*. The complex formed by Cu^{2+} ion with ethylenediamine is an example of a chelate.



$[Cu(en)_2]^{2+}$

The following are the characteristics of chelates:

a. Chelating ligands form more stable complexes than monodentate ligands. This is called chelating effect, all types of polydentate ligands can act as chelating ligands.

b. The chelates containing 5 or 6 membered rings including metal atom are comparatively more stable. Chelating ligands which do not contain unsaturated groups (double bonds), in general, form five membered stable complexes while chelating ligands having unsaturated groups (double bonds) form six membered stable complexes.

c. Ligands with larger groups form more unstable rings than with smaller groups due to steric hindrance.

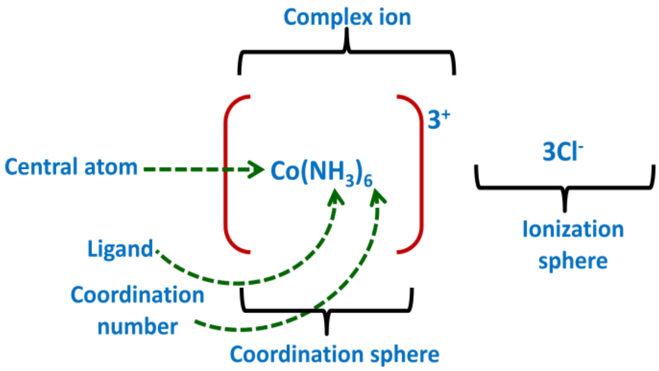
3. Co-ordination number:

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

4. Co-ordination 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, as 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.

Thus, the various terms used in a coordination compound can be illustrated as below:



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 0 respectively.

Complex ion:

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:

S.No	Complex compound (ion)	Charge on complex ion
(i)	$[Cu(NH_3)_4]^{2+}$	(+2) of Cu + (0) of NH_3 ∴ Net charge = +2
(ii)	$[Fe(CN)_6]^{4-}$	(+2) of Fe + (-6) of 6 CN ∴ Net charge = -4
(iii)	$(Co(NH_3)_5Cl]^{2+}$	(+3) of Co + (0) of NH_3 + (-1) of Cl ∴ Net charge = +2
(iv)	$[Co(NH_3)_3Cl_3]$	(+3) of Co + (0) of NH_3 + (-3) of Cl ∴ Net charge = 0

Nomenclature of Co-ordination compounds (IUPAC system):

The following rules are adopted for naming all types of coordination compounds:

1. If a coordination compound is ionic, the name of cation is given whether or not it is the complex ion followed by the name of the anion just like naming a simple salt. The names of cation and anion are separated by a space.
2. Within a complex ion, the ligands are named first followed by the metal ion

Naming of the ligands:

a. Anionic ligands ending with – ide are named by replacing – ide with suffix – o or replacing – e by – o.

Anion	Symbol	Name as ligand
Chloride	Cl^-	Chlorido
Bromide	Br^-	Bromido
Cyanide	CN-	Cyano
Oxide	O^{2-}	Oxo
Peroxide	O_2^{2-}	Peroxo
Hydroxide	OH^-	Hydroxo
Sulphide	S^{2-}	Sulphido
Amide	NH_2^-	Amido

Nitride	N^{3-}	Nitrido
Phosphide	P^{3-}	Phosphido

Ligand whose names end in – ite or – ate become – ito or – ato, *i.e.,* by replacing the ending – e with – o.

Anion	**symbol**	**Name of the ligand**
Carbonate	CO_3^{2-}	Carbonato
Oxalate	$C_2O_4^{2-}$	Oxalato
Sulphate	SO_4^{2-}	Sulphato
Nitrate	NO_3^-	Nitrato
Sulphite	SO_3^{2-}	Sulphito
Acetate	CH_3COO^-	Acetato
Nitrite	ONO^- NO_2^-	(bonded through oxygen) Nitrito – O (bonded through nitrogen) Nitrito – N or Nitro

b. Neutral ligands are called with the same names as their neutral molecules or with their special names, e.g.,

H_2O Aquo (Aqua) NH_3 Ammine
CO Carbonyl;   NO Nitrosyl;
CS Thiocarbonyl;   NS Thionitrosyl

c. Positively charged ligands have suffix – ium.

NH_2 - NH_3^+ Hydrazinium; NO_2^+ Nitronium

d. If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek prefixes such as di, tri, tetra, penta, hexa etc.

e. When more than one ligand is present, they are named in alphabetical order without separation by hyphen.

3. The oxidation state of the central metal is shown by Roman numerical in bracket immediately following its name.

4. Complex positive ions and neutral coordination compounds have no special ending.

5. Complex negative ions always end in the suffix – ate. In most of the cases, the suffix – ate is fixed to names of the metals.

   Name of components present in coordination sphere are written continuously without a gap, *e.g.,*

   $K_3[Fe(CN)_5NO]$ potassium $\underbrace{\text{pentacyanonitrosylferrate (II)}}$

   Some names of the metals in the anionic complexes are given below.

Element	**Metal as named in ionic complex**
Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

6. The name of the neutral coordination compound is given in one word only as the name of $Ni(CO)_4$ is tetracarbonylnickel (0). The following examples will make the rules more clear.

Coordination compounds containing complex cations:

$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum(IV) chloride
$[CO(NH_3)_4(H_2O)Cl]Cl$	Tetraammineaquochloridocobalt(III) chloride
$[Fe(H_2O)_4(C_2O_4)]_2SO_4$	Tetraaquooxalatoiron(III) sulphate
$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride

Coordination compounds containing complex anions:

$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
$Na[Ag(CN)_2]$	Sodium dicyanoargentate(I)
$Na_3[Co(NO_2)_6]$	Sodium hexanitrocobaltate(III)

$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosylferrate(II)

Coordination compounds containing complex cations and anions:

$[Cr(NH_3)_6][Co(CN)_6]$	Hexaamminechromium (III), hexacyanocobaltate (III)
$[Pt(NH_3)_4][CuCl_4]$	Tetraammineplatinum (II), tetrachloroidocuprate (II)

Non-ionic coordination compounds:

$Fe(CO)_5$	Pentacarbonyliron (0)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt (III)

Writing the formula of a coordination compound from its IUPAC name:

Following rules are followed in writing the formula of a coordination compound:

1. Formula of the cation whether simple or complex is written first followed by that of an anion
2. The coordination sphere is written in square brackets
3. The following sequence of symbols within the coordination sphere is followed:
    - i. Metal atom
    - ii. Anionic ligands
    - iii. Neutral ligands
    - iv. Cationic ligands
    - a. If there are number of ligands of same type (anionic, neutral or cationic), they are listed alphabetically according to first alphabet of their names. For example if NO_3^-, SO_4^-, OH^-, Br^- etc., are present, they are written as Br^-, NO_3^-, OH^- and SO_4^{2-}.

      When two ligands have same donor atom, the ligands with fewer such atoms is cited first followed by the ligand having more atoms. For example, SO_4^{2-}, precedes $S_2O_3^{2-}$.

      When the numbers of defining atoms are same, subsequent symbol decides the sequence. For example, NH_2^- precedes NO_2 because H comes before O.
4. Polyatomic ligands are enclosed in parentheses but all ligands are formulated without any space in between

5. The number of cations or anions to be written in the formula is calculated on the basis of total negative charge on the anion, as the complex as a whole is electrically neutral.
6. Sometimes abbreviations for certain ligands are used in parentheses instead of their structural formulae. For example,

(en)	ethylenediamine (ethane – 1, 2 – diamine)
(dien)	diethylenetriamine
(trien)	triethylenetetraamine
(edta or EDTA)	ethane – 1, 2 – diamine tetraacetato
(dmg)	dimethylglyoximato

Few examples are given here to explain the above rules.

Example 1:

Trichlorotriamminecobalt(III)

The metal complex is a neutral substance. The name of the central metal is written first. Its oxidation state, then the ligands and their numbers are written.

Therefore the formula is written as $[Co^{III}(NH_3)_3(Cl_3)]$

Example 2:

Tetramminecopper(II) hydroxide. The complex is a cationic complex. The formula of the cation is written in the same order as in neutral complex. *i.e.* the central metal, its oxidation state; ligands and their numbers.

Therefore $[Cu^{II}(NH_3)_4]^{+2}$

The name of the anion only is given and not its number. Therefore hydroxide. The number is inferred from the oxidation state of the complex species.

Therefore complete formula is $[Cu(NH_3)_4](OH)^2$

Example 3:

Potassium tetrachloropalatinate(II)

The complex is an anionic complex

The cation is potassium. From the oxidation state of the complex anion, the number of cations is 2.

The anion, obtained by applying the above procedure, is $[Pt^{II}(Cl_4)]^{-2}$

Therefore complete formula is $K_2[PtCl_4]$

Assignment Questions:

1. Mention which of the following substances is a double salt and which is a complex compound?
   a. Potash alum
   b. Carnallite
   c. Mohr's salt
   d. Potassium ferricyanide
2. Define the terms
   a. Ligand
   b. Chelate
3. Give the coordination number of the metal in the following compounds
   a. $[Ag(NH_3)_2]Cl$
   b. $[Cu(H_2O)_4]SO_4$
   c. $K_4[Fe(CN)_6]$
   d. $[Pt(en)_3]Cl_4$
4. Write the names of the following complexes
   a. $Ag[NH_3]_2Cl$
   b. $[Co(en)_2Cl_2]^+$
   c. $K_4[Fe(CN)_6]$

Example Set:

1. Oxidation state of Fe in $K_4[Fe(CN)_6]$ is
   a. +2
   b. +3
   c. -2

   d. -3

Solution: a)

2. All ligands are
   a. Lewis acids
   b. Lewis bases
   c. Neutral
   d. Both a) and b)

Solution: b)

3. The number of ions formed in aqueous solution by the compound $[Co(NH_3)_4Cl_2]Cl$ is
   a. 2
   b. 3
   c. 4
   d. 7

Solution: a)

4. $[Co(NH_3)_6]Cl_3$ is called
   a. Hexamminecobalt(III) chloride
   b. Aminocobalt chloride(III)
   c. Cobalt chloride hexammine
   d. Hexammine tricobalt chloride

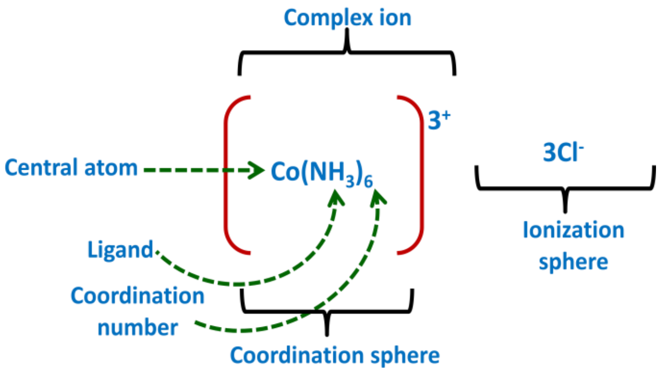
Solution: a)

5. Explain the terms co-ordination sphere and oxidation number of a central metal atom.

Solution:

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, as 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.

Thus, the various terms used in a coordination compound can be illustrated as below:



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 is similar to the calculation of oxidation states in the compounds as we know it from earlier studies.

6. State the principles involved in the nomenclature of co-ordination compounds

Solution:

Nomenclature of co-ordination compounds (IUPAC system):

The following rules are adopted these days for naming all types of coordination compounds:

1. If a coordination compound is ionic, the name of cation is given whether or not it is the complex ion followed by the name of the anion just like naming a simple salt. The names of cation and anion are separated by a space.
2. Within a complex ion, the ligands are named first followed by the metal ion

a. Neutral ligands are called with the same names as their neutral molecules or with their special names, e.g.,

   H_2O Aquo (Aqua) NH_3 Ammine
   CO Carbonyl;   NO Nitrosyl;
   CS Thiocarbonyl;   NS Thionitrosyl

b. Positively charged ligands have suffix – ium.

   NH_2 - NH_3^+ Hydrazinium; NO_2^+ Nitronium

c. If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek prefixes such as di, tri, tetra, penta, hexa etc.

d. When more than one ligand is present, they are named in alphabetical order without separation by hyphen.

3. The oxidation state of the central metal is shown by Roman numerical in bracket immediately following its name.
4. Complex positive ions and neutral coordination compounds have no special ending.
5. Complex negative ions always end in the suffix – ate. In most of the cases, the suffix – ate is fixed to names of the metals.

7. Write a short note on complex compounds.

Solution:

Complex compounds:

The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions, are called coordination compounds or complex compounds. The properties of their solutions are different from those of their constituents. When crystals of $CuSO_4.4NH_3$ are dissolved in water there is hardly any evidence for the presence of Cu^{2+} ions or ammonia molecules. A new ion, $[Cu(NH_3)_4]^{2+}$, is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of $Fe(CN)_2.4KCN$ does not give tests of Fe^{2+} and CN^- ions but gives the test for a new ion, $Fe(CN)_6]^{4-}$. The ions $[Cu(NH_3)_4]^{2+}$ and $[Fe(CN)_6]^{4-}$ are called complex ions.

$$CuSO_4 \cdot 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

$$Fe(CN)_2 \cdot 4KCN \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Thus, a coordination or complex compound may be defined as a molecular compound that results from the combination of two or more simple, stable, molecular compounds and retains its identity in the solid as well as in dissolved state.

Problem Set:

1. The IUPAC name of $[Cr(NH_3)_4Cl_2]NO_3$ is
   a. Tetra amino dichloro chromium nitrate
   b. Tetra amino dichloro chromium (II) nitrate
   c. Tetra amminedichlorochromium(III) nitrate
   d. Tetra amino dichloro chromium (II) nitrate

Solution: c)

2. EDTA is a ___ ligand
   a. Monodentate
   b. Hexadentate
   c. Bidentate
   d. Tridentate

Solution: b)

3. $K_3[Al(C_2O_4)_3]$ is called
   a. Potassium alumino oxalate
   b. Potassium alumino (III) oxalate
   c. Potassium trisoxalatoaluminate(III)
   d. Potassium trioxalato aluminate (III)

Solution: c)

4. The IUPAC name for $[Co(NH_3)_6][Cr(CN)_6]$ is

a. Hexamminecobalt(III) hexacyano chromate(III)
b. Hexacyano chromium, cobalt hexa ammine (VI)
c. Hexa ammine cobalt (III) hexa cyano chromium (VI)
d. Hexa cyano chromium (III) hexa amine cobalt (III)

Solution: a)

5. Distinguish between double salt and complex compound.

Solution:

Double salt	Complex compound
1. It is formed by combination of two salts. They lose their identity when dissolved in water **Ex:** $KCl + MgCl_2 + 6H_2O \longrightarrow KCl.\ MgCl_2.\ 6H_2O$ Carnalite is dissolved in water to give Mg^{+2}, K^+ and Cl^- which answer their tests Other examples are	1. It is formed by combination of two salts which have lost their identity after union **Ex:** $4KCN + Fe(CN)_2 \longrightarrow 4K[Fe(CN)_6]$ Potassium ferrocyanide It is dissolved in water to give K^+ and $[Fe(CN)_6]^{4-}$ ions. Here Fe^{+2} and CN^- ions Other examples are
2. Potash alum	2. $[Co(NH_3)_6]Cl_3$
3. Cryolite	3. $[Ni(CN)_4]^{2-}$

6. What is the coordination number of the central metal ions in the following complexes

a. $[Cu(NH_3)_4]^{+2}$
b. $[Fe(C_2O_4)_3]^{3-}$
c. $[Pt(en)_2]Cl_2$
d. $[Mo(CN)_8]^{4-}$
e. $[Fe(EDTA)]^-$
f. $[Pd(H_2O)_2(ONO)_2I_2]$

Solution:

a. NH_3 is a monodentate ligand

No. of points of attachment with Cu^{2+} = 4 × 1 = 4
C.N of Cu^{+2} = 4

b. $C_2O_4^{2-}$ is a bidentate ligand
No. of points of attachment Fe^{+3} = 3 × 2 = 6
C.N of Fe^{+3} = 6

c. "en" is a bidentate ligand and Cl^- is a monodentate ligand
No. of points of attachment with Pt^{+2} = 2 × 2 + 2 × 1 = 6
C.N of Pt^{+2} = 6

d. CN^- is a monodentate liquid
No. of points of attachment with Mo^{4+} = 8 × 1 = 8
C.N of Mo^{4+} = 8

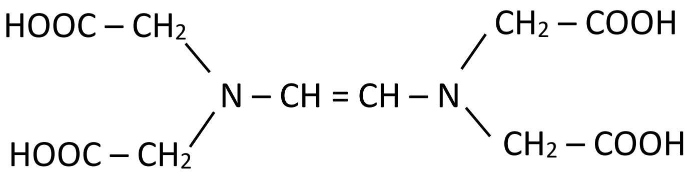
e. EDTA is a hexadentate liquid
No. of points of attachment with Fe^{+3} = 6 × 1 = 6
C.N of Fe^{+3} = 6

f. No. of points of attachment with Pd^{+4} = 2 × 1 + 2 × 1 + 2 × 1 = 6
C.N of Pd^{+4} = 6

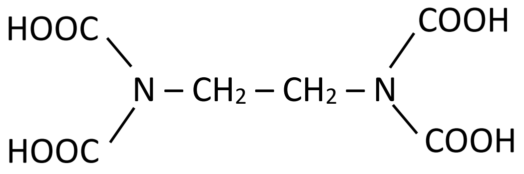
Exercise Questions:

1. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is
   a. Tetrachloronickel(II) tetramminenickel (II)
   b. Tetramminenickel (II) tetrachloronickel (II)
   c. Tetramminenickel(II) tetrachloronickelate(II)
   d. Ttrachloronickel (II) tetrachloronickelate (0)

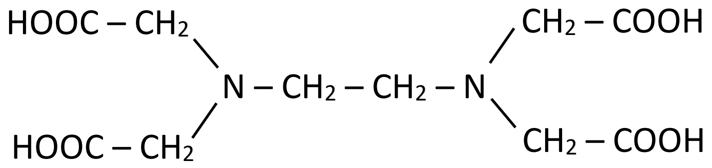
2. The correct structure of ethylenediaminetetraacetic acid (EDTA) is
   a.



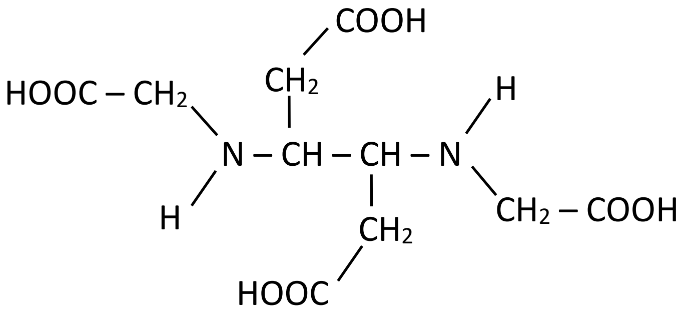
b.



c.



d.



3. **3.** What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.
4. **4.** Specify the oxidation number of the metals in the following coordination entities.
   a. $[Co(H_2O)(CN)(en)_2]^{2+}$
   b. $[Co(Br)_2(en)_2]^{2+}$
   c. $[PtCl_4]^{2-}$
   d. $K_3[Fe(CN)_6]$
   e. $[Cr(NH_3)_3Cl_3]$
5. **5.** Write down the IUPAC names of the following compounds.
   a. $[Co(NH_3]_5(ONO)]Cl_2$
   b. $K_3[Cr(CN)_6]$

6. **Write the formulae of the following complexes**
   a. Pentammine chlorocobalt (III) ion
   b. Lithium tetrahydrogen aluminate (III)
7.

   Identify A and B. Write the IUPAC names of A and B.
8. Write down the IUPAC names of the following compounds:
   I. $[Co(NH_3)_5ONO]Cl_2$
   II. $K_3[Cr(CN)_6]$
   III. $[Cr(NH_3)_5CO_3]Cl$
9. Compare qualititatively the first and second ionization potentials of copper and zinc. Explain the observation.
10. Write the IUPAC name of the compound $[Cr(NH_3)_5(NCS)][ZnCl_4]$. Is this compound coloured?
11. Write the formulae of the following complexes:
   i. Pentamminechlorocobalt(III) ion
   ii. Lithium tetrahydroaluminate(III) ion

Solutions to Exercise Questions:

1. c
2. c
3. A ligand may contain one or more unshared pair of electrons which are called the donor sites of ligands. Now, depending on the number of these donor sites, ligands can be classified as follows.

a. Unidentate ligands:

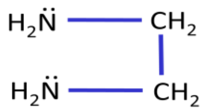
Ligands with only one donor site are called unidentate ligands.

Example: $\dot{N}H_3$, Cl^- etc

b. Bidentate ligands:

Ligands that have two donor sites are called bidentate ligands.

Example: **(a) Ethane – 1, 2 - diamine** **(b) Oxalatie ion**



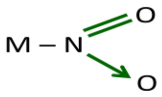
$$\begin{matrix} H_2\ddot{N} - CH_2 \\ \quad | \\ H_2\ddot{N} - CH_2 \end{matrix}$$

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$$

c. Ambidentate ligands:

Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands.

Example: **Nitro group** **Oxygen group**



The donor atom is N

$M - O - N = O$

The donor atom is oxygen

4.

a. $[Co(H_2O)(CN)(en)_2]^{2+}$

Let the oxidation number of Co is be x

The charge on the complex is +2

$[Co(H_2O)(CN)(en)]^{+2}$

$[x + 0 + (-1) + 2(0)] = +2$

$(x - 1) = +2$

$x = +3$

b. $[Pt(Cl)_4]^{2-}$

Let the oxidation number of Pt be x

The charge on the complex is -2

$[Pt(Cl)_4]^{2-}$

$[x + 4(-1)] = -2$

$(x - 4) = -2$

$x = +2$

c. $[Co(Br)_2(en)_2]^{2+}$

$[x + 2(-1) + 2(0)] = +1$

$(x - 2) = +1$

$x = +3$

d. $K_3[Fe(CN)_6]$

i.e., $[Fe(CN)_6]^{3-}$

$[x + 6(-1)] = -3$

$(x - 6) = -3$

$x = -3 + 6$

$x = +3$

e. $[Cr(NH_3)_3Cl_3]$

$[x + 3(0) + 3(-1)] = 0$

$(x - 3) = 0$

$x = +3$

5.

a. Pentammine nitrito cobalt (II) chloride

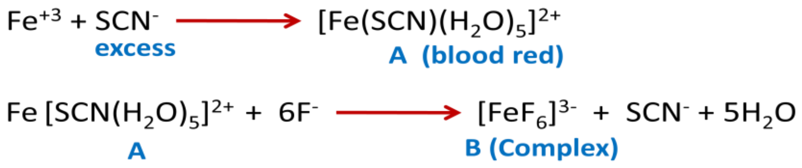
b. Potassium hexacyano chromate (III)

6.

a. $[Co(NH_3)_5Cl]$

b. $Li[AlH_4]$

7.



IUPAC name of A = pentaaquathiocyanatoferrate (III) ion

B = Hexafluoroferrate (III)

8.

I. Pentamminenitritocobalt (III) chloride

II. Potassium hexacyanochromate (III)

III. Pentamminecarbonatochromium (III) chloride.

9.

$_{29}Cu = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$

$_{30}Zn = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2$

On the basis of configuration of Cu and Zn, first ionization potential of Zn is greater than that of copper because in zinc the electron is removed from $4s^2$ configuration while in copper it is removed from $4s^1$ configuration. So more amount of energy is required for the removal of electron of $4s^2$ (completely filled orbital) than that of $4s^1$ while the second ionization potential of Cu is higher than that of zinc because Cu^+ has $3d^{10}$ (stable configuration) in comparison to Zn^+ ($4s^1$ configuration).

10. Pentammine isothiocyanato chromium (III) tetra chlorozincate.

This compound is coloured because Cr^{3+} has $3d^3$ configuration (has unpaired electron in d – orbitals) which show colour, through d - d transition.

11.

i. Formula of pentamminechlorocobalt (III) is $[CoCl(NH_3)_5]^{2+}$.
ii. Formula of lithium tetrahydroaluminate (III) is $LiAlH_4$

Co-ordination Compounds

Module 24.2: Theories of Co-ordination compounds

To explain the formation of complex compounds many theories have been suggested. The most successful of the earliest theories is Werner's theory. It is based on certain assumptions which are listed here.

Werner's Theory of Co-ordination compounds:

Postulates

1. A complex has always a central metal atom. This may be an ion or a neutral atom.
2. A metal in a complex compounds has two types of valencies, namely primary and secondary valencies.
3. Primary valency (Ionisable valency) corresponds to the oxidation state of metal atom or ion. Secondary valency (Non-ionisable valency) corresponds to the co-ordination number of the central metal.
4. Every metal has a fixed number of secondary valencies or co-ordination number in each of its oxidation states.
5. The co-ordination number of the metal is the number of ligands, which gives the number of coordinate covalent bonds formed with central metal atom or ion, in a complex compound.

   In majority of the commonly found complex compounds, the co-ordination number 2 or 4 or 6.

   i) Co(III) and Pt(IV) have 6 co-ordination number

   Ex: $[Co(NH_3)_6]Cl_3$; $K_2[Pt(Cl)_6]$

   ii) Cu(II), Pt(II), Zn(II) have 4 Co-ordination number

   Ex: $[Cu(NH_3)_4]^{2+}$; $[Cu(OH)_4]^{2-}$; $[Pt(NH_3)_4]^{+2}$; $[Zn(CN)_4]^{-2}$; $[ZnCl_4]^{-2}$

   iii) Ag(I) has 2 Co-ordination number

   Ex: $[Ag(NH_3)_2]^{+}$; $[Ag(CN)_2]^{-}$
6. The secondary valencies of the central metal may be satisfied by negative ions (Cl^-, Br^-, CN^- etc..) or by neutral molecules (H_2O, NH_3 etc), or by positive ions (NH_2-NH_3^+, NO^+ etc)

In some complex compounds both primary and secondary valencies may be satisfied by negative ions.

Ex: $[Co(NH_3)_4Cl_2]Cl$

7. The primary valency can be satisfied by negative ions.
8. The ligands are directed in space around the central atom symmetrically in such a way that the complex has a definite structure.

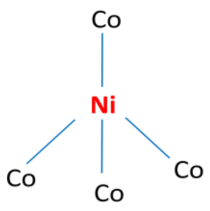
Ex: i) If the complex has 2 ligands, it gives linear structure.

$[Ag(NH_3)_2]^+$; $[H_3N - Ag - NH_3]^+$

ii) If the complex has 4 ligands, it assumes either a tetrahedral or a square planar structure.

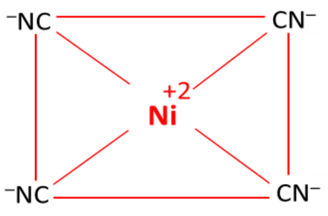
Ex:

$Ni(Co)_4$



Tetrahedral

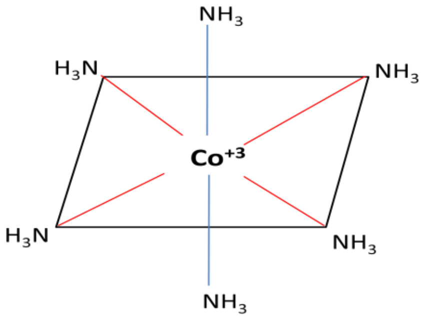
$[Ni(CN)_4]^{2-}$



Square planar

iii) If the complex has 6 ligands it gives octahedral structure.

Ex: $[Co(NH_3)_6]^{+3}$



Octahedral structure

9. The charge of complex ion is equal to the sum of charges of metal and ligands.

Ex 1 : **$K_4[Fe(CN)_6]$**

Oxidation state of Fe is +2

Oxidation state of CN^- is –1

Charge of complex ion [2+6(-1)] = – 4

i.e., $[Fe(CN)_6]^{4-}$

<u>Ex 2 :</u> **$[Co(NH_3)_6]^{+3}\ [Cl^-]_3$**

Oxidation state of Co is +3

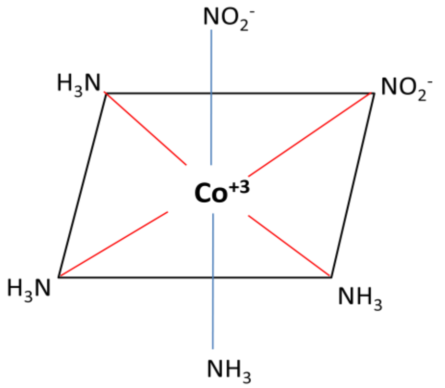
Oxidation state of NH_3 is 0

Charge of complex ion (+3) + 6(0) = +3

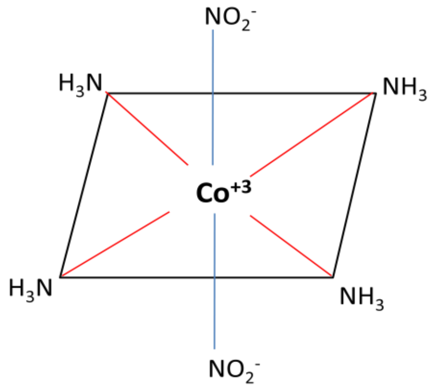
i.e., $[Co(NH_3)_6]^{3+}$

Advantages of Werner's theory:

a) Werner's theory can explain the isomerism in complex compounds.
Ex: $[Co(NH_3)_4(NO_2)_2]^+$ give two isomers



Cis



Trans

b) We can distinguish the following complex compounds of same molecular formula

$[Co(NH_3)_5SO_4]Br$ (I)

$[Co(NH_3)_5Br]SO_4$ (II)

$[Co(NH_3)_5SO_4]Br$ gives yellow precipitate with $AgNO_3$.

$[Co(NH_3)_5Br]SO_4$ gives white precipitate wit $BaCl_2$ solution.

Defects in Werner's theory:

Inspite of the capacity to explain the formation of complex compounds, Werner's theory is having many defects. Some of the important drawbacks are enumerated here.

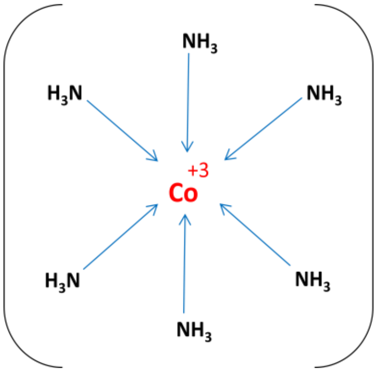
1. Werner's theory does not correlate electronic configuration of the central metal with the formation of the complex compounds. Now it is known that the central metal try to acquire the next inert gas structure through coordinate bond formation. Hence complexes are formed.
2. The postulates of Werner do not offer any explanation to the colour of the complex compounds. It is appropriate at this juncture, to know how the d – d transition takes place and result in the colour to the complex.
3. Werner's theory is incapable of explaining the magnetic behavior. The magnetic property depends on the number of unpaired electrons present in the metal ion. Werner's theory is not related to electronic configuration and so this property could not be explained.

Sidgwick Theory of Co-ordination compounds:

Sidgwick suggested that the bond between the ligands and the metal ion is co-ordinate covalent or semipolar bond. He says that the ligands donate the electron pair to metal ion forming a coordinate covalent bond. Here ligand (L) is donor and metal ion (M) is acceptor.

It is denoted by "L → M"

According to Sidgwick's concept, the structure of the complex ion $[Co(NH_3)_6]^{3+}$ is represented as



Here, each NH_3 donates a lone pair of electrons to cobalt (III) ion. The donation is represented by an arrow. In the process the central atom acquires the same or nearest number of electrons as that of its nearest inert gas. This number is known as EAN. The principle is referred commonly as EAN rule.

Effective atomic number (EAN):

"The total number of electrons the central metal ion possesses including those gained from ligands in the bonding, is called Effective Atomic Number (EAN)"

In many complexes it is equal to the atomic number of the nearest inert gas.

EAN value of metal can be calculated as follows using the relation.

EAN = {(Atomic number of metal) – (Oxidation state of metal) + [2×number of ligands]}

Many complexes obey EAN rule

S.No	**Complex compound**	**Central metal**	**At. no. of the metal**	**No. of e's lost = Ox. State(x)**	**No. of e's gained (y)**	**EAN of the metal = (z-x+y)**	**At. No. of next inert gas**
1.	$[Co(NH_3)_6]Cl_3$	Co	27	3	12	(27-3+12)=36	36(Ar)
2.	$K_4[Fe(CN)_6]$	Fe	26	2	12	(26-2+12)=36	36(Ar)
3.	$[Pd(NH_3)_6]SO_4$	Pd	46	4	12	(46-4+12)=54	54(Xe)
4.	$[PtCl_6]^{-2}$	Pt	78	4	12	(78-4+12)=86	86(Rn)

Some complexes do not obey EAN rule

Ex: 1) $[Fe(CN)_6]^{3-}$ (26-3+12) = 35
2) $[Ni(CN_4)]^{2-}$ (28-2+8) = 34

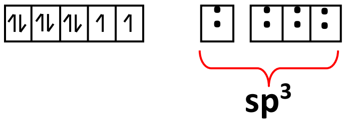
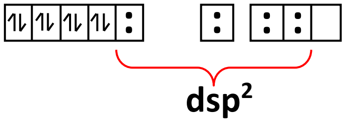
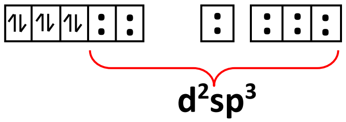
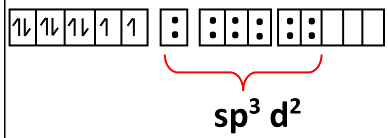
Valence Bond Theory:

This theory was developed by Pauling. This can explain the kind of bonding, shape and magnetic properties of complex compounds. Main points are…

1. The central metal atom or ion makes available the necessary number of vacant orbitals to suit its co-ordination number. These orbitals are hybridized together, depending on the structure and shape hybrid orbitals.
2. The ligands must have at least one lone pair of electrons.
3. The vacant metal orbitals and lone pairs of electrons of the ligand orbitals overlap to form coordinate covalent bonds.

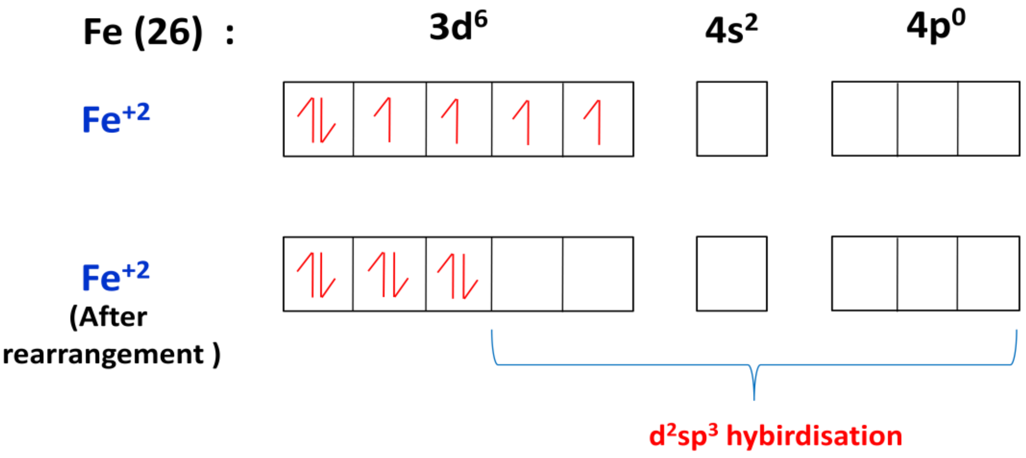
4. The non-bonding metal electrons occupy the inner d-orbital which do not involve in the hybridization.
5. If a complex contains unpaired electrons, it is paramagnetic in nature; if it does not contain unpaired electrons it is diamagnetic in nature.
6. The number of unpaired electrons in complex may indicate the geometry of the complex.
7. From the number of unpaired electrons in the complex the extent of paramagnetism can be calculated.
8. The central metal atom may utilize the d-orbitals of either the penultimate shell or the valence shell resulting in the inner d-orbital complexes or outer d-orbital complexes respectively.
9. Sometimes the electrons undergo rearrangement against the Hund's max multiplicity rule.

Geometry (shape) and magnetic nature of some complexes (application of Valence bond Theory)

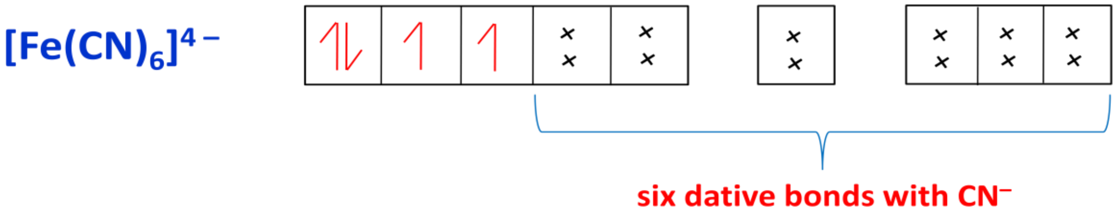
Complex	Configuration	Ox. state	Hybridization	Geometry shape	No. of Unpaired electrons	Magnetic nature
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{-}$		+2	dsp^2	Square planar	0	Diamagnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3	Octahedral	0	Diamagnetic
$[Co(H_2O)_6]^{+2}$		+2	sp^3d^2	Octahedral	3	Paramagnetic

Examples of inner orbital complexes and outer orbital complexes:

Ex 1: **Formation of $[Fe(CN)_6]^{4-}$** : The electronic configuration of Fe and Fe^{+2} ion in Ferrocyanide ion is given below



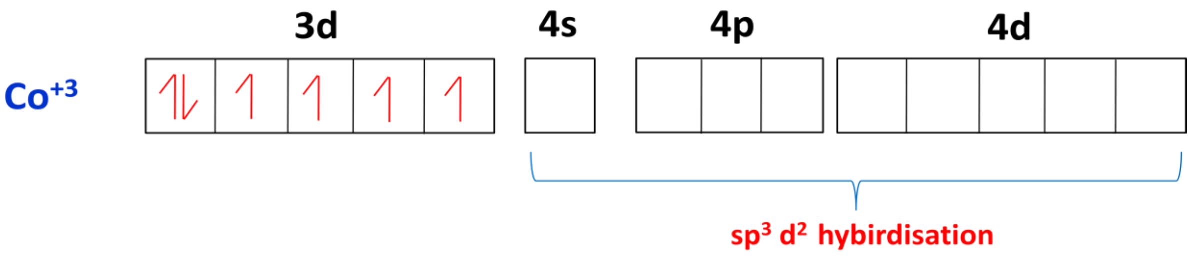
In presence of cyanide ligand, the electrons in the 3d orbitals are forced to pair up. Here Fe^{+2} undergoes d^2sp^3 hybridisation to form six d^2sp^3 hybrid orbitals, each of them accepts electron pair donated by cyanide ion



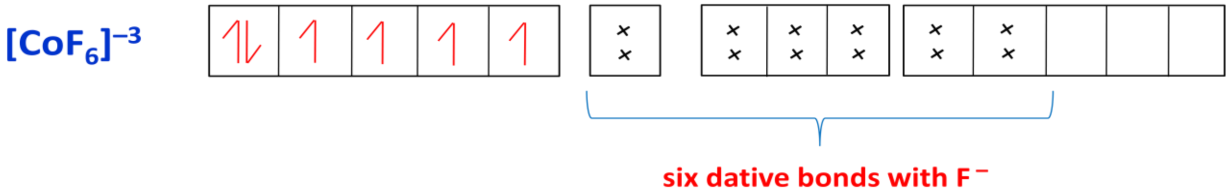
Another inner orbital complex is $[Co(NH_3)_6]^{3+}$

Outer orbital complex:

Ex-1: **Formation of $[CoF_6]^{3-}$**: The electronic configuration of Co^{+3} ion is given below (outer orbitals configuration is $3d^6$ $4s^0$)



The fluoride ion is a weak ligand and cannot force the pairing up of electrons.



Drawbacks of Valence Bond Theory:

1. It is a qualitative approach describing bonding in co-ordination compounds.
2. The theory fails to explain the finer aspects of the magnetic properties of co-ordination compounds.
3. This theory does not provide an answer to the origin of characteristic colours of complex ions.
4. It does not explain why [Co(NH$_3$)$_6$]$^{+3}$ is an inner orbital complex and [CoF$_6$]$^{-3}$ is an outer orbital complex.

Assignment Questions:

(1) Write the postulates of Werner's theory.

(2) Explain Werner's theory giving one example.

(3) Write the postulates of Valence Bond Theory.

(4) Explain the formation of [Fe(CN)$_6$]$^{4-}$ and [CoF$_6$]$^{-3}$ on the basis of VBT (Z of Fe = 26; Z of Co = 27).

(5) Define EAN.

Example Set:

1. EAN of Fe in [Fe(CN)$_6$]$^{3-}$ is

a) 36 b) 27 c) 38 d) 35

Solution: d

2. The hybridisation undergone by Ni in [Ni (CN)$_4$]$^{2-}$ ion is

a) dsp^2 b) sp^{2}d^2 c) d^{2}sp d) sp^2

Solution: a

3. Which of the following has a central metal atom that has undergone d^{2}sp^3 hybridisation?

a) $[Cr(NH_3)_6]^{2+}$ b) $[Fe(CN)_6]^{3-}$

c) $[Co(NH_3)_6]^{3+}$ d) all are correct

Solution: d

4. According to Werner's Theory the primary valency of the transition metal ion is equal to
   a) Oxidation state
   b) Co-ordination number
   c) Number of electrons in the outer most orbit
   d) Atomic number

   Solution: a

5. Write the formula to calculate the EAN of a central metal atom / ion.

   Solution: **EAN = {(Atomic number of metal) – (Oxidation state of metal) + [2×number of ligands]}**

6. What type of hybridisation undergone by Co in the complex $[Co(NH_3)_6]^{3+}$?

   Solution: d^2sp^3 hybridisation

7. Write a short not on i) Primary valency ii) Secondary valency of a metal in a complex.

   Solution:

   i) Primary valency (Ionisable valency) corresponds to the oxidation state of metal atom or ion.

   ii) Secondary valency (Non-ionisable valency) corresponds to the Co-ordination number of the central metal.

8. What are the possible shapes of complex ion with Co-ordination number 4 and 6?

   Solution: Tetrahedral and square planar.

Problem Set:

1. According to Werner's Theory the number of secondary valencies of a transition metal ion is equal to the
   a) Oxidation state
   b) Atomic number
   c) Co-ordination number
   d) Unpaired electrons

Solution: c

2. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate?

a. $Cu(CN)_2$
b. $K_2[Cu(CN)_4]$
c. $K[Cu(CN)_2]$
d. $K_3[Cu(CN)_4]$

Solution: d

3. In the process of extraction of gold,

Roasted gold ore + $CN^- + H_2O \xrightarrow{O_2} [X] + O^-$
$[X] + Zn \rightarrow [Y] + Au$

Identify the complexes [X] and [Y]

a. $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$
b. $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$
c. $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$
d. $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

Solution: a

4. The EAN of nickel in $K_2[Ni(CN)_4]$ is

a) 35 b) 34 c) 36 d) 38

Solution: b

5. Which of the following pairs contain only tetrahedral complexes?

a) $[Ni(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$
b) $[Ni(CO)_4]$ and $[ZnCl_4]^{2-}$
c) $[Ni(NH_3)_4]$ and $[Cu(NH_3)_4]^{2-}$
d) $[Ni(NH_3)_4]$ and $[Ni(CO)_4]^{2-}$

Solution: b

6. The hybridisation state of the Fe among $[Fe(CN)_6]^{3-}$, $Fe(CO)_5$, $[Fe(H_2O)_6]^{2+}$

a) sp^3d^2, dsp^3, sp^3d^2
b) d^2sp^3, dsp^3, sp^3d^2
c) d^2sp^3, sp^3d, sp^3d^2
d) sp^3d^2, sp^3d, d^2sp^3

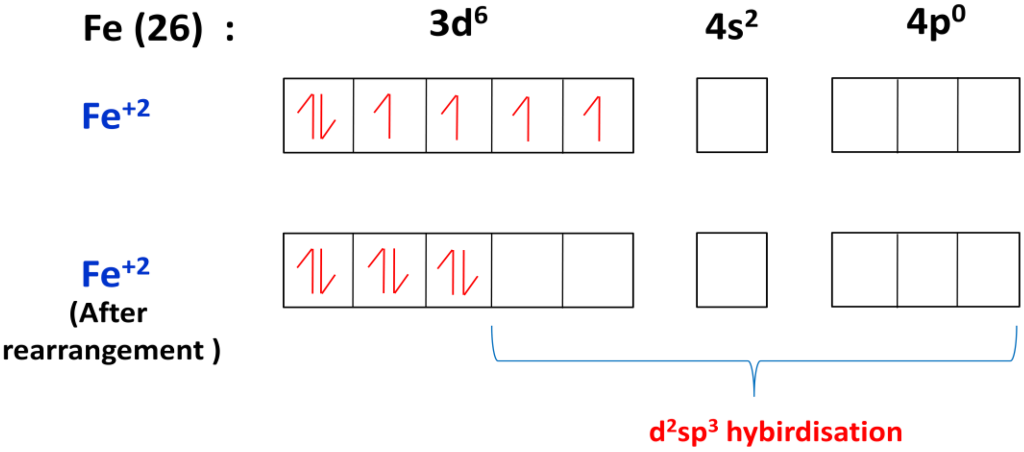
Solution: b

7. Explain the terms inner orbital complex and outer orbital complex.

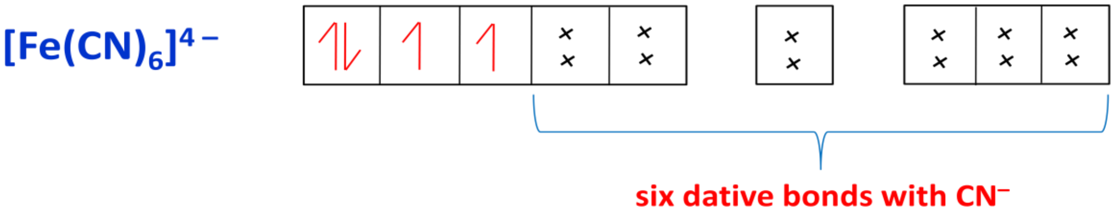
Solution:

Examples of inner orbital complexes and outer orbital complexes:

Ex 1: **Formation of $[Fe(CN)_6]^{4-}$** : The electronic configuration of Fe and Fe^{+2} ion in Ferrocyanide ion is given below



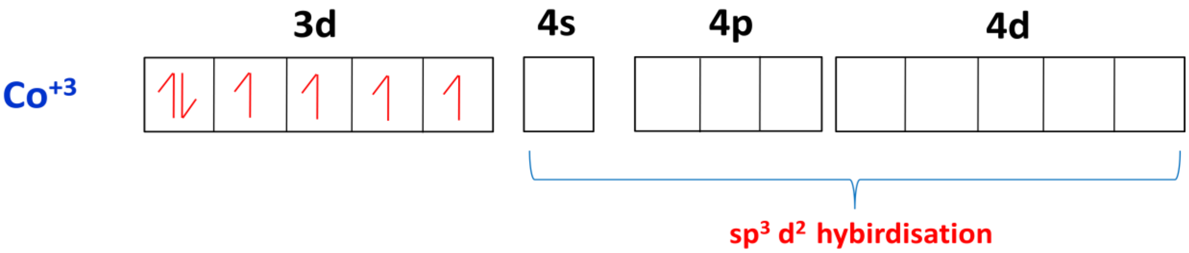
In presence of cyanide ligand, the electrons in the 3d orbitals are forced to pair up. Here Fe^{+2} undergoes d^2sp^3 hybridisation to form six d^2sp^3 hybrid orbitals, each of them accepts electron pair donated by cyanide ion



Another inner orbital complex is $[Co(NH_3)_6]^{3+}$

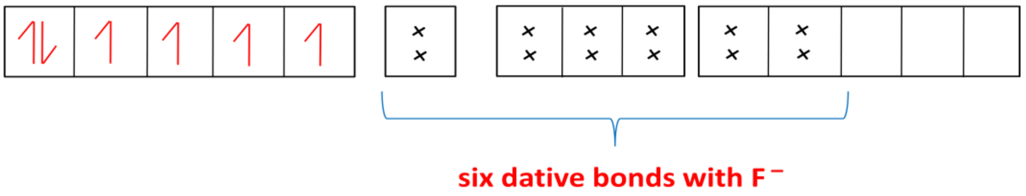
Outer orbital complex:

Ex-1: **Formation of $[CoF_6]^{3-}$**: The electronic configuration of Co^{+3} ion is given below (outer orbitals configuration is $3d^6\ 4s^0$)



The fluoride ion is a weak ligand and cannot force the pairing up of electrons.

$[CoF_6]^{-3}$



8. Calculate the EAN of the following metals in the following complexes

a) $[Co(NH_3)_6]^{3+}$ b) $[Pd(NH_3)_6]SO_4$ c) $[Fe(CN)_6]^{4-}$ d) $[PtCl_6]^{-2}$

Solution:

S.No	Complex compound	Central metal	At. no. of the metal	No. of e's lost = Ox. State(x)	No. of e's gained (y)	EAN of the metal = (z-x+y)	At. No. of next inert gas
1.	$[Co(NH_3)_6]Cl_3$	Co	27	3	12	(27-3+12)=36	36(Ar)
2.	$K_4[Fe(CN)_6]$	Fe	26	2	12	(26-2+12)=36	36(Ar)
3.	$[Pd(NH_3)_6]SO_4$	Pd	46	4	12	(46-4+12)=54	54(Xe)
4.	$[PtCl_6]^{-2}$	Pt	78	4	12	(78-4+12)=86	86(Rn)

9. Discuss the nature of bonding in the following co-ordination entities on the basis of valence bond theory.

i) $[Fe(CN)_6]^{4-}$ ii) $[FeF_6]^{3-}$

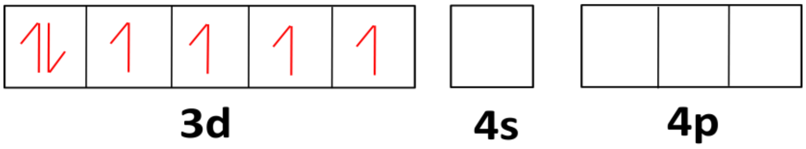
Solution:

i) $[Fe(CN)_6]^{4-}$

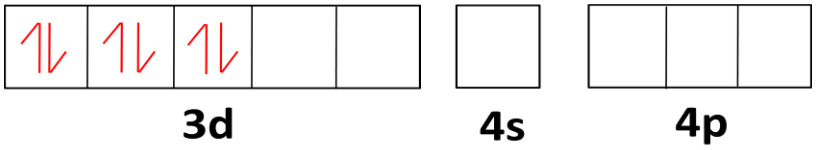
In the above co-ordination complex, iron exists in the +II oxidation state.

Electronic configuration of Fe^{+2} is $3d^6\ 4s^0$.

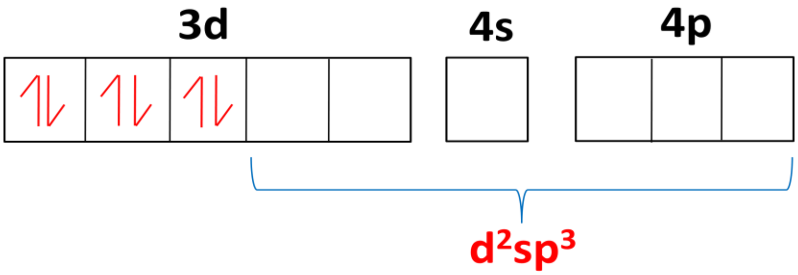
Orbitals of Fe^{+2} ion:



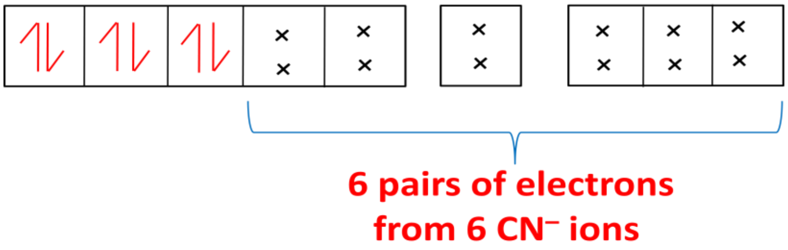
As CN^- is a strong ligand, it causes pairing of the unpaired 3d electrons.



Since there are six ligands around the central metal ion, the most feasible hybridisation is d^2sp^3.
d^2sp^3 hybridized orbitals of Fe^{+2} are



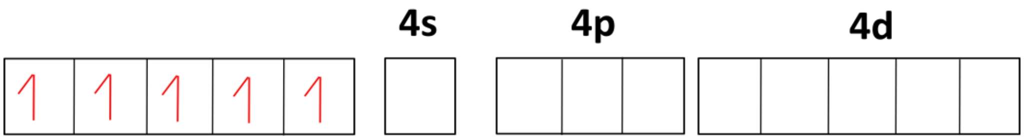
6 electron pairs form CN^- ions occupy the six hybrid d^2sp^3 orbitals
Then,



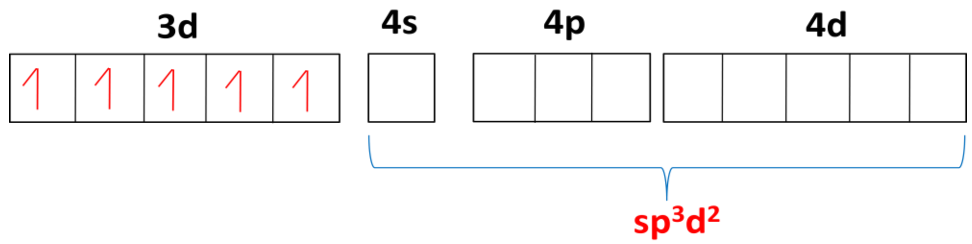
Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons)

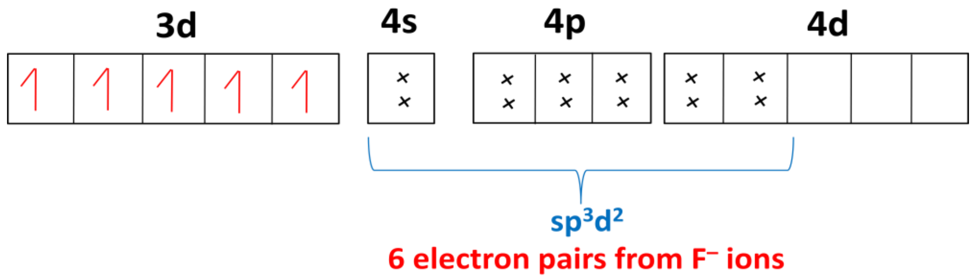
ii) $[FeF_6]^{3-}$

In this complex, the oxidation state of Fe is $^{+3}$.
Orbitals of Fe^{+3} ion are



There are $6F^-$ ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridisation. As F^- is a weak ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridisation is sp^3d^2.





Hence, the geometry of the complex is found to be octahedral.

Exercise Questions:

1. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$
   a. $Ni(CO)_4$ and $NiCl_4^{2-}$ diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic.
   b. $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic
   c. $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic
   d. $Ni(CO)_4$ is diamagnetic and $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic
   Answer: c
2. Among the following, the compound that is both paramagnetic and colored is
   a. $K_2Cr_2O_7$
   b. $(NH_4)_2(TiCl_6)$
   c. $CoSO_4$
   d. $K_3[Cu(CN)_4]$
   Answer: c

3. The geometry of $Ni(CO)_4$ and $[Ni(PPh_3)_2]Cl$ are
   a. Both square planar

b. Tetrahedral and square planar, respectively
c. Both tetrahedral
d. Square planar and tetrahedral, respectively:

Answer: c

4. The complex ion which has no ‘d’ electrons in the central metal atom is

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

Answer: a

5. The species having tetrahedral shape is ___

a. $[PdCl_4]^{2-}$
b. $[Ni(CN)_4]^{2-}$
c. $[Pd(CN)_4]^{2-}$
d. $[NiCl_4]^{2-}$

Answer: b

6. The spin magnetic moment of cobalt in the compound $Hg[Co(SCN)_4]$is

a. $\sqrt{3}$
b. $\sqrt{8}$
c. $\sqrt{15}$
d. $\sqrt{24}$

Answer: c

7. Which kind of isomerism is exhibited by octahedral $Co(NH_3)_4 Br_2Cl$

a. Geometrical and ionization
b. Geometrical and optical
c. Optical and ionization
d. Geometrical only

Answer: a

8. Among the following metal carbonyls, the C – O bond order is lowest in

a. $[Mn(CO)_6]^+$
b. $[Fe(CO)_5]$
c. $[Cr(CO)_6]$

d. $[V(CO)_6]^-$

Answer: d

9. Among the following the colored compound is

a. CuCl
b. $K_3[Cu(CN)_4]$
c. CuF_2
d. $[Cu(CH_3CN)_4]BF_4$

Answer: c

10. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridization of nickel in these complexes, respectively are

a. sp^3, sp^3
b. sp^3,dsp^2
c. dsp^2, sp^3
d. dsp^2 , sp^2

Answer: b

11. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is

a. 0
b. 2.84
c. 4.90
d. 5.92

Answer: a

12. The complex showing a spin – only magnetic moment of 2.82 B.M. is

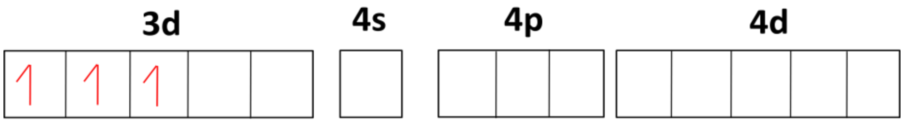
a. $Ni(CO)_4$
b. $[NiCl_4]^{2-}$
c. $Ni(PPh_3)_4$
d. $[Ni(CN)_4]^{2-}$

Answer: b

13. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

Solution:

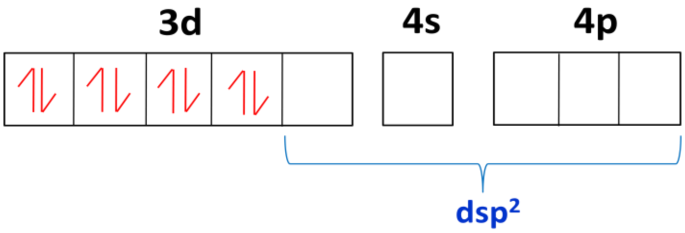
Cr is in the +3 oxidation state i.e. d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.



Therefore it undergoes d^2sp^3 hybridisation and the electrons in the 3d orbitals remain unpaired. Hence it is paramagnetic in nature.

In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state *i.e.,* it has $d^8 4s^0$ configuration.

CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridisation

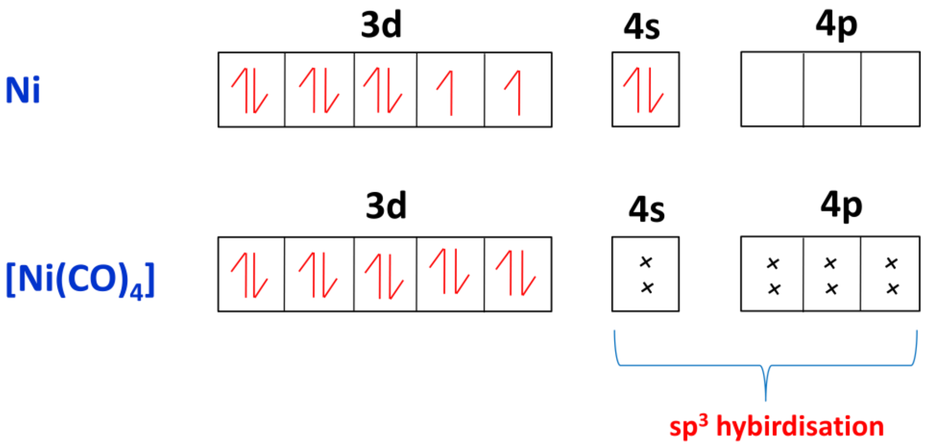


As there are no unpaired electrons it is diamagnetic.

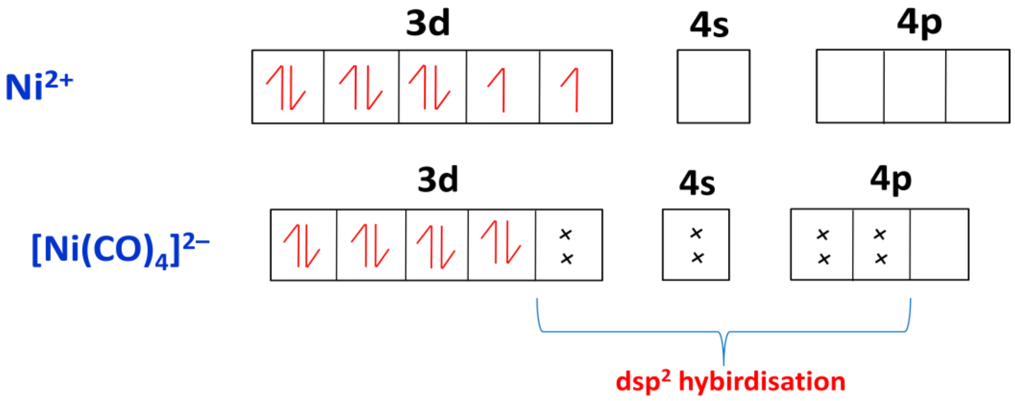
14. $[Ni(CO)_4]$ possesses tetrahedral geometry while $[Ni(CN)_4]^{2-}$ is a square planar. Explain why?

Solution:

In the formation of $Ni(CO)_4$ nickel is in zero oxidation state. It undergoes sp^3 hybridisation; hence it is tetrahedral in shape.



In the formation of $[Ni(CN)_4]^{2-}$, Ni^{2+} ion undergoes dsp2 hybridisation, hence it is square planar in shape.



15. Explain, why NH_4^+ ion does not form complexes?

Solution:

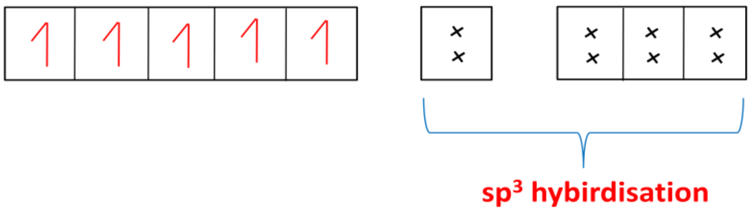
NH_4^+ Ion does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.

16. Calculate the magnetic moment of Mn in $[MnCl_4]^{2-}$.

Solution:

In $[MnCl_4]^{2-}$ ion, Mn^{+2} ion undergoes sp^3 hybridisation. It contains 5d-orbitals singly occupied. Hence, it has high value of magnetic moment.

$[MnCl_4]^{2-}$



Number of unpaired electrons = 5

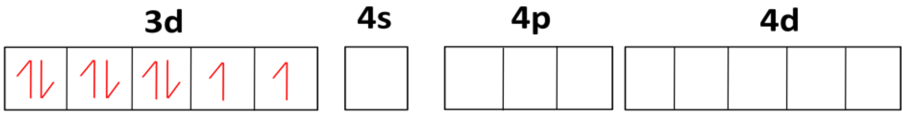
$$\therefore \quad \mu = \sqrt{n(n+2)}$$

$$= \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

17. Explain why octahedral complexes of Ni^{2+} must be outer orbital complexes.

Solution:

Ni^{2+}



During rearrangement only one 3d-orbital may be made available by pairing the electrons. Thus, inner d^2sp^3 hybridisation is not possible. So, only sp^3d^2 (outer) hybridisation can occur.

18. Identify the complexes which are expected to be colored. Explain

i. $[Ti(NO_3)_4]$ ii. $[Cu(NCCH_3)_4]^+ BF_4^-$ iii. $[Cr(NH_3)_6]^{3+} 3Cl^-$ iv. $K_3[VF_6]$

Solution:

i. $[Ti(NO_3)_4]$; ${}_{22}Ti^{4+}$: $[Ar]3d^0\ 4s^0$

ii. $[Cu(NCCH_3)_4]^+ BF_4^-$; ${}_{29}Cu^+$: $[Ar]3d^{10}\ 4s^0$

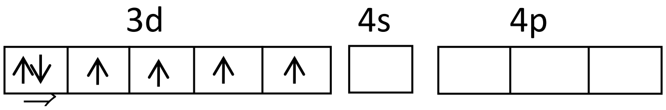
iii. $[Cr(NH_3)_6]^{3+} 3Cl^-$; ${}_{24}Cr^{3+}$: $[Ar]3d^3\ 4s^0$

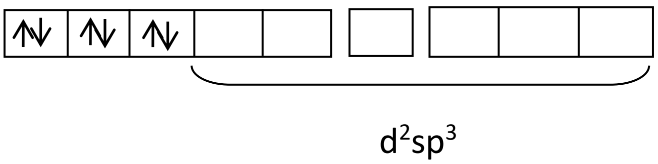
iv. $K_3[VF_6]$; ${}_{23}V^{+3}$: $[Ar]3d^2\ 4s^0$

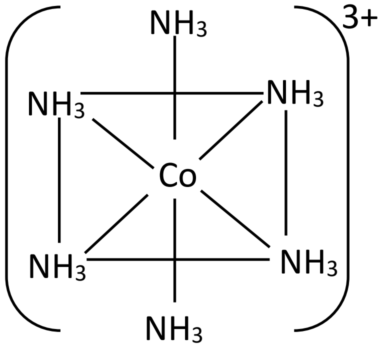
19. Draw the structures of $Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridization of atomic orbitals of the transition metal in each case.

Solution:

Co^{3+}

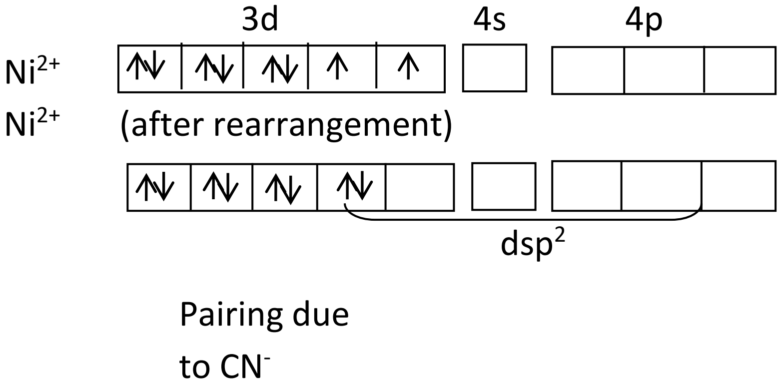


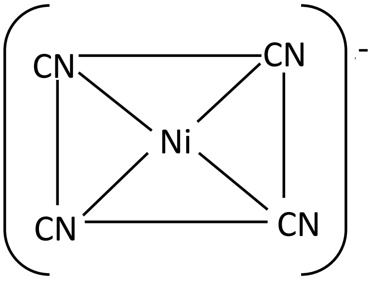




Octahedral

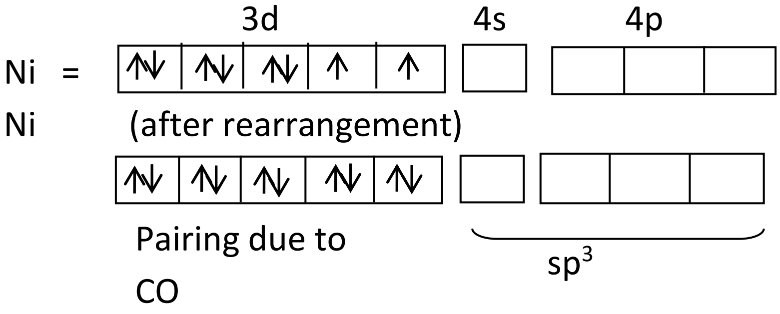
$[Ni(CN)_4]^{2-}$

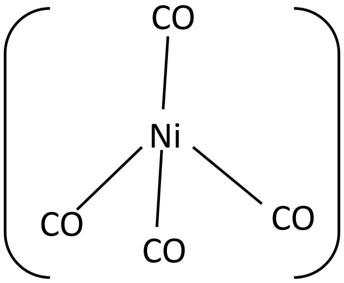




Square planar

$[Ni(CO)_4]$





Tetrahedral

20. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (A) and (B). The form (A) reacts with $AgNO_3$ 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 hybridization of chromium in each. Calculate their magnetic moments (spin only values).

Solution:

Compound (A) on treatment with $AgNO_3$ gives white precipitate of AgCl, which is readily soluble in dil.aq.NH_3. Therefore it has at least one Cl^- ion in the ionization sphere furthermore chromium has co-ordination number equal to 6. So its formula is **$[Cr(NH_3)_4BrCl]Cl$.**

Compound (B) on treatment with $AgNO_3$ give pale yellow precipitate of AgBr soluble in conc.NH_3. Therefore it has Br- in the ionization sphere. So its formula is **$[Cr(NH_3)_4Cl_2]$ Br**.

Cr^{3+} (Z = 24) has $3d^3$ configuration

Hybridization of chromium in both (A) and (B) is d^2sp^3.

Spin magnetic moment of (A) or (B),

$\mu_{spin} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87BM$

21. Deduce the structure of $[NiCl_4]^{2-}$ and $[Ni(CN_4)]^{2-}$ considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species.

Solution:

Cl^- is a weak ligand which is unable to pair the electrons of Ni^{2+}, Hybridisation is sp^3 and shape will be tetrahedral, with 2 unpaired electrons.

Electronic configuration of Ni^{2+} in presence of Cl^- ion, a weak ligand.

Magnetic moment = $\sqrt{2(2+2)}$ = 2.82 BM

On the other hand CN^- is a strong ligand which pairs up the electrons of Ni^{2+}. Therefore, here hybridization is dsp^2 and shape will be square planar, with unpaired electrons. u = 0

22. Write the IUPAC nomenclature of the given complex along with its hybridization and structure

$K_2[Cr(NO)(NH_3)(CN)_4]$, $\mu = 1.73$ BM

Solution:

The spin magnetic moment, μ of the complex in 1.73 BM.

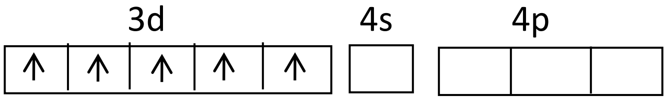
$\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$

It means that nucleus of the complex; chromium ion has one unpaired electron. So the ligand NO is unit positively charged.

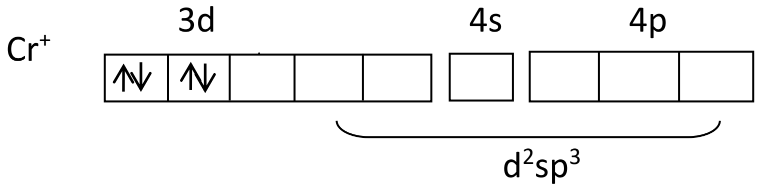
IUPAC name:

Potassium amminetetracyanonitrosochromate(I).

(a) Electronic configuration of Cr^+:



(b) Electronic configuration of Cr^+ under the influence of strong field ligand CN^-



So, hybridization is d^2sp^3 and shape is octahedral

Co-ordination Compounds

Module 24.3: Isomerism

Two or more molecules having the same molecular formula but different structural or spatial arrangement are called **isomers**.

They are of two types.

a. Structural isomerism
b. Stereo isomerism

Stereo isomerism in complex compounds:

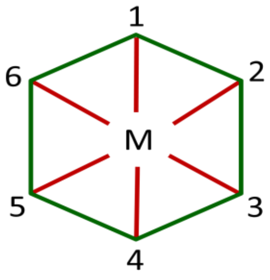
Two or more complexes having same molecular composition but different arrangement of atoms (or) groups in space is called as stereoisomerism.

It is of two types.

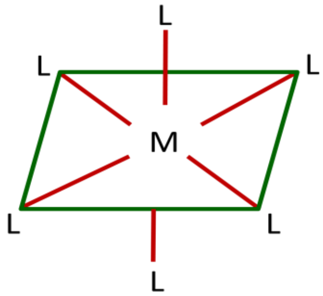
a. Geometrical isomerism
b. Optical isomerism

Geometrical isomerism in co-ordination number 6 compounds:

The arrangement of six ligands in a complex around the central metal ion is possible in two different ways. Those are regular hexagon and regular octahedron.



Hexagon



Octahedron

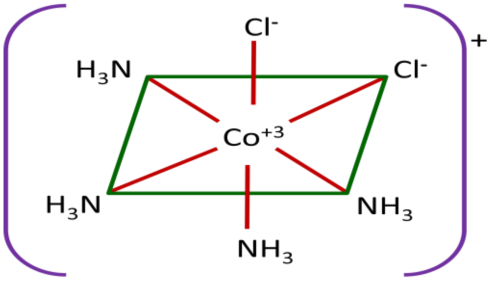
If the complex Ma_4b_2 (where M = central metal atom; a,b = ligands) has hexagonal structure it can give three isomers corresponding to (1, 2), (1, 3) and (1, 4) positions of a and b, while octahedral arrangement can give only two isomers. X – ray analysis confirmed that co-ordination number 6 complexes exhibit octahedral arrangement by giving two isomers of Ma_4b_2 type. Hence co-ordination number 6 complexes have octahedral structure.

1. No isomerism is possible in $[Ma_6]$ or Ma_5b of complexes

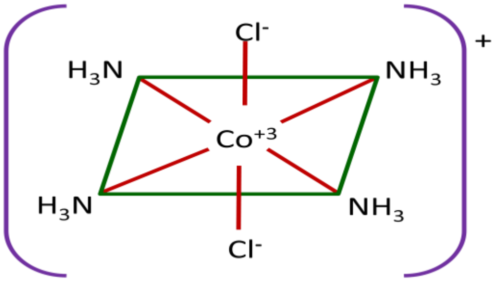
   Example: $[Co(NH_3)_6]^{3+}$; $[Co(NH_3)_5Cl]^{2+}$

2. $[Ma_4b_2]$ and $[Ma_4bc]$ type of complexes can give two isomers. Those are cis and trans – isomers.

   Example: $[Co(NH_3)_4Cl_2]^+$ gives cis and trans isomers.



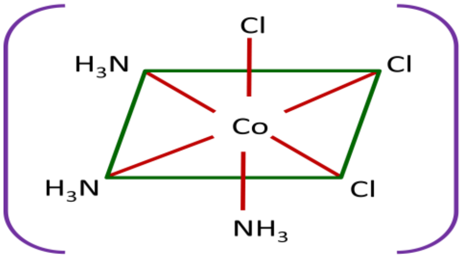
Cis



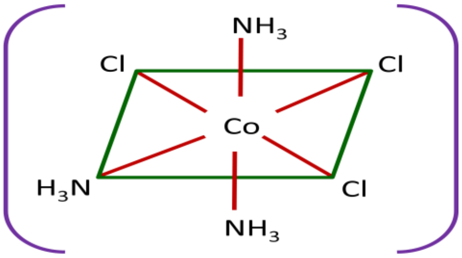
Trans

3. $[Ma_3b_3]$ type of complexes can exhibit geometrical isomerism.

   Example: $[Co(NH_3)_3Cl_3]$ gives Cis – trans isomers.



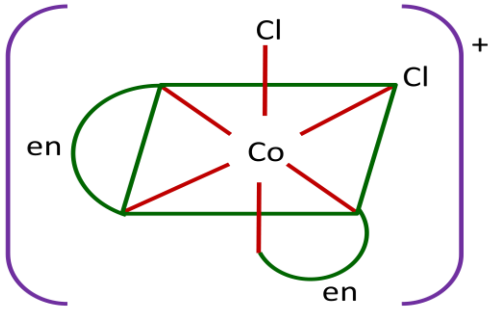
Cis



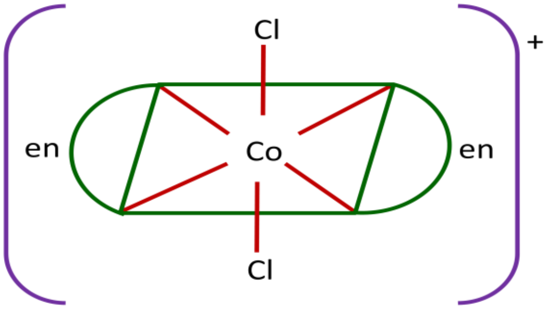
Trans

4. $[M(aa)_2b_2]$ (where aa = bidentate ligand) type of complexes having two bidentate ligands, can exhibit geometrical isomerism.

   Example: $[Co(en)_2Cl_2]^+$ gives cis and trans isomers.



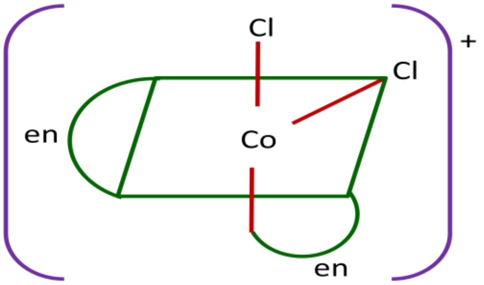
Cis



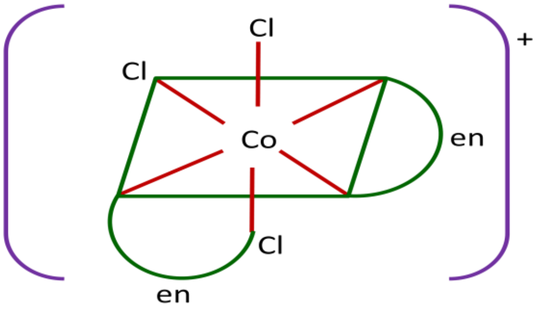
Trans

Optical isomerism in co-ordination number 6 compounds::

1. The cis isomer of $[M(aa)_2b_2]$ type complexes has no plane of symmetry. So it can give two isomers (d and l)

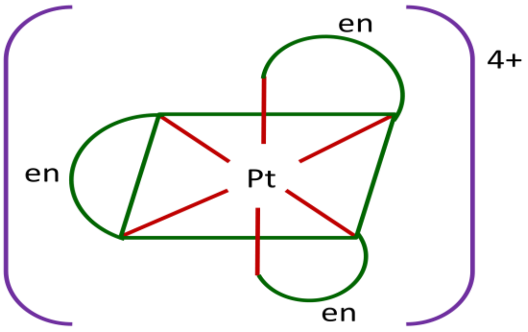


d - form

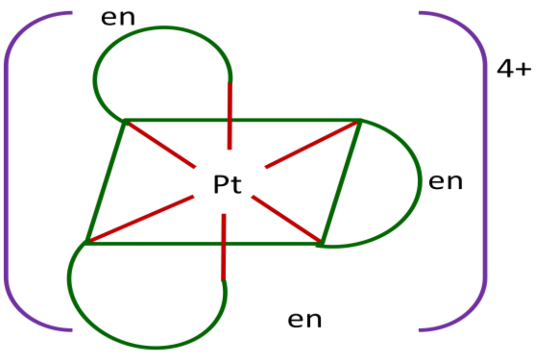


2. Complexes of $[M(aa)_3]$ type having three bidentate ligands are also unsymmetrical and gives optical isomerism.

   Example: $[Pt(en)_3]^{4+}$ gives optical isomers.



d – form



l – form

Stereo isomerism in co-ordination numbers 4 compounds:

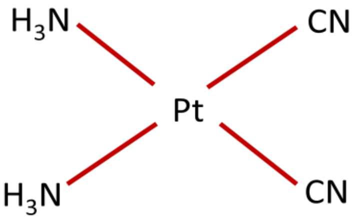
Complex compounds with co-ordination number 4 give either tetrahedral or square planar structure.

1. No isomers are possible [Ma_4], [Ma_3b] types complexes (square planar or tetrahedral)

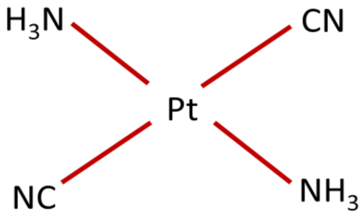
   Example: $Ni(CO)_4$, $[Cu(NH_3)_4]^{2+}$

2. [Ma_2b_2] and [Ma_2bc] complexes of some metals like Pt (II), Pd (II), Ni (II), Cu (II) give square planar structure having dsp^2 hybridization.

   Example: $[Pt(NH_3)_2(CN)_2]$ gives cis, trans isomers

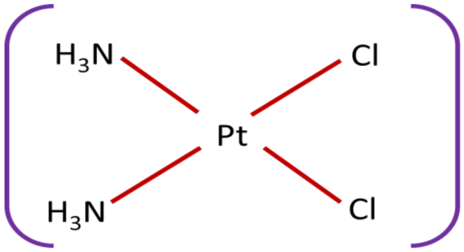


Cis

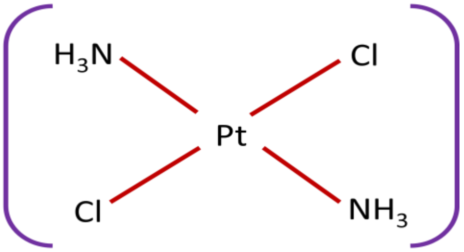


Trans

The geometrical isomers of $[Pt(NH_3)_2Cl_2]$ are



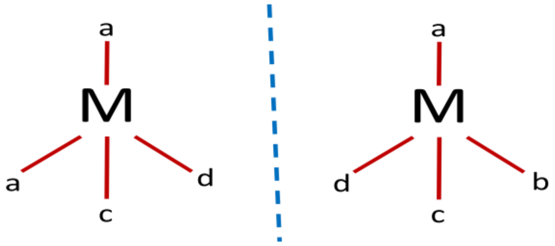
Cis – isomer



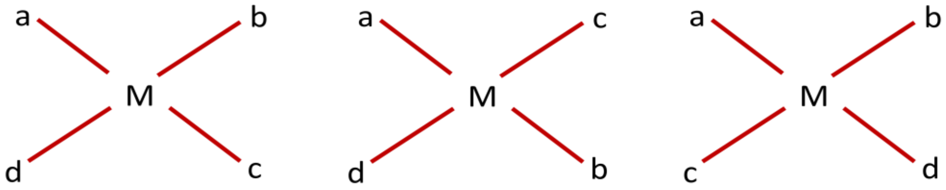
Trans – isomer

Some complex compounds of Cu, Zn, Ni can give tetrahedral structure. These metals undergo sp^3 hybridisation

$[M_{abcd}]$ type of complex gives optical isomerism, if it has tetrahedral structure.



Three geometrical isomers are possible, if they have square planar structures.



Example: $[Pt(NH_3)(Py)ClBr]$ gives three isomers.

Assignment Questions:

1. Draw the structures of optical isomers of
   a. $[Pt(en)_3]^{4+}$
   b. $[Co(en)_2Cl_2]^+$

Example Set:

1. Which one of the following square planar complexes will show cis – trans isomerism

a. Ma_4
b. Ma_3b
c. Ma_2b_2
d. M_{abcd}

Solution: c)

2. The number of isomers possible for square planar complex $K_2[PdClBr_2(SCN)]$
a. 2
b. 4
c. 5
d. 6

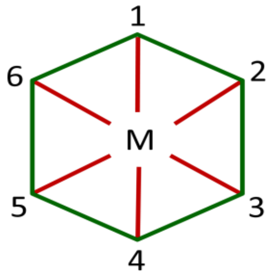
Solution: a)

3. Write an account on geometrical isomerism in complexes giving examples.

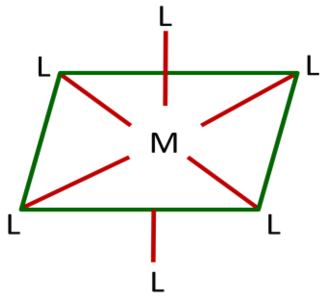
Solution:

Geometrical isomerism in co-ordination number 6 compounds:

The arrangement of six ligands in a complex around central metal ion is possible in two different ways. Those are regular hexagon and regular octahedron.



Hexagon



Octahedron

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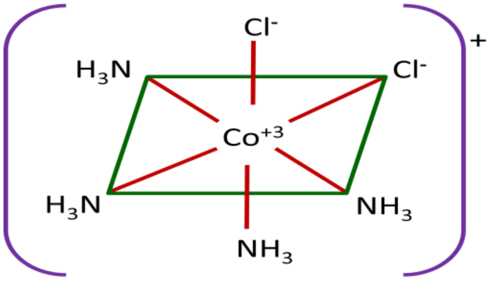
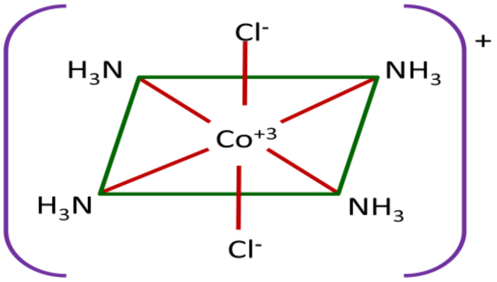
   Example: $[Co(NH_3)_4Cl_2]^+$ gives cis and trans isomers.



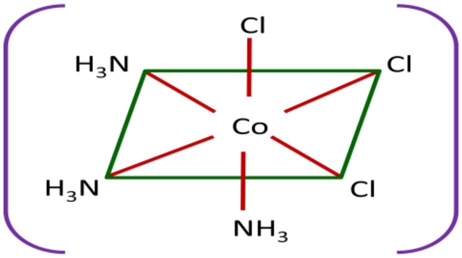
Cis



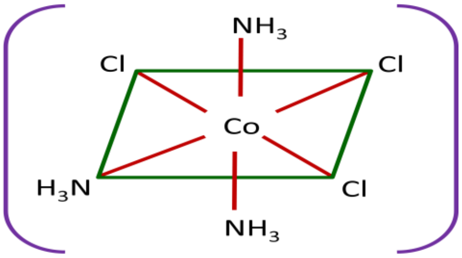
Trans

3. $[Ma_3b_3]$ type of complexes can exhibit geometrical isomerism.

   Example: $[Co(NH_3)_3Cl_3]$ gives cis – trans isomers.



Cis



Trans

Problem Set:

1. Geometrical isomerism would be expected from?

   a. $[Zn(NH_3)_2(H_2O)_2]^{2+}$
   b. $[Cu(CN)_4]^{3-}$
   c. $[Pt(NH_3)_2Cl_2]$
   d. $[Ag(NH_3)_2]^+$

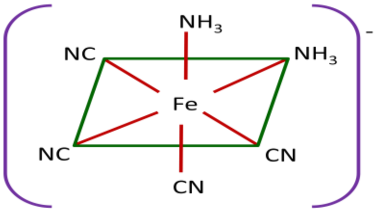
Solution: c)

2. **2.** Which of the following octahedral complexes does not show geometrical isomerism (a and b are monodentate ligands)?
   a. Ma_3b_3
   b. Ma_4b_2
   c. Ma_5b
   d. Ma_2b_4

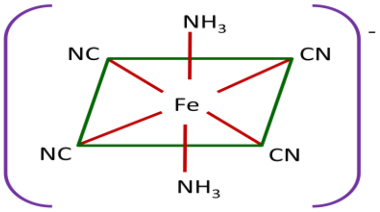
Solution: c)

3. Draw structures of the geometrical isomers of $[Fe(NH_3)_2(CN)_4]$.

Solution:



Cis



Trans

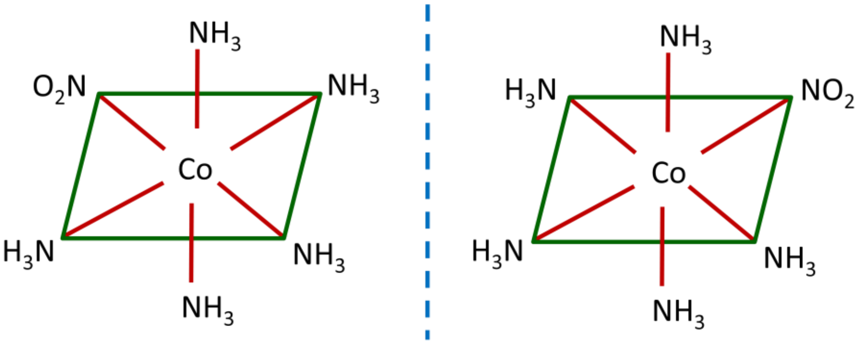
Exercise Questions:

1. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands?
2. Give evidence that $[Co(NH_3)_5Cl)SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionization isomers?
3. Platinum (II) forms square planar complexes and platinum (IV) forms octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Draw their structures.
   a. $[Pt(NH_3)_3Cl]^+$
   b. $[Pt(NH_3)Cl_5]^-$
   c. $[Pt(NH_3)_2Cl(NO_2)]$
   d. $[Pt(NH_3)_4ClBr]^{+2}$

Solutions to Exercise Questions:

1. b
2. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same w.r.t each other.

3.
   a. A pair of optical isomers



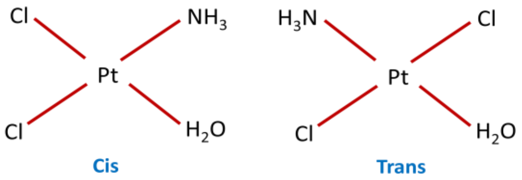
It can also show linkage isomerism

$[Co(NH_3)_5(NO_2)](NO_3)_2$ and $[Co(NH_3)_5(ONO)](NO_3)_2$

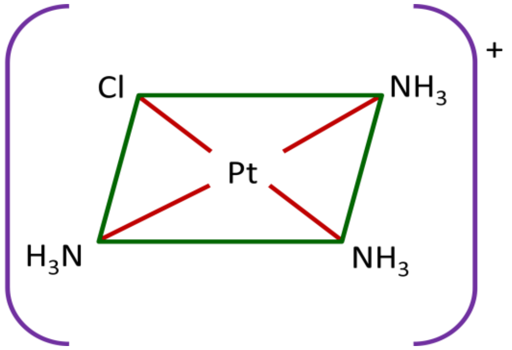
It can also show ionization isomerism

$[Co(NH_3)_5(NO_2)](NO_3)_2$ and $[Co(NH_3)_5](NO_3)](NO_2)(NO_3)$

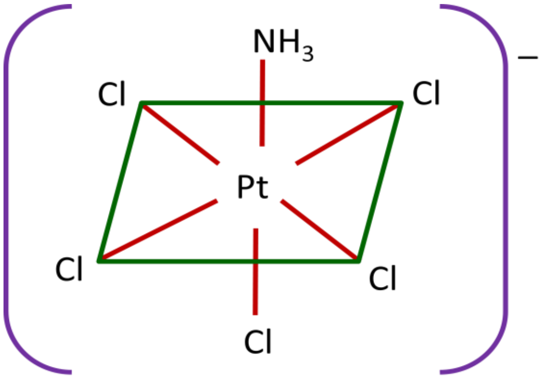
   b. Geometrical (cis-, trans-) isomers of $[Pt(NH_3)(H_2O)Cl_2]$ can exist



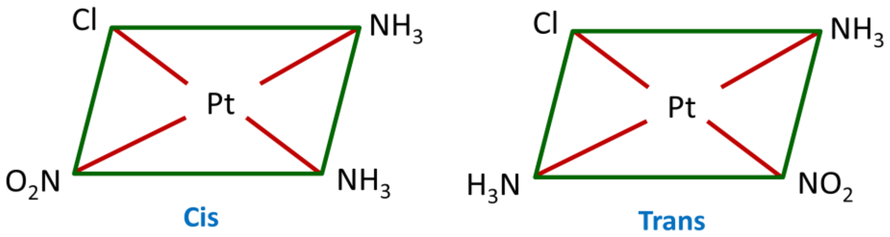
4.
   a. No isomers are possible for a square planar complex of the type Ma_3b. It is $[Ma_3b]$ type of a complex



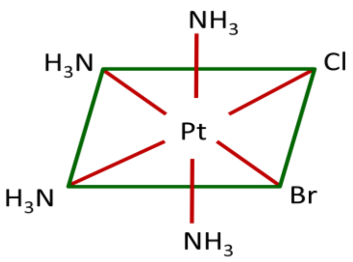
b. No isomers are possible for an octahedral complex of the type Mab_5. This is a complex of the type Ma_5b or Mab_5



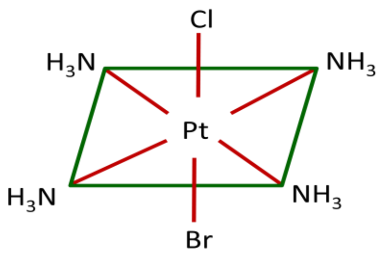
c. cis and trans isomers are possible for a square planar complex of the type Ma_2bc



d. cis and trans isomers are possible for an octahedral complex of the type Ma_4bc



Cis



Trans

5. A, B and C are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4, whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively , on treatment with concentrated H_2SO_4 identify A , B and C.

Solution:

The compound A does not react with concentrated H_2SO_4 implying that all water molecules are coordinated with Cr^{3+} ion. Hence, its structure would be $[Cr(H_2O)_6]Cl_3$. The compound B loses 6.75% of its original mass when treated with concentrated H_2SO_4. This loss is due to the removal of water molecules which is/are not directly coordinated to Cr^{3+} ion.

The mass of water molecules removed per mole of the complex

$$= \frac{6.75}{100} \text{ X molar mass of the complex}$$

$$= \frac{6.75}{100} \text{ X } 266.5 \text{ g} = 17.98 \text{ g (one mole } H_2O)$$

Compound B will be $[Cr(H_2O)_5Cl](H_2O)Cl_2$

The compound C loses 13.5 % of its mass when treated with concentrated H_2SO_4 which is twice of the mass lost by the compound B. Hence compound C will be $[Cr(H_2O)_4Cl_2](H_2O)_2Cl$.

7. The acidic, aqueous solution of ferrous ion forms a brown complex in the presence of NO_3^-, by the following two steps. Complete and balance the equations.

$[Fe\ (H_2O)_6]^{2+} + NO_3^- + H^+ \rightarrow \ldots\ldots + [Fe(H_2O)_6]^{3+} + H_2O$

$[Fe(H_2O)_6]^{2+} + \ldots\ldots \rightarrow \ldots\ldots + H_2O$

Solution:

$3[Fe\ (H_2O)_6]^{2+} + NO_3^- + 4H^+ \rightarrow NO + 3[Fe(H_2O_6)]^{3+} + 2H_2O$

$[Fe\ (H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5\ NO]^{2+} + H_2O$

8. Write the chemical reaction associated with the brown ring test.

Solution:

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$6\ FeSO_4 + 2HNO_3 + 3\ H_2SO_4 \rightarrow 3\ Fe_2(SO_4)_3 + 4\ H_2O + 2\ NO$

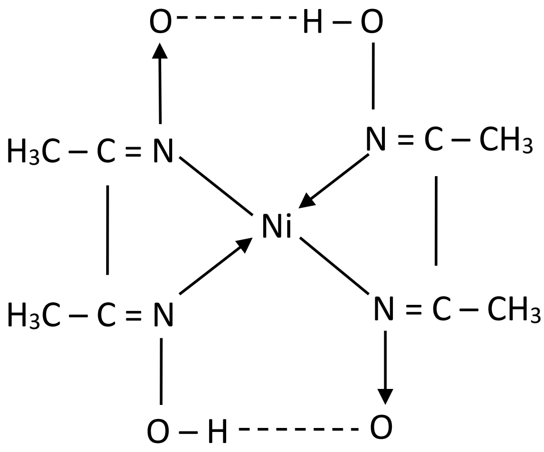
$[Fe(H_2O)_6]SO_4.H_2O + NO \rightarrow \underset{\text{(brown ring)}}{[Fe(H_2O)_5\ NO]\ SO_4} + 2\ H_2O$

9. Nickel chloride, when treated with dimethyl gyloxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following.

a) Draw the structure of the complex showing H- bonds
b) Give oxidation state of nickel and its hybridization
c) Predict the magnetic behavior of the complex.

Solution:

(a)



Bis(dimethylglyoximato) nickel (II).

(b) Charge on Ni in the complex is +2 and it is dsp^2 hybridized.

(c) Since number of unpaired electrons in Ni^{2+} is zero, the complex is diamagnetic.

10. $Fe^{3+} \xrightarrow[\text{excess}]{SCN^-} (A) \xrightarrow[\text{excess}]{F^-} (B)$

Blood red Coloration ***Colorless***

What are (A) and (B)? Give IUPAC Name of (A). Find the spin only magnetic moment of (B).

Solution:

$$\underset{}{Fe^{3+}} + \underset{\text{(excess)}}{SCN^-} \rightarrow \underset{\text{(A)(blood red)}}{[Fe\,(SCN)(H_2O)_5]^{2+}}$$

$$[Fe\,(SCN)(H_2O)_5]^{2+} + 6F^- \rightarrow [FeF_6]^{3-} + SCN^-$$

IUPAC name of A is pentaaquathiocyanato ferrate (III) ion

IUPAC name of B is hexafluoroferrate (III)

In $[FeF_6]^{3-}$ co-ordination no.of Fe = 6

In $[FeF_6]^{3-}$ oxidation state of Fe = +3

$\therefore$ It has 3 unpaired electrons, n = 5

Magnetic moment = $\sqrt{35}$ = 5.92 B.M.

11.(Colourless liquid) $MCl_4 \xrightarrow{Zn}$ Purple color compound ; M = Transition metal

$$MCl_4 \xrightarrow{Zn} \underset{\text{White fumes}}{(B)}$$

Identify (A), (B) and MCl_4. Explain color difference between MCl_4 and (A).

Solution:

(A) $[Ti(H_2O)_6]Cl_3$ (B) HCl

$$TiCl_4 \xrightarrow[\text{heat}]{\text{Zn}} TiCl_3 \xrightarrow{H_2O} [Ti(H_2O)_6]Cl3$$

Purple (A)

$$TiCl_4 + (n + 2)\, H_2O \rightarrow TiO_2\, (H_2O)_n + 4\, HCl \uparrow$$

White fumes

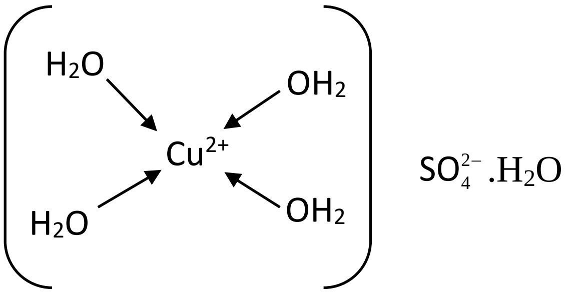
(B) $Ti^{4+} = [Ar]\, 3d^0$; $Ti^{3+} = [Ar]3d^1$

$TiCl_4$ is colorless since Ti^{4+} has no d electrons. Hence d-d transition is impossible. On the other hand, Ti^{3+} is colored due to d-d transition. Ti^{3+} absorbs greenish yellow compound of white light, hence its aqueous solution is purple which is complementary color of greenish yellow in white light.

12. The number of water molecules (s) directly bonded to the metal centre in $CuSO_4.5H_2O$ is

Solution:

The number of water molecules directly bonding to the metal centre in $CuSO_4.5H_2O$ is 4



13. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is

Solution:

Four different ligands and hence three different arrangements.