Transition Element & Coordination Compound

TRANSITION ELEMENTS & COORDINATION COMPOUND

Introduction

Definition and Electronic Configuration of Atoms

The elements lying between s and p-block elements of the periodic table are collectively known as transitional elements **(T.E.'s) :** These elements either in their atomic state or in any of their common oxidation state have partly filled (n-1) orbitals of (n-1)th main shell. In these elements the differentiating electron enters (n-1)d orbitals of (n-1)th main shell and such these are called d-block elements.

The valence shell configurations of these elements can be represented by $(n\text{-}1)d^{1-10}.ns^{0,\,1,\,2}$. The configurations clearly show that strictly, according to the definition of d-block elements, Cu, Ag and Au should be excluded from d-block elements, since these elements, both in their atomic state [with configuration $(n\text{-}1)d^{10}ns^1$] and in their + 1 oxidation state [with configuration $(n\text{-}1)d^{10}$], do not have partly filled (n-1)d-orbitals. Similarly Zn, Cd and Hg which, both in their atomic state [$(n\text{-}1)d^{10}ns^2$] and in + 2 oxidation [$(n\text{-}1)d^{10}$] do not contain partly filled (n-1)d orbitals, should also be excluded from d-block elements. Similar is the case with Pd atom with configuration $4d^{10}5s^0$. Yet, in order to maintain a rational classification of elements, these elements (viz Cu, Ag, Zn, Cd, Hg and Pd) are also generally studied with d-block elements.

All the d-block elements are classified into four series viz 3d, 4d, 5d and 6d series corresponding to the filling of 3d, 4d, 5d and 6d orbitals of (n-1)th main shell. Each of 3d, 4d and 5d series has ten elements while 6d series has at present only one element viz AC_{89} whose valence shell configuration is $6d^1\ 7s^2$.

Important Points To be remembered

(i) Electron configuration of Cr and Cu

Cr (24)	$[Ar]_{18}3ds^5s^1$
Cu (29)	$[Ar]_{18}3d^{10}4s^1$

The $3d^5s^1$ and $3d^{10}4s^1$ configuration are preferred due to greater stability of half and fully filled orbitals (HUND's Rule).

(ii) Electron configuration of second and third transition series elements is not similar to first transition series. The full explanation is beyond the scope of IIT-JEE. It can only be said this point that small energy gap with increasing atomic number is one of the reasons.

(iii) Zinc, Cd and Hg have fully filled $(n\text{-}1)d^{10}$ orbitals in their configuration.

Zn	$3d^{10}4s^2$
Cd	$4d^{10}5s^2$
Hg	$5d^{10}6s^2$

These elements exhibit oxidation state of + 2 in their compounds. In + 2 oxidation state d-orbitals are fully filled,

$Zn^{+2} - 3d^{10}$, $Cd^{+2} - 4d^{10}$, $Hg^{+2} - 5d^{10}$

Therefore, Zn, Cd and Hg do not exhibit general properties shown by transition elements but form a group (12) by themselves with similar properties.

(iv) Elements Sc, Y and La exhibit the common oxidation states + 3, in which (n – 1)d orbitals are vacant (d^0). Therefore, these elements also do not show general characteristic properties of transition elements.

(v) True transition elements, thus, are

3d	(i)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
4d	(ii)	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
5d	(iii)	Hf	Ta	W	Re	Os	Ir	Pt	Au
6d	(iv)	Rf	Db	Sg	Bh	Hs	Mt		

It is because all the above elements have partially filled (n -1)d orbitals in their atoms or in one or more of the of the chemically important ions. Therefore, these are true transition elements in the strict sense.

General Properties

(a) They all are metals.
(b) They are hard, strong, high melting, high boiling metals that conduct heat and electricity.
(c) Many are electropositive to dissolve in mineral acids, a few are noble (Pt, Au etc.)
(d) They exhibit variable oxidation states.
(e) Form paramagnetic compounds.
(f) Form variety of complex compounds.
(g) Many of the compounds are coloured.
(h) Compounds undergo hydrolysis.
(i) Many of the transition metals and their compounds act as catalyst.
(j) Form very important alloys.

Atomic and Ionic radii

The atomic and ionic radii decrease from Sc to Cu, but the variation is small. The outer most electron configuration is $(n - 1)d^X ns^2$. The screening power of d-orbitals is small and electrons are being added in inner orbitals [(n – 1)d orbitals. Therefore, change in radii, atomic and ionic both, are small.

Ionic radii

	Ti^{2+}	V^{+2}	C^{+2}	Mn^{+2}	Fe^{2+}	Co^{+2}	Ni^{2+}	Cu^{+2}	Zn^{+2}
r (Å)	0.80	0.73	0.80	0.90	0.85	0.80	0.76	0.69	0.74

In a group, the atomic and the ionic radii increase with increase in atomic number (because new orbitals are added in the configuration). It is followed in the first and the second transition series. But the radii of the third transition series elements are almost equal to the second transition series elements. The reason for this equality, in radii is the lanthanide contraction.

Radii in Å

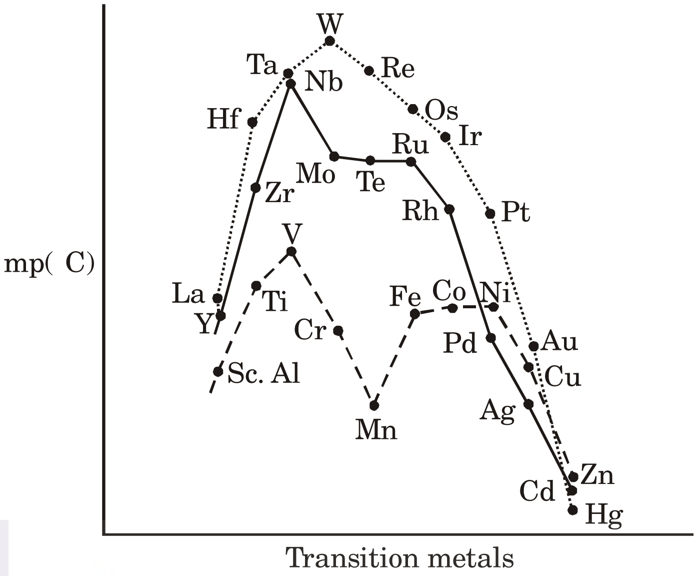
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
r (Å)	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
r (Å)	1.62	1.45	1.34	1.29	–	1.24	1.25	1.28	1.34	1.41
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
r (Å)	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

Bonding in Transition metals and its effect on properties

All transition elements are metals. They are high melting, high boiling and have high heat of atomization and high densities. All these properties show that the atoms in transition elements are held together by strong metallic bonds. The strength of metallic bond very much depends upon number of valence electrons. Larger the number of valence electrons stronger the metallic bond. In the transition elements a minimum of three electrons are present, $(n-1)d^1ns^2$. The presence of d-electrons contribute much towards metallic bonding (d – d overlap) and the strength increases with in the number of unpaired electrons in the orbitals. Also the difference between the mp and the bp is large. This indicates that metallic bond is present in molten state also.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
mp	1660	1710	1600	1260	1535	1490	1450	1083
bp	3260	3450	2660	2150	3000	2900	2730	2600

Melting points of Transition metals



The above graph shows that–

(i) 5d metals have highest mp.

(ii) mp increases with increase in the number of unpaired electron in d orbitals and then decreases, when number of unpaired electrons in d–orbitals decreases.

(iii) Mn and Tc show anomalous values.

(iv) W has highest mp.

Ionization Energy

In a period, the first ionization energy gradually increases from left to right. This is mainly due to increase in nuclear charge. Generally, the ionization energies of transition elements are intermediate between those of s and p-block elements. The first ionization potential of the 5d-elements are higher than those of 3d and 4d-elements due to poor shielding of 4f-electrons.

From 3d → 4d series, general trend is observed but not from 4d → 5d series because of incorporation of the 14 lanthanides elements between La and Hf. Third period of transition elements have the highest ionization energy. This reflects the fact that increase in radius due to addition of extra shell is compensated by the decrease in radius due to lanthanide contraction.

As the radius of 4d and 5d-elements more or less remains the same, due to which Z_{eff} of elements of 5d series is higher, which results in high ionization energy of the 5d-elements of transition series.

Oxidation states

All transition metals exhibit variable oxidation states. It arises due to removal of electrons from inner d-orbital.

Fe(26)	$[Ar]_{18}3d^6 4s^2$
Fe^{2+}	$[Ar]_{18}3d^6$
Fe^{3+}	$[Ar]_{18}3d^5$

Element and oxidation states	Electron configuration	Arrangement of outermost electrons	Unpaired electrons
Ti(22)	$[Ar]_{18}3d^2 4s^2$	$\overset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}}\quad\overset{4s}{\boxed{\uparrow\downarrow}}$	2
Ti^{2+}	$[Ar]_{18}3d^2$	$\overset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}}$	2
Ti^{+3}	$[Ar]_{18}3d^1$	$\overset{3d}{\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{}}$	1
V(23)	$[Ar]_{18}3d^3 4s^2$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\quad\boxed{\uparrow\downarrow}$	3
V^{+2}	$[Ar]_{18}3d^3$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}$	3
V^{+3}	$[Ar]_{18}3d^2$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}$	2
V^{+5}	$[Ar]_{18}$	————	0
Cr(24)	$[Ar]_{18}3d^5 4s^1$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad\boxed{\uparrow}$	6
Cr^{+2}	$[Ar]_{18}3d^4$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$	4
Cr^{+3}	$[Ar]_{18}3d^3$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}$	3
Cr^{+6}	$[Ar]_{18}$	————	0
Mn(25)	$[Ar]_{18}3d^5 4s^2$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad\boxed{\uparrow\downarrow}$	5
Mn^{+2}	$[Ar]_{18}3d^5$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	5
Mn^{+4}	$[Ar]_{18}3d^3$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}$	1
Mn^{+6}	$[Ar]_{18}3d^1$	$\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{}$	3
Mn^{+7}	$[Ar]_{18}$	————	0

Element and oxidation states	Electron configuration	Arrangement of outermost electrons	Unpaired electrons
Fe(26)	$[Ar]_{18}3d^6 4s^2$	[↑↓][↑][↑][↑][↑] [↑↓]	4
Fe^{2+}	$[Ar]_{18}3d^6$	[↑↓][↑][↑][↑][↑]	4
Fe^{3+}	$[Ar]_{18}3d^5$	[↑][↑][↑][↑][↑]	5
Co(27)	$[Ar]_{18}3d^7 4s^2$	[↑↓][↑↓][↑][↑][↑] [↑↓]	3
Co^{+2}	$[Ar]_{18}3d^7$	[↑↓][↑↓][↑][↑][↑]	3
Co^{+3}	$[Ar]_{18}3d^6$	[↑↓][↑][↑][↑][↑]	4
Ni(28)	$[Ar]_{18}3d^8 4s^2$	[↑↓][↑↓][↑↓][↑][↑] [↑↓]	2
Ni^{2+}	$[Ar]_{18}3d^8$	[↑↓][↑↓][↑↓][↑][↑]	2
Ni^{+4}	$[Ar]_{18}3d^6$	[↑↓][↑][↑][↑][↑]	4
Cu(29)	$[Ar]_{18}3d^{10} 4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓] [↑]	1
Cu^{+}	$[Ar]_{18}3d^{10}$	[↑↓][↑↓][↑↓][↑↓][↑↓]	0
Cu^{+2}	$[Ar]_{18}3d^9$	[↑↓][↑↓][↑↓][↑↓][↑]	1

Besides, the above given oxidation states, lower oxidation state (0 or + 1) are also exhibited by transition metals. But these are stable only in complexes especially with π–acid ligands. Compounds in different oxidation states differ in properties. Common observations are :

(i) Most common oxidation state is + 2 for first series. (It shows greater stability of 3d orbitals over 4s)

(ii) The + 1 state is stable (dry state) only for Cu in simple compounds.

(iii) Bonds in + 2 or + 3 states are mostly ionic.

(iv) + 2 state forms basic oxide and hydroxides.

(v) Higher oxidation states + 4, + 5, + 6, + 7 etc. form covalent compounds (MnO_4^- has covalent Mn – O bond).

(vi) Oxides (or hydroxides) in higher oxidation states are acidic

VO	Basic
V_2O_5	Acidic
CrO	Basic
CrO_3	Acidic

(vii) Higher oxidation state is more stable down a group

Fe	+ 2, + 3	Mn	+ 7, MnO_4^- S O agent
Ru	+ 4, + 6	Te	
Os	+ 8 (OsO_4)	Re	+ 7, ReO_4^- not an O agent

(viii) Higher oxidation states are found in oxygen and fluorine compounds only

Mn_2O_7, MnF_7, CrO_4^-, MnO_4^- etc.

(ix) Oxides in intermediate oxidation states are amphoteric.

$$\left.\begin{array}{r} TiO_2 \\ VO_2 \\ Mn_2O_3 \end{array}\right\} \text{Amphoteric}$$

Magnetic properties

The substances can be either paramagnetic or diamagnetic. A paramagnetic substance is one which is weakly attracted into a magnetic field and a diagmagnetic substance is one which is repelled by a magnetic field. The paramagnetic behaviour arises due to the presence of one or more singly occupied atomic orbitals, while diamagnetic behaviour is due to presence of unpaired electrons in the atomic orbitals.

It is represent as μ in Bohr magnetons,

$$\mu = \sqrt{n(n+2)} \text{ BM},$$

where n = number of unpaired electrons.

Transition metals and most of their compounds contain unpaired electrons in their different oxidation states. Therefore, they are paramagnetic.

Example 1

Compare the magnetic moments of Fe^{2+} and Fe^{3+}.

Solution :

Following the same procedure as above try to calculate the magnetic moments of the two given species

n for $Fe^{2+} = 4\mu = \sqrt{n(n+2)}$ B.M. $= \sqrt{4 \times 6} = \sqrt{24}$ B.M.

n for Fe3+= $5\mu = \sqrt{n(n+2)}$ B.M. $= \sqrt{5 \times 7} = \sqrt{35}$ B.M.

$$\frac{\mu Fe^{2+}}{\mu Fe^{3+}} = \frac{\sqrt{24}}{\sqrt{35}}$$

Example 2

Find the oxidation state of Cr in the given complex $K_2[Cr(NO)(NH_3)(CN)_4]$, $\mu = 1.73$ BM.

Solution :

$\mu = 1.73$

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

$n(n+2) = 3$

$\therefore$ $n = 1$

$\therefore$ Number of unpaired electron = 1

$\therefore$ Cr is in + 1 oxidation state.

Colour of Complex Compounds

Many ionic and covalent compounds of transition elements are coloured. In contrast compounds of the s– and p–block elements are almost always white. When light passes through a material, it is deprived of those wavelengths that are absorbed. If wavelength of the absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the complementary colour to the colour of the light absorbed. Absorption in the visible and UV regions of the spectrum is caused by changes in electronic energy. Thus, the spectra are sometimes called electronic spectra.

Colour may arise from an entirely different cause in ions with incomplete d or f-subshells. This source of colour is very important in most of the transition metal ions.

In a free isolated gaseous ion, the five d–orbitals are degenerate that is they are identical in energy. In actual practice, the ion will be surrounded by solvent molecules if it is in solution, by other ligands if it is in a complex, or by other ions if it is in a crystal lattice. The surrounding groups affect the energy of some d–orbitals more than others. Thus, the d–orbitals are no longer degenerate and at their simplest they form two groups of orbitals of different energy. Thus, in transition element ions with a partly filled d–subshell it is possible to promote electrons from one d–level to another d–level of higher energy. This corresponds to a fairly small energy difference and so light it absorbed in the visible region. The colour of a transition metal complex is dependent on how big the energy difference is between the two d–levels. This in turn depends on the nature of the ligand and on the type of complex formed. Thus, the octahedral complex $[Ni(NH_3)_6]^{2+}$ is blue, $[Ni(H_2O)_6]^{2+}$ is green and $[Ni(NO_2)_6]^{4-}$ is brown-red. The colour changes with the ligand used. The colour also depends on the number of ligands and the shape of the complex formed.

The source of colour in the lanthanides and the actinides is very similar, arising from f $\longrightarrow$ f transitions. With the lanthanides, the 4f–orbitals are deeply embedded inside the atom and are well-shielded by the 5s and 5p-electrons. The f–electrons are practically unaffected by complex formation. Hence, the colour remains almost constant for the particular ion regardless of the ligand.

Some compounds of the transition metal are white, for example Cu_2Cl_2, $ZnSO_4$ and TiO_2. In this compounds, it is not possible to promote electrons within the d–level. Cu^+ and Zn^{2+} has a d^{10} configuration and the d–level is completely filled. Ti^{4+} has a d^0 configuration and d–level is empty. In the series Sc(III), Ti(IV), V(V), Cr(VI) and Mn(VII), these ions may all be considered to have an empty d–subshell; hence d–d spectra are impossible and they should be colourless. However, as the oxidation state increases, these states become increasingly covalent. Rather than forming highly charged simple ions, they form oxoions like TiO^{2+}, VO_2^+, VO_4^{3-}, CrO_4^{2-} and MnO_4^-. VO_2^+ is pale yellow, but CrO_4^{2-} is strongly yellow coloured and MnO_4^- has an intense purple colour in solution, though the solid is almost black. The colour arises by charge transfer mechanism. In MnO_4^-, an electron is momentarily transferred from O to the metal, thus momentarily changing O^{2-} to O^- and reducing the oxidation state of the metal from Mn(VII) to Mn(VI). Charge transfer requires the energy levels on the two different atoms to be fairly close. Charge transfer always produces more intense colours than the colours generated due to d–d transitions. Charge transfer is also possible between metal–ion and metal–ion as seen in prussian blue, $Fe_4[Fe(CN_6)]_3$.

The s and p–block elements do not have a partially filled d–subshell, so there cannot be any d–d transitions. The energy required to promote an s or p–electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus, compounds of s and p–block elements are typically not coloured.

Complex Formation

The transition elements have a huge tendency to form coordination compounds with Lewis Base, i.e., with groups which are able to donate an electron pair. These groups are called ligands. A ligand may be a neutral molecule such as NH_3 or ion such as Cl^- or CN^- etc.

$$Co^{3+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{3+}$$

$$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$$

The reason for transition elements are good in forming complexes are :

(i) Small size and high effective nuclear charge

(ii) Availability of low lying vacant d–orbitals which can accept lone pair of electrons donated by a ligand.

Catalytic Properties

Transition metals and their compounds are known to act as good catalyst due to the following reasons :

(i) Due to the variable oxidation states, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (Intermediate compound formation theory)

(ii) In some cases the finely divided metals or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact (Adsorption theory)

1.	$TiCl_3$	Used as Natta catalyst for coordination polymerization of ethene to polyethene
2.	V_2O_5	Converts SO_2 to SO_3 in the contact process for making H_2SO_4
3.	MnO_2	Used as a catalyst to decompose $KClO_3$ to give O_2
4.	Fe	Used in Haber–Bosch process for making NH_3 (as promoter)
5.	Pd	Catalyst for hydrogenation
6.	Pt/PtO	Adam catalyst used for reduction of triple bond to double bond
7.	$CuCl_2$	Deacon process or making Cl_2 from HCl
8.	Ni	As Raney nickel for hydrogenation reaction

Formation of Alloys

As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and often have high melting point.

Interstitial Compound

Transition metals form a number of interstitial compounds. In which they take up atoms of small size e.g. H, C, B and N in the vacant spaces in their lattices. The presence of these atoms results in decrease in malleability and ductility of the metals but increases their tensile strength.

Zinc, Cadmium and Mercury

(a) These are the elements of group 12 having electronic configuration (n – 1) d^{10} ns^2 and + 2 oxidation state. In these elements the d-subshell is full, hence these are regarded as non-transition elements which is evident from the following characteristics.

  (i) They do not show variable valency except mercury.

  (ii) Many of their compounds are white

  (iii) Their melting and boiling points are very low.

(b) Unique structure of mercurous ion – Unlike Zn and Cd, Hg exhibits + 1 well as + 2 oxidation state. Thus mercurous ion exists are Hg_2^{2+} and not as Hg^+.

(c) Structure of mercurous ion – It consists of two atoms linked by a covalent and $(-Hg-Hg-)^{2+}$ and explains the diamagnetic character of mercurous ions if it was Hg^+ (presence of an unpaired electron in 6s orbital), mercurous salt should have been paramagnetic.

(d) Anomalous behaviour of mercury,

  (i) It is liquid at ordinary temperature while Zn and Cd are solids.

  (ii) It is less electropositive than hydrogen and therefore does not displace hydrogen from acids while Zn and Cd does.

  (iii) It does not form hydroxide or peroxide, while Zn and Cd do so

  (iv) Mercuric oxide, on heating, gives metallic mercury and oxygen while oxides of Zn and Cd are stable towards heat.

  (v) $HgCl_2$ is covalent while zinc and Cd chlorides are ionic. With NH_3, $HgCl_2$ gives a white ppt. of $Hg(NH_2)Cl$, while Zn and Cd salts from complex ions, $[M(NH_3)_4]^{2+}$.

COMPOUNDS OF IRON

Ferrous Sulphate or Green vitriol ($FeSO_4.7H_2O$)

The name green vitriol is given because of its green colour.

(i) On heating, green $FeSO_4.7H_2O$ gives a white anhydrous salt. On strong heating it forms Fe_2O_3, SO_2 and SO_3.

$$FeSO_4.7H_2O \xrightarrow{\text{heating}} \underset{\text{White}}{FeSO_4} + 7H_2O$$

$$2FeSO_4 \xrightarrow{\text{heating}} \underset{\text{Brown}}{Fe_2O_3} + SO_2\uparrow + SO_3\uparrow$$

(ii) With nitric oxide, ferrous sulphate turns brown due to the formation of nitroso ferrous sulphate $FeSO_4.NO$.

Ferric Oxide – Fe_2O_3 (Reddish Brown)

Preparation :

(i) In lab, it can be prepared by heating ferrous sulphate or ferric hydroxide.

$$2FeSO_4 \longrightarrow Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O$$

(ii) It is also obtained as a by product in the manufacture of sulphuric acid from iron pyrites.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Properties :

It is a reddish brown powder, insoluble in water but soluble in acid. Amphoteric in nature and reacts with acids and alkalies.

$$NaFeO_2 + H_2O \longrightarrow Fe_2O_3 + NaOH$$

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$

$$Fe_2O_3 + Na_2CO_3 \longrightarrow \underset{\text{Sodium ferrate}}{2NaFeO_2} + CO_2$$

Ferric Chloride (Red Black)

Anhydrous ferric chloride, Fe_2Cl_6 is obtained by heating iron filing in a stream of dry chlorine. The compound sublimes and collects in the form of deep red-black flaky crystals.

$$2Fe + 3Cl_2 \rightarrow Fe_2Cl_6$$

It dissociates on heating above 973 K first into $FeCl_3$ and then into $FeCl_2$ and Cl_2.

$$Fe_2Cl_6 \xrightarrow{973K} 2FeCl_3 \xrightarrow{\Delta} 2FeCl_2 + Cl_2\uparrow$$

Its aq. solution is acidic in nature due to hydrolysis.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + HCl$$

It is soluble in water, alcohol and ether and forms hydrates. The most common hydrate of iron $FeCl_3.6H_2O$ is yellow in colour.

Ferrous Ammonium Sulphate (Mohr's Salt), $FeSO_4.(NH_4)_2SO_4.6H_2O$

It is prepared by crystallising a solution containing equivalent amounts of iron (II) sulphate and ammonium sulphate. It is a pale green crystaline compound which does not effloresce like ferrous sulphate.

COMPOUNDS OF COPPER

Cupric chloride, $CuCl_2.2H_2O$ (Green Crystal)

Preparation :

$$2Cu + 4HCl + O_2 \longrightarrow 2\,CuCl_2 + 2H_2O$$

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

Properties :

(i) It is deliquescent compound and is readily soluble in water. The dilute solution is blue but concentrated solution is, however, green. The blue colour is due to complex cation $[Cu(H_2O)_4]^{2+}$

(ii) On heating forms Cu_2Cl_2

$2CuCl_2 \rightarrow Cu_2Cl_2 + Cl_2$

(iii) $CuCl_2 + Cu \rightarrow Cu_2Cl_2$

$2CuCl_2 + 2H \rightarrow Cu_2Cl_2 + 2HCl$

$2CuCl_2 + SnCl_2 \rightarrow Cu_2Cl_2 + SnCl_4$

Copper Sulphate (Blue Vitriol), $CuSO_4.5H_2O$

Preparation :

(i) It is prepared by dissolving copper (II) oxide or copper (II) carbonate in dil. sulphuric acid.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$$

On evaporation, solution is concentrated, blue crystals of $CuSO_4.5H_2O$ separate out on cooling.

(ii) On a large scale, copper (II) sulphate is obtained by passing air through a hot mixture of copper and dil. H_2SO_4.

$$2Cu + 4H^+ + O_2 \longrightarrow 2Cu^{2+} + 2H_2O$$

Properties :

(i) On heating $CuSO_4.5H_2O$ loses water molecules as follows.

$$CuSO_4.5H_2O \xrightarrow[\text{Strong } 100°C]{373\,K} CuSO_4.H_2O \xrightarrow[150°C]{423\,K} CuSO_4 \longrightarrow CuO + SO_3$$

(ii) $CuSO_4 + 6NH_4OH \rightarrow [Cu(NH_3)_4]\,(OH)_2 + (NH_4)_2SO_4 + 4H_2O$

Schweitzer's reagent

(iii) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2\downarrow + I_2\uparrow + 2K_2SO_4$.

A mixture of copper sulphate and lime, under the name of Bordeaux mixture is used as a fungicide in agriculture.

Cupric Oxide, CuO (Black)

It is called black oxide of copper.

Preparation :

(i) It is prepared by heating following copper compounds :

$$Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$$

$$2Cu + O_2 \longrightarrow 2CuO$$

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

$$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$$

(ii) On commercial scale, it is obtained by heating malachite, which is found in nature.

$$CuCO_3.Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$$

Properties :

It is black powder, insoluble in water but dissolves in acids. It is reduced to metallic copper by reducing agents like H, C and Co.

$$CuO + H_2 \longrightarrow Cu + H_2O$$

Compounds of Silver

Silver Nitrate, $AgNO_3$ (Lunar Caustic)

Preparation :

$$3Ag + \underset{\text{(Dilute)}}{4HNO_3} \xrightarrow{\text{Heat}} 3AgNO_3 + 2H_2O + NO\uparrow$$

Properties :

(i) $$2AgNO_3 \xrightarrow{\text{Heat}} 2AgNO_2 + O_2$$

$$2AgNO_3 + \xrightarrow{\text{red Heat}} 2Ag + 2NO_2 + O_2$$

(ii) It reacts with iodine in two ways.

(a) When iodine is in excess

$$5AgNO_3 + 3I_2 + 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3$$

(b) When $AgNO_3$ is in excess

$$6AgNO_3 + 3I_2 + 3H_2O \longrightarrow AgIO_3 + 5AgI + 6HNO_3$$

(iii) When treated with alkali, it gives precipitate of silver oxide, which dissolves in excess of NH_4OH

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{brown ppt}}{Ag_2O \downarrow} + 2NaNO_3 + H_2O$$

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O \downarrow + 2NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

(iv) $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$

$Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow 2Na_3[Ag(S_2O_3)_2$

Silver Bromide, AgBr

Preparation :

By adding $AgNO_3$ solution to soluble bromide solution.

Properties :

(i) It is insoluble in water and conc. acid but soluble in excess of strong solution of ammonia (e.g. AgCl is soluble in dilute solution of NH_4OH, AgI is insoluble in NH_4OH solution.

(ii) Silver halides, are also soluble in KCN and hypo solutions

(iii) On heating, it melts to red liquid.

(iv) It is used as the light sensitive material in photographic films. It is the most sensitive silver halide to photo-reduction.

COMPOUNDS OF ZINC

Zinc Oxide – ZnO

Preparation :

It is prepared by burning zinc metal in air or by heating the zinc carbonate or zinc nitrate.

$$2Zn + O_2 \longrightarrow 2ZnO$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$$

Properties :

Zinc oxide is a white power and becomes yellow on heating and the colour disappears on colling.

(i) It dissolves readily in mineral acids and forms the corresponding salts with alkalies, it forms zincates $[Zn(OH)_4]^{2-}$

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH + H_2O \longrightarrow Na_2[Zn(OH)_4]$$

(ii) It reduced to metallic zinc when heated with carbon or hydrogen

$$ZnO + C \longrightarrow Zn + CO$$

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

Chloride of Lead

Lead chloride, $PbCl_2$

Preparation :

Prepared by slow direct combination or by the action of boiling concentrated HCl on lead (its oxide or carbonate).

$$Pb + Cl_2 \xrightarrow{\Delta} PbCl_2$$

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2 \uparrow$$

$$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$

The usual method of preparation is to precipitate $PbCl_2$ as a white crystalline precipitate by adding a soluble chloride to a lead salt solution.

$$Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2 + 2NaNO_3$$

Properties :

It is sparingly in cold water but more soluble in hot water. In concentrated solutions of Cl^- ions, it dissolves forming complex ions, $[PbCl_3]^-$ and $[PbCl_4]^{2-}$.

Lead tetrachloride, $PbCl_4$

Properties :

$PbCl_4$ is a yellow only liquid. it is heavy and dissolves in organic solvents. It is a covalent and unstable compound, readily decomposes on heating.

$$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2 \uparrow$$

It is easily hydrolysed by water and forms a double salt with NH_4Cl.

$$PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$$

Lead tetrabromide and tetraiodide are unknown, so the dihalides dominate the halogen chemistry of lead.

OXIDES OF LEAD

Lead monoxide, PbO

Preparation :

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 \uparrow + O_2 \uparrow$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2 \uparrow$$

Dry air has no action on lead, but in moist air it tarnishes, forming a film of oxide first and finally basic carbonate, which protects it from further action. On heating in air or oxygen, it forms litharge, PbO. But prolonged heating gives red lead, Pb_3O_4.

$2Pb + O_2 \longrightarrow 2PbO$

$6PbO + O_2 \longrightarrow 2Pb_3O_4$

Properties :

(i) At room temperature, it is a yellow amorphous powder that is insoluble in water but dissolves in acids as well as alkalies.

$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$

$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$

Thus, it behaves as an amphoteric oxide. The acetic properties being rather feeble.

(ii) It is easily reduced to the metallic state by hydrogen, carbon or carbon monoxide.

(iii) In the red form of PbO, the Pb(II) ions are four co-ordinate but the O^{2-} ions around the Pb(II) lie in a square.

Lead dioxide, PbO_2

Preparation :

Action of cold concentrated nitric acid on red lead gives lead nitrate in solution while lead dioxide is thrown as a chocolate powder.

$Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2 \downarrow + 2Pb(NO_3)_2 + 2H_2O$

Properties :

(i) It is a chocolate coloured powder insoluble in water and dilute acids.

(ii) It liberates oxygen on gentle heating.

$2PbO_2 \longrightarrow 2PbO + O_2 \uparrow$

(iii) At 440 C, it is converted into red lead, Pb_3O_4.

$$3PbO_2 \xrightarrow{440°C} Pb_3O_4 + O_2 \uparrow$$

(iv) PbO_2 is an amphoteric oxide.

$PbO_2 + 4HCl \longrightarrow PbCl_2 \downarrow + Cl_2 \uparrow + 2H_2O$

$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 \downarrow + 2H_2O + O_2 \uparrow$

(v) It is a good oxidizing agent. It oxidizes manganous salts to pink permanganic acid when boiled in nitric acid solution.

$2MnSO_4 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$

(vi) In alkaline medium, chromium hydroxide is oxdized to yellow chromate by PbO_2.

$2Cr(OH)_3 + 10KOH + 3PbO_2 \longrightarrow 2K_2CrO_4 + 3K_2PbO_2 + 8H_2O$

The maroon form of lead(IV) oxide, PbO_2, crystallizes in the rutile structure. This oxide is a component of the cathode of a lead-acid battery.

Red lead, Pb_3O_4

Preparation :

Roasting of litharge in air at 450 C gives a bright red powder.

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

It is also known as sindur.

Properties :

Sparingly soluble in water but dissolves in dilute nitric acid.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 \downarrow + 2H_2O$$

The above reaction indicates that red lead may be considered as plumbous ortho plumbate, $2PbO.PbO_2$.

POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

When chromite $[Fe(CrO_2)_2]$ is fused with Na_2CO_3 in air (or $NaNO_3$) sodium chromate Na_2CrO_4 is formed.

$$2\,Fe\,(CrO_2)_2 + 4\,Na_2CO_3 + O_2 \xrightarrow{\Delta} 4Na_2CrO_4 + 4CO_2 + Fe_2O_3$$

The fused mass is extracted with water and filtered. The filterate is concentrated and acidified with H_2SO_4. It produces $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

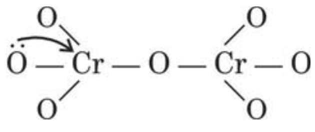
The sodium is concentrated and then saturated with KCl orange crystal of $K_2Cr_2O_7$ separates out.

$$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium dichromate is hygroscopic but not the $K_2Cr_2O_7$. Therefore, $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$.

Properties :

(i) It is orange crystalline solid. Soluble in water, colour is due to charge transfer.



(ii) With alkali (i.e. pH > 7) it turns yellow due to the formation of chromate.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

(iii) When $K_2Cr_2O_7$ is heated it gives O_2

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

But $(NH_4)_2Cr_2O_7$ on heating gives N_2

$$\underset{\text{(Orange)}}{(NH_4)_2CrO_7} \xrightarrow{\Delta} \underset{\text{(Green)}}{Cr_2O_3} + 4H_2O + N_2$$

(iv) Solid $K_2Cr_2O_7$ with conc. H_2SO_4 forms a red solution. The red is dichromic acid.

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow H_2Cr_2O_7 + K_2SO_4$$

When the solution is concentrated bright orange (or red) crystals of CrO_3 are formed.

$$\text{Red solution} \xrightarrow{\text{Crytallisation}} CrO_3$$

That is $K_2Cr_2O_7$ is dehydrated by conc. H_2SO_4 to bright orange solid CrO_3. The ($K_2Cr_2O_7$ + conc. H_2SO_4) mixture is used for cleaning glassware as it is highly oxidizing.

(v) $K_2Cr_2O_7$ as oxidizing agent

$K_2Cr_2O_7$ is a good oxidizing agent in acid medium and reacts as

$$Cr_2O_7^{-2} + 6e + 14H^+ \longrightarrow \underset{\text{(green)}}{2Cr^{3+}_{(aq)}} + 7H_2O \qquad E = 1.36 \text{ V}$$

It oxidizes :

$Fe^{2+} \longrightarrow Fe^{3+}$

(H_2S) $S^{-2} \longrightarrow S$

$I^- \longrightarrow I_2$

$SO_2 \longrightarrow SO_4^{-2}$

Reactions :

$$\begin{array}{l} Cr_2O_7^{-2} + 6e + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O \\ Fe^{2+} \longrightarrow Fe^{3+} + e] \times 6 \\ \hline Cr_2O_7^{-2} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{+3} + 6Fe^{2+} + 7H_2O \end{array}$$

Thus SO_2 and H_2S turn orange solution of $K_2Cr_2O_7$ (acidic) to green due to the reduction of $Cr_2O_7^{-2}$ ion to $Cr^{+3}_{(aq)}$.

(vi) $K_2Cr_2O_7$ as qualitative reagent

To test H_2O_2 : $K_2Cr_2O_7$ (or K_2CrO_4) in acid solution + amyl alcohol, when treated with H_2O_2, CrO_5 is formed. It dissolves in amyl alcohol making deep blue solution.

$$CrO_4^{-2} + 2H^+ + 2H_2O_2 \longrightarrow CrO_5 + 3H_2O$$

$$CrO_7^{-2} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$$

CrO_5 + amyl alcohol $\longrightarrow$ deep blue

CrO_5 is not stable in aq. medium and decomposes to Cr^{+3} and O_2.

$4CrO_5 + 12H^+ \longrightarrow 4Cr^{+3} + 7O_2 + 6H_2O$

(vii) $K_2Cr_2O_7$ as quantitative reagent

The acidic solution of K_2Cr_2O is an oxidizing agent. The solution is a primary standard as :

(a) $K_2Cr_2O_7$ prepared very pure

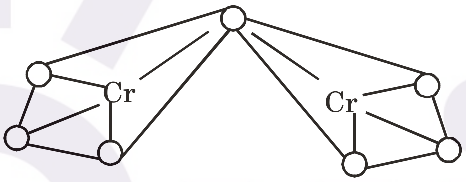
(b) Solution of K_2Cr_2O stable

(c) The solution is much less readily reduced by organic substances

(d) Not affected by light.

Structure of $Cr_2O_7^{-2}$

The structure involves two tetrahedra joined through O–atom. Cr is sp^3 in $Cr_2O_7^{-2}$. The structure is



Cr – O (bridging) = 1.78 Å

Cr – O (terminal) = 1.61 Å

$\underset{\text{(bridging)}}{\mathrm{Cr}\overset{\mathrm{O}}{\diagup\diagdown}\mathrm{Cr}} = 131$

The Cr – O bonds have multiple bond nature due to (d – p) interaction.

POTASSIUM PERMANGNATE ($KMnO_4$)

When MnO_2 (Pyrolusite) is fused with KOH and KNO_3 (O.A.) K_2MnO_4 (green) is formed. It (K_2MnO_4) is oxidized by Cl_2 to $KMnO_4$.

$$MnO_2 + 2KOH + KNO_3 \xrightarrow[\text{(ii) water}]{\text{(i) fuse}} K_2MnO_4 + KNO_2 + H_2O$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

Oxidation of K_2MnO_4 may be caused electrolytically (better).

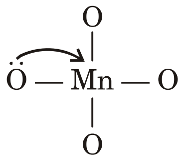
Anode reaction $2MnO_4^{-2} \longrightarrow 2MnO_4^{-} + 2e^{-}$

Cathode reaction $2H_2O + 2e^- \longrightarrow 2HO^- + H_2$

Oxidized solution on concentration gives violet (deep purple) crystals of $KMnO_4$ (The crystals however, appear almost black).

Properties :

(i) Violet solid colour is due to charge transfer.



(ii) $KMnO_4$ is soluble in water and the solution is red violet.

(iii) $KMnO_4$ is widely used as a laboratory oxidizing agent. It is oxidant in neutral, acid and basic solutions. The reaction are :

(a) In acid medium :

$$\underset{\text{(pink)}}{MnO_4^-} + 5e + 8H^+ \longrightarrow \underset{\text{(colourless)}}{Mn^{+2}} + 4H_2O,\ E = 1.54\ V$$

(b) Neutral or dil. alkali :

$$MnO_4^- + 3e + 2H_2O \longrightarrow \underset{\text{(black solid)}}{MnO_2} + 4HO^-$$

(c) conc. alkali :

$$MnO_4^- + e \longrightarrow MnO_4^{-2}$$

Hydrochloric acid (HCl) is not used to create acid medium as MnO_4^- oxidizes Cl^- to Cl_2 ($Cl^- - Cl_2$, E = 1.34 V).

$$MnO_4^- + 5Cl^- + 8H^+ \longrightarrow Mn^{+2} + {}^5/_2Cl_2$$

In acid medium MnO_4^- oxidizes,

$S^{-2} \longrightarrow S$

$Fe^{2+} \longrightarrow Fe^{3+}$

$I^- \longrightarrow I_2$

$NO_2^- \longrightarrow NO_3^-$

$SO_2 \longrightarrow SO_4^{-2}$

$H_2O_2 \longrightarrow O_2$

$C_2O_4^{-2} \longrightarrow CO_2$

and itself is reduced to Mn^{+2}. Therefore, pink solution of $KMnO_4$ is decolourised in all of the above reactions. In the case of S^{-2}, white S precipitates.

$$MnO_4^- + 5e + 8H^+ \longrightarrow Mn^{+2} + 4H_2O] \quad 2$$

$$C_2O_4^{-2} \longrightarrow 2CO_2 + 2e\ ] \quad 5$$

$$2\,MnO_4^- + 16H^+ + 2C_2O_4^{-2} \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

Other reactions can be written in the same way.

$FeSO_4$ solution (light green) decolourises MnO_4^- solution in acid medium. But if excess MnO_4^- is added a black ppt. is formed. It is due to oxidation of Mn^{+2} to MnO_2.

$$\underset{\text{(pink)}}{MnO_4^-} + 5Fe^{2+} + 8H^+ \xrightarrow{\text{acid}} \underset{\text{(colourless)}}{Mn^{+2}} + 5Fe^{3+} + 4H_2O$$

$$Mn^{+2} + 2H_2O \longrightarrow MnO_2 + 2e + 4H^+] \quad 3$$

$$MnO_4^- + 3e + 4H^+ \longrightarrow MnO_2 + 2H_2O\ ] \quad 2$$

$$3\,Mn^{+2} + 2\,MnO_4^- + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

In alkaline solution (I^-) is oxidized by MnO_4^- to iodate (IO_3^-)

$$I^- + 6HO^- \longrightarrow IO_3^- + 6e + 3H_2O$$

$$MnO_4^- + 3e + 2H_2O \longrightarrow MnO_2 + 4HO^-\ ] \quad 2$$

$$I^- + 2\,MnO_4^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$$

(iv) $KMnO_4$ as volumetric reagent

Standard acidic solution of $KMnO_4$ is oxidizing agent and is used as a volumetric reagent. But it is a secondary standard (not a primary standard like $K_2Cr_2O_7$), because $KMnO_4$ converts to MnO_2 in water and oxidizes H_2O to O_2. The reaction is, however, very slow.

$$MnO_4^- + 3e + 4H^+ \longrightarrow MnO_2 + 2H_2O] \quad 2$$

$$H_2O \longrightarrow 2H^+ + 2e + {}^1/_2\ O_2\,] \times 3$$

$$2\,MnO_4^- + 2H^+ \longrightarrow 2MnO_2 + H_2O + {}^3/_2\ O_2$$

It is for the above reason; $KMnO_4$ solution in volumetric analysis is standardized before every use.

Titration with $KMnO_4$ solution does not require indicator. It acts as a self-indicator because even a drop of dil. $KMnO_4$ imparts pale pink colour to the solution.

It is used for the estimation of iron, H_2O_2, NO_2^-, MnO_2 (in pyrolusite) etc.

Example 3

50 mL aqueous solution of $FeSO_4$ required 12 mL of 0.02 M $KMnO_4$ in acid medium for complete oxidation. Calculate the molarity of ferrous sulphate solution.

Solution :

Balanced redox reaction for oxidation of ferrous ion to ferric ion is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

1 mole of $KMnO_4$ = 5 mole of $FeSO_4$

$$\text{Number of moles of } KMnO_4 \text{ used} = \frac{MV}{1000}$$

$$= \frac{0.02 \quad 12}{1000} = 2.4 \times 10^{-4}$$

$\therefore$ Number of moles of $FeSO_4$ in 50 mL solution $= 5 \quad 2.4 \quad 10^{-4}$

$= 12.0 \quad 10^{-4}$

$$\text{Thus, molarity of } FeSO_4 = \frac{n}{V} \times 1000$$

$$= \frac{12 \times 10^{-4}}{50} \times 1000 = 0.024$$

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f-Block Elements

These are also referred as 'inner transition elements'. These are two series of elements, formed by filling of 4f and 5f-subshells. The elements in which 4f-subshell is filled are called **lanthanides** and the elements in which 5f-subshell is filled are called **actinides.**

Electronic Configuration

(i) Lanthanides

Ce (Z = 58) to Lu (Z = 71) – (6th period)

General configuration : [Xe] $4f^{1-14}\ 5d^{0-1}\ 6s^2$

(ii) Actinides

Th (Z = 90) to Lr (Z = 103) – (7th period)

General configuration [Rn] $5f^{1-14}\ 6d^{0-1}\ 7s^2$

General Characteristics

Lanthanides exhibits (III) oxidation state (some elements show (II) and (IV) also).

Many of the compounds are coloured. In the Lanthanide elements, there is a regular decrease in the radius as the period is traversed. This is known as **"Lanthanide contraction".**

The reason for this contraction is that as we proceed from one element to the next element in the Lanthanide series, the nuclear charge, i.e., atomic number increases by one unit and one electron is added to the 4f- energy shell. On account of the very diffused shapes of f-orbitals, the 4f electrons shield each other quite poorly from the nuclear charge. Thus, the effect of nuclear charge increase is more than the changed shielding effect. This brings valence shell nearer to the nucleus and hence the size of atom or ions goes on decreasing as we move in the series.

CO-ORDINATION COMPOUND

Some Basic terms

To be read from NCERT book

Classification of Ligands

There are two ways ligands can be classified :

(I) Classification based on donor and acceptor properties of the ligands.

- (i) Ligands having one or more lone pair(s) of electrons are further classified as
  - (a) Ligands containing vacant π-type orbitals can receive back donated π-electrons from the metal ion in low oxidation state. Such ligands have filled donor orbitals in addition to unsaturated organic molecules. Such ligands have filled donor orbitals in addition to vacant π-acceptor orbitals. Thus, in the complexes formed by such ligands, both metal and the ligand act as donor and acceptors $\left(M \underset{\sigma}{\overset{\pi}{\rightleftharpoons}} L\right)$.
  - (b) Ligands, which have no vacant orbitals to get back donated electrons from the metal. e.g. H_2O, NH_3, F^- etc.
- (ii) Ligands having no lone pair of electrons but π-bonding electrons. e.g. C_2H_4, C_6H_6 $C_5H_9^-$ etc.

(II) Classification based on te number of donor atoms present in the figuers :

Such ligands are of following types :

(i) Monodentate or unidentate ligands

The ligands that can co-ordinate to the central metal ion at one site only are called monodentate ligands. Such ligands may be neutral molecules, negatively or positively charged ions. For example,

$$F^-, Cl^-, CN^-, OCN^-, H_2O, NH_3, NO_2, NO^+, NH_2NH_3^+ \text{ etc.}$$

A monodentate ligand having more than one lone pair of electrons may simultaneously co-ordinate with two or more atoms and thus acts as a bridge between the metal ions. In such a case, it is called a bridging ligand and the complex thus formed is known as bridged complex. For example, OH^-, F^-, NH_2^-, CO, O^{2-}, SO_4^{2-} etc.

(ii) Bidentate ligand : Ligands, which have two donor atoms and have the ability to co-ordinate with the central atom/ion at two different sites are called bidentate ligands. For example,

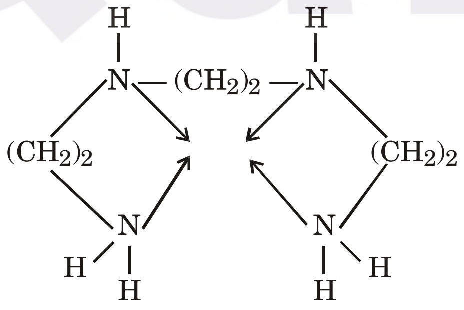
$$H_2\ddot{N}-(CH_2)_2-\ddot{N}H_2 \text{ (ethylenediamine)}$$

(iii) Tridentate ligands : The ligands having three coordination sites are called tridentate ligands. For example,

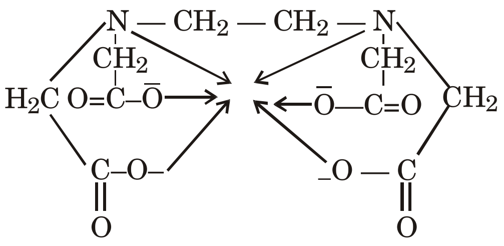
e.g. $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H-CH_2-\ddot{N}H_2$

Diethylenetriamine

(iv) Polydentate ligands : The ligands having four or more co-ordination sites are called polydentate ligands. For example,



Triethylenetetramine
(trine)



Ethylenediamine
tetraacetate ion (EDTA)

(v) Ambidentate ligands : They have two or more donor atoms but, while forming complexes only one donor atom is attached to the metal ion. The examples of such ligands are CN^-, NO_2^- NCS^-, NCO^- etc.

(vi) **Chelating ligands :** When a bidentate or a polydentate ligand is attached through two or more donor atoms to the same metal ion forming a ring structure, the ligand is called chelating ligand.

The chelating ligands form more stable complexes than ordinary unidentate ligands.

IUPAC NOMENCLATURE OF COMPLEXES

The following rules are used for naming all types of complexes :

(1) In case of ionic complexes, the cationic part is named first followed by the anionic part, irrespective of the fact, whether cation or anion or both are complex.

(2) In naming of complex ion, the ligands are namd first in the alphabetical order followed by name of the metal ion.

(3) When there are several ligands of the same type then prefix di, tri, tetra, penta are provided to the ligands. If in ligand's name any of this prefix is already present, then to avoid confusion bis, tris etc. are provided rather than di, tri etc. and ligand's name is placed in paranthesis.

(4) Name of all negative ligands ends with 'O' while the name of all positively charged ligands ends with '-ium'. Neutral ligands have no special ending.

Name of negative ligands

Ligand	Name	Ligand	Name
F^-	Fluoro	NH_2^-	Amido
Cl^-	Chloro	NO_2^-	nitro
Br^-	Bromo	NO_3^-	nitrato
I^-	Iodo	$S_2O_3^{2-}$	thiosulphato
O^{2-}	Oxo	SO_4^{2-}	Sulphato
O_2^{2-}	Peroxo	CO_3^{2-}	Carbonato
OH^-	Hydroxo	SCN^-	Thiocynato
CN^-	Cyano	SO_3^{2-}	Sulphito
NC^-	Isocyanido	CH_3COO^-	Acetato
N^{3-}	Nitrido	H^-	Hydrido
N_3^-	azido	S^{2-}	Sulphide

Note : Negative organic ligand having –yl suffix is NOT replaced by – O.

Eg. CH_3^- — methyl

$CH_3 — CH_2^-$ ethyl

 — cyclopentadienyl

Name of positive ligands

NO^- — nitrosonium

NO_2^+ — nitronium

$NH_2NH_3^+$ — hydrazinium

(5) Usually common names are provided to the neutral ligands except :

H_2O – Aqua / Auqo

NH_3 – ammine

CO – carbonyl

NO – Nitrosyl

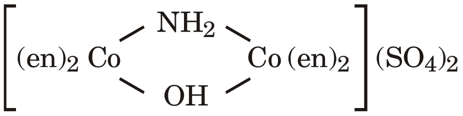
(6) Oxidation state of Central metal as is represented by roman numerals including zero immediately after metal's name in small bracket (paranthesis).

In case of naming of complex anion, central metal atom has suffix – ate along with its English/Latin name. But in case of complex cation or complex neutral molecule, central metal atom has no specific suffix.

Usually latin names are used for those metals of which chemical symbol is derived from their latin name except

	English name	Latin name
Hg	Mercury	Hydragesium
Sb	Antimony	Stibine
W	Tungston	Wulfrum

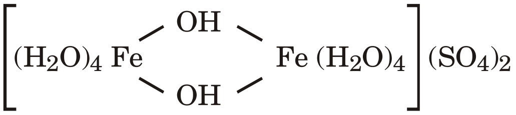
(7) In case of polynuclear or bridging complex compound (having 2 or more bridging compounds) a prefix µ – before the name of each different bridging group is added. Two or more bridging groups of the same type are indicated by di-µ –, tri – µ – etc. When a bridging ligand is attached to more than two metal atoms or ions, this is indicated by a subscript to µ.

(a) 

$$\left[(en)_2Co\begin{matrix}NH_2\\ \\ OH\end{matrix}Co(en)_2\right](SO_4)_2$$

Bis(ethylenediamine) Cobalt (III)– µ–amido – µ – hydroxo – bis(ethylene diamine)cobalt (III)sulphate

(b)



Tetraaquoiron (III) – di – μ – hydroxo – tetraaquoiron (III) sulphate

(8) For deciding the alphabetical order of ligands, the first letter of the ligand's name is to be considered and prefixes di, tri, tetra, bis etc. are not considered.

Some Examples :

$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum (IV) Chloride
$[Co(NH_3)_4(H_2O))Cl]Cl$	Tetraamineaquochlorocobalt (II) chloride
$[Cr(H_2O)_4Cl_2]^+$	Tetraaquodichlorochromium (III) ion
$[Co(NH_3)_5(NCS)]Cl_2$	Penta amineisothiocyanatocobalt (III) chloride
$[Ni\ (CN)_4]^{2-}$	Tetracyanonickelate (II) ion
$Na_3[CO(NO_2)_6]$	Sodium hexanitro cobaltate (III)
$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosyl ferrate (II)
$Fe(CO)_5$	Pentacarbonyliron (0)
$Ni(DMG)_2$	Bis (dimethylglyoximato) nickel (II)

Example 1

Give the systematic names for the following coordination compounds :

1. $\mathbf{[Cr(NH_3)_3(H_2O)_3]Cl_3}$

Answer :

triamminetriaquachromium(III) chloride

Solution :

The complex ion is inside the parentheses, which is a cation.

The amine ligands are named before the aqua ligands according to alphabetical order.

Since there are three chlorides binding with the complex ion, the charge on the complex ion must be + 3 (since the compound is electrically neutral).

From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the the ligands are neutral molecules. Therefore, the oxidation number of chromium must be same as the charge of the complex ion, + 3.

2. $[Pt(NH_3)_5Cl]Br_3$

Answer : pentaamminechloroplatinum (IV) bromide

Solution :

The complex ion is a cation, the counter anion is the 3 bromides.

The charge of the complex ion must be + 3 since it bonds with 3 bromides.

The NH_3 are neutral molecules while the chloride carries – 1 charge.

Therefore, the oxidation number of platinum must be + 4.

3. $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$

Answer : dichlorobis (ethylenediamine) platinum (IV) chloride

Solution : ethylenediamine is a bidentate ligand, the bis-prefix is used instead of di-.

4. $[Co(H_2NCH_2CH_2NH_2)_3]_2\ (SO_4)_3$

Answer : tris(ethylenediamine)cobalt (III) sulfate

Solution :

The sulfate is the counter anion in this molecule. Since it takes 3 sulfates to bond with two complex cations, the charge oneach complex cation must be + 3.

Since ethylenediamine is a neutral molecule, the oxidation number of cobalt in the complex ion must be + 3.

Again, remember that you never have to indicate the number of cations and anions in the name of an ionic compound.

5. $K_4[Fe(CN)_6]$

Answer : potassium hexacyanoferrate(II)

Solution :

potassium is the cation and the complex ion is the anion.

Since there are 4 K^+ binding with a complex ion, the charge on the complex ion must be – 4.

Since each ligand carries – 1 charge, the oxidation number of Fe must be + 2.

The common name of this compound is potassium ferrocyanide.

6. $Na_2[NiCl_4]$

Answer : sodium tetrachloronickelate(II)

Solution :

The complex ion is the anion so we have to add the suffix –ate in the name of the metal.

7. $Pt(NH_3)_2Cl_4$

Answer : diamminetetrachloroplatinum (IV)

Solution :

This is a neutral molecule because the charge on Pt^{+4} equals the negative charges on the four chloro ligands.

If the compound is $[Pt(NH_3)_2Cl_2]Cl_2$, eventhough the number of ions and atoms in the molecule are identical to the example, it should be named : diamminedichloroplatinum (II) chloride, a big difference.

8. $Fe(CO)_6$

Answer : pentacarbonyliron (0)

Solution :

Since it is a neutral complex, it is named in the same way as a complex cation. The common name of this compound, iron carbonyl, is used more often.

9. $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$

Answer : ammoniumdiaquabis (oxalato) nickelate(II)

Solution :

The oxalate ion is a bidentate ligand.

10. $[Ag(NH_3)_2][Ag(CN)_2]$

Answer : diamminesilver(I) dicyanoargentate(I)

WERNER'S THEORY

When aqueous ammonia is added to a solution of cobalt dichloride, $CoCl_2$, a blue precipitate forms of the corresponding hydroxide, $Co(OH)_2$, which dissolves on the addtion of an excess of ammonia to give a solution that immediately begins to absorb oxygen and turn brown. From the oxidized solution, the following compounds can be isolated :

	Composition	**Colour**
(I)	$CoCl_3.6NH_3$	Orange-yellow
(II)	$CoCl_3.5NH_3.H_2O$	Pink
(III)	$CoCl_3.5NH_3$	Purple

A great many other compounds of this type can be prepared, (i) by starting with other cobalt salts, and (ii) by carrying out further reactions with the compounds first obtained. Among these other compounds are two other chlorides :

(IV)	$CoCl_3.4NH_3$	Violet
(V)	$CoCl_3.4NH_3$	Green

At first sight, the properties of compounds (I) - (V) are very puzzling :

(i) All of them fail to give a brown precipitate of $Co(OH)_3$ when treated with sodium hydroxide solution - a property expected of compounds containing the Co^{3+} ion. Only on boiling does a precipitate form.

(ii) All of them fail to give ammonium chloride when treated with concentrated hydrochloric acid - a reaction that would be expected of a compound containing ammonia. Only on boiling with sodium hydroxide is ammonia evolved.

(iii) While all of them give a precipitate of silver chloride when treated with silver nitrate in aqueous solution, the amount that is precipitated in the cold is in some cases less than expected, as shown in the table below. In these cases the full amount is only obtained by leaving the solution to stand for a long time or by boiling it.

(iv) The five compounds give different numbers of ions in solution, as judged from (a) the electrical conductivities of their solution in comparison with those of other electrolytes, (b) the extent to which they depress the freezing point of water. The number of ions judged to be present are shown in the table below.

		Moles of AgCl precipitated per mole	**Number of ions present in solutions per $CoCl_3$**
(I)	$CoCl_3.6NH_3$	3	4
(II)	$CoCl_3.5NH_3.H_2O$	3	4
(III)	$CoCl_3.5NH_3$	2	3
(IV)	$CoCl_3.4NH_3$	1	2

These properties, and those of many other compounds of a similar kind, were brilliantly rationalized by Alfred Werner in 1893. He proposed what is now referred to as his "coordination theory", for which he was awarded a Nobel prize in 1913. Its principal postulates are as follows :

The first theory was called the Werner's theory of co-ordination compounds.

(1) Metals possess two types of valencies :

(a) **Primary valency or ionizable valency :** It is also referred to oxidation state. Primary valences were obvious from the stoichiometries of simple compounds such as $NiCl_2$, $Fe_2(SO_4)_3$ and $PtCl_2$.

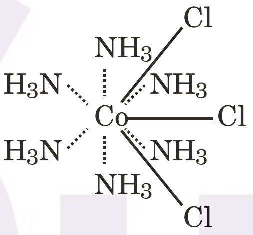
(b) **Secondary valency :** The valency which a metal atom or cation exercises towards neutral molecules or negative groups (ligands) in the formation of complex ions. The secondary valency is also called the coordination number. New materials were frequently observed when other, independently stable substances, e.g. H_2O, NH_3 and KCl, were added to these simple compounds giving, for example, $NiCl_2.\ 4H_2O$, $Co_2(SO_4)_3.12NH_3$ or $PtCl_2.2KCl$. Such species were called complex compounds, in recognition of the stoichiometric complications they represented, and were considered characteristic of certain metallic elements. The number of species considered to be added to the simple compounds give rise to the concept of secondary valence.

Example : In $[Pt(NH_3)_6]Cl_4$ secondary valency of Pt is 6

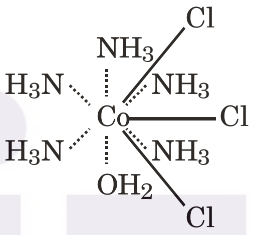
(2) Primary valencies are satisfied by negative ions, secondary valencies may be satisfied by negative ions or neutral molecules.

(3) Ligands satisfying secondary valencies are directed towards fixed positions in space giving a definite geometry to the complex, but the primary valencies are non-directional. Six valencies are directed towards a regular octahedron while four are directed towards either a tetrahedral manner or square planar.

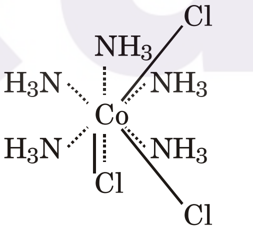
On the basis of postulates (1) and (2) & (3), Werner formulated compounds (I)–(IV) as shown diagrammatically below. Ordinary valency bonds are designated by black lines (———) and bonds between neighbouring atoms by dotted lines (...........). The cobalt atoms have their ordinary valency of three (as in CoF_3) and are given a coordination number of six. The other atoms are given coordination numbers to match (e.g. four for the nitrogen atom in NH_3, leaving one for the cobalt).



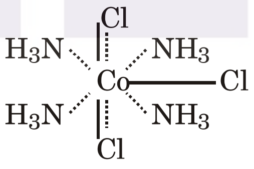
$CoCl_3.6NH_3$



$CoCl_3.5NH_3.H_2O$



$CoCl_3.5NH_3$



$CoCl_3.4NH_3$

Now if in these formulations the black lines are taken to be ionic bonds, and the dotted and double lines are taken to be bonds of a non-ionic character, the properties of compounds (I)–(IV) given above are fully explained. Thus (I) and (II) would be expected to give three Cl^- ions in solution, (III) only two, and (IV) only one. This leads to the customary formulations :

(I) $[Co(NH_3)_6]Cl_3$ containing the $[Co(NH_3)_6]^{3+}$ ion;

(II) $[Co(NH_3)_5H_2O]Cl_3$ containing the $[Co(NH_5)_6H_2O]^{3+}$ ion;

(III) $[CoCl(NH_3)_5]Cl_2$ containing the $[CoCl(NH_3)_5]^{2+}$ ion;

(IV) $[CoCl_2(NH_3)_4]Cl$ containing the $[CoCl_2(NH_3)_4]^+$ ion.

Example 2

A, B & C are three complexes of chromium (III) with the empirical formula $H_{12}O_6\ Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4 where as complexes B and C lose 6.75% & 13.5% of their original mass respectively on treatment with concentrated H_2SO_4. Identify A, B & C.

Solution :

A = $(Cr(H_2O)_6]Cl_3$

$[Cr(H_2O_6]Cl_3 + H_2SO_4 \longrightarrow$ No reaction because in it all H_2O molecules are present in coordinate sphere.

B = $[Cr(H_2O)_5Cl]Cl_2.\ H_2O$

$[Cr(H_2O)_5Cl]Cl_2.\ H_2O + H_2SO_4 \longrightarrow$ One mole of H_2O is removed because its is present outside the coordination sphere)

Molecular wt of complex = 266.5

$$\therefore \quad \%\ \text{loss} = \frac{18}{266.5} \times 100 = 6.75\%$$

C = $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

$[Cr(H_2O)_4Cl_2]Cl.2H_2O + H_2SO_4 \longrightarrow$ Two mole of H_2O are removed

(Because these are present outside the coordination sphere

$$\therefore \quad \%\ \text{loss} = \frac{2 \times 18}{266.5} \times 100 = 13.50\%$$

Example 3

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 hybridisation of chromium in each case. Also calculate their magnetic moments (spin - only value).

Solution :

Formula of A is $[Cr(NH_3)_4ClBr]Cl + AgNO_3 \longrightarrow AgCl \downarrow$ (white)

Formula of B is $[Cr(NH_3)_4Cl_2]Br + AgNO_3 \longrightarrow AgBr \downarrow$ (yellow)

Cr is in + 3 oxidation state i.e. $3d^3$ system

Therefore the hybridisation of Cr is sp^3d^2 and spin only magnetic moment.

$$\mu_S = \sqrt{n(n+2)}\text{BM}$$

$$\mu_S = \sqrt{3(3+2)}\text{BM} = 3.87\ \text{BM}$$

VALENCE BOND THEORY

To be read from NCERT book

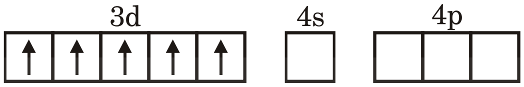
Example 4

The magnetic moment of $[MnBr_4]^{2-}$ is 5.9 B.M. What is the geometry of this complex ion?

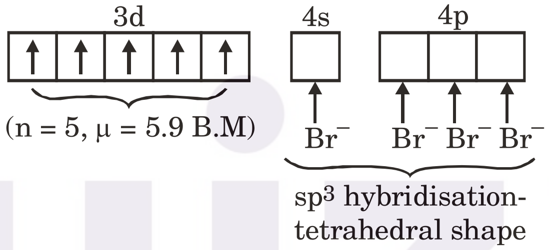
Solution :

Since the coordination number of 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 BM. Shows that it should be tetrahedral in shape rather than square-planar.

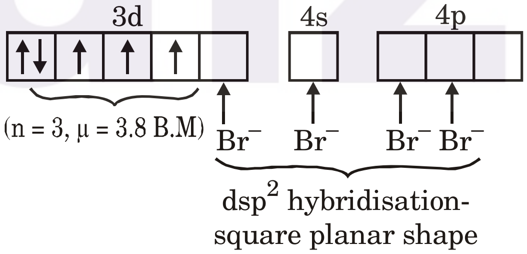
(a) Mn^{2+} ion ($3d^5$)



(b) $[MnBr_4]^{2-}$ (sp^3 hybridisation– tetrahedral shape)



(c) $[MnBr_4]^{2-}$ (dsp^2 hybridisation– square planar shape)



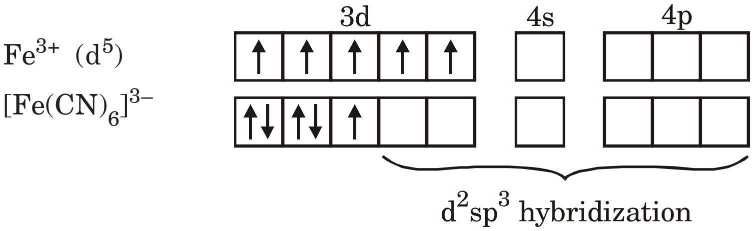
Example 5

How would you account for the following ?

- **(a)** **$[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN_6]^{4-}$ is diamagnetic.**
- **(b)** **$Ni(CO)_4$ possesses tetrahedral geometry while $[Ni(CN)_4]^{2-}$ is square planar.**
- **(c)** **$[Ni(CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic.**

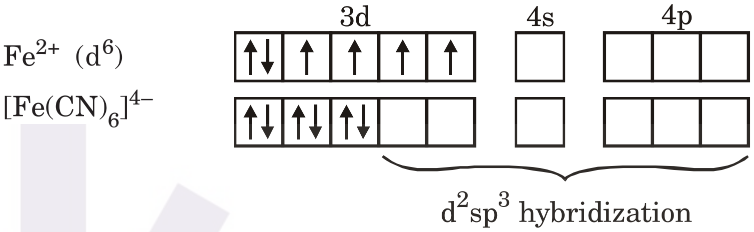
Solution :

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



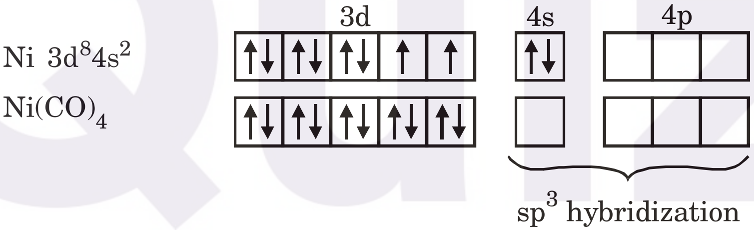
One d–orbital is singly occupied, hence it is weakly paramagnetic in nature.

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

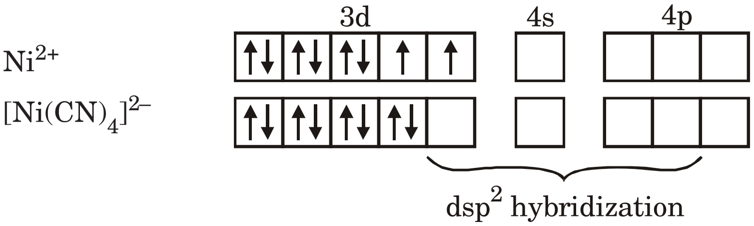


All orbitals are doubly occupied, hence it is diamagnetic in nature.

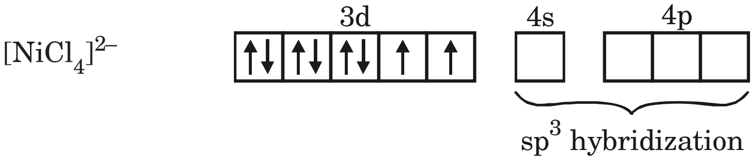
(b) In the formation of $Ni(CO)_4$, nickel undergoes sp^3 hybridization, hence it is tetrahedral in shape.



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



In $[Ni(CN)_4]^{2-}$, all orbitals are doubly occupied, hence it is diamagnetic; while in $[Ni(Cl_4]^{2-}$, two orbitals are singly occupied, hence it is paramagnetic in nature.

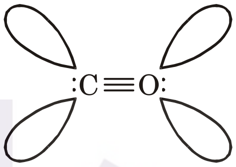


Strong field ligands like CN^-, CO, en, NO_2^- have very strong electron donating tendency, hence electrons of central metal ion pair up against Hund's rule and low spin complexes are formed.

Important points on Back bonding

Back bonding is more dominant than σ bonding in carbonyl complexes.

- If back bonding increases, electrons in π orbitals of CO increases, thus its bond order decreases, consequently bond length increases and vice versa.
- Shape of anti bonding orbital of CO is



Therefore back bonding takes place with dry orbital metal which is identical in shape.

Example 6

In the following compounds, which has greater bond length of CO ?

$[V(CO)_6]^-$ & $[Mn(CO)_6]^+$

Solution :

V = [Ar] $[4s^2]$ $[3d^3]$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }\boxed{\ }$

Mn = [Ar] $[4s^2]$ $[3d^5]$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

V^- = $\boxed{\uparrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Mn^+ = $\boxed{\uparrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

V can easily donate the electron to CO through backbonding as compared to Mn has it has half of orbital.

So backbonding is greater with vandium thus, CO has greater bond length in $[V(CO)_6]^-$.

Example 7

How will you distinguish between the following isomer pairs

(a) (i) $[CoBr(NH_3)_5]SO_4$ and

(ii) $[Co(SO_4)(NH_3)_5]Br$

(b) **(i)** **$[Cr(H_2O)_6]Cl_3$ and**

  (ii) **$[CrCl(H_2O)_5]Cl_2H_2O$**

(c) **(i)** **Cis $[PtCl_2(NH_3)_2]$ and**

  (ii) **trans $[PtCl_2(NH_3)_2]$**

(d) **The two enantiomers of $[CoCl_2(en)_2]^+$**

Solution :

(a) Isomer (i) gives white ppt of $BaSO_4$ with $BaCl_2$ whereas isomer (ii) does not form a precipitate with $BaCl_2$.

(b) The water molecule in isomer (ii) is lost easily on heating leading to weight loss whereas the water molecule in isomer (i) are not easily, being coordinated to the central atom.

(c) Cis isomer (i) has dipole moment, the trans isomer (ii) does not.

(d) One isomer is dextrorotatory whereas the other is laevorotatory.

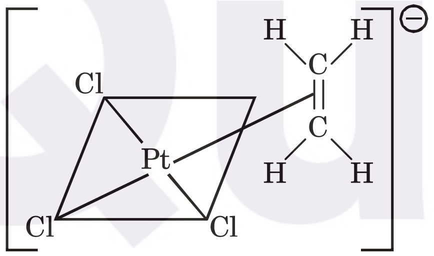
Example 8

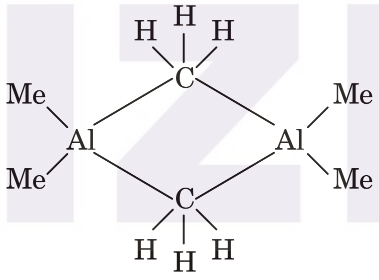
Draw structure of

(i) **Zeise's salt anion $[PtCl_3(\eta^2 - C_2H_4)]^-$**

(ii) **$[Al(CH_3)_3]_2$.**

Solution :





Example 9

Write down the formulae of the following coordination compounds.

(i) **Hexaaqua Iron (II) sulphate**

(ii) **Potassium tetracyanonickelate (III)**

(iii) **Potassium trioxalatoaluminate (III)**

(iv) **Chloronitrodiammineplatinum (II)**

(v) **Potassium hexacyanoferrate (II)**

(vi) **Chlorodiammineplatinum (II) ion**

(vii) **Dichlorobis (enthylenediamine) cobalt (III) ion**

(viii) Dichlorotetraamminecobalt (III) ion

(ix) Potassium pentacyanonitrosylcobaltate (III)

(x) Sodium ethylnediaminetetraacetato chromate (II)

Solution :

(i) $[Fe(H_2O)_6]SO_4$

(ii) $K[Ni(CN)_4]$

(iii) $K_3[Al(C_2O_4)_3]$

(iv) $[PtCl(NO_2)(NH_3)_2]$

(v) $K_4[Fe(CN)_6]$

(vi) $[PtCl(NH_3)_2]^+$

(vii) $[CoCl_2(en)_2]^+$

(viii) $[CoCl_2(NH_3)_4]^+$

(ix) $K_2[Co(CN)_5NO]$

(x) $Na_2[Cr(CH_3COO)_4(en)]$

Example 10

A solution containing 0.319 g of complex $CrCl_3.6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 ml of 0.125 M NaOH. 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 Cl^- ions outside = milliequivalent of HCl formed

= milliequivalent of NaOH used

$= 28.5 \quad 0.125$

$= 3.56$

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

1 mole of complex will give 3 mole of Cl^-, i.e. all the three Cl atoms are outside the co-ordination sphere. Thus, the complex is $[Cr(H_2O)_6Cl_3$.

Example 11

(A), (B) and (C) are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_{13}Cr$. All the three complexes have water and chloride ions 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 weight, respectively, on treatment with concentrated H_2SO_4. Identify the octahedral complexes (A), (B) and (C).

Solution :

(A) : $[Cr(H_2O)_6]Cl_3$ (Violet)

(B) : $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (Green) Molecular weight = 266.5

(C) : $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (Dark green)

Compound (A) contains six water molecules as co-ordinated water and thus, does not lost H_2O on treatment with H_2SO_4. Compound (B) contains five water molecules as co-ordinated water and one molecule as lattice water which is lost to H_2SO_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 H_2SO_4 to show a loss of 13.5%.

Example 12

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

$K_2[Cr(NO)(NH_3)(CN)_4]$; $\mu = 1.73$ B.M.

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

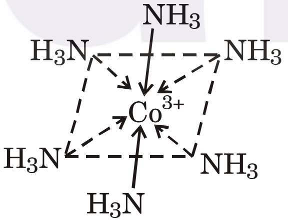
Solution :

(a) Potassium amminetetracyanonitrosoniumchromate (I)

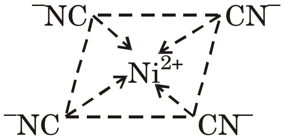
Cr is in + 1 oxidation state and possess d^2sp^3 hybridisation with one unpaired electron.

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

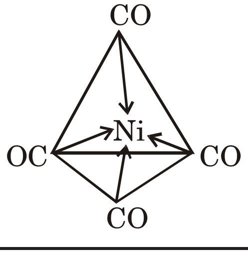
(b) $[Co(NH_3)_6]^{3+}$: Co^{3+} is d^2sp^3 hybridised to show octahedral shape.



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



$[Ni(CO)_4]$: Ni is sp^3 hybridised to show tetrahedral shape.

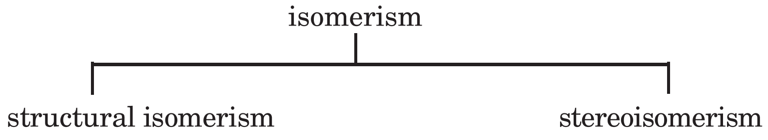


CRYSTAL FIELD THEORY

To be done from NCERT

ISOMERISM :

Two or more substances having the same molecular formula but different structural or spatial arrangements are called isomers. They are of two types :



structural isomerism

(i) ionization isomerism
(ii) Coordination isomerism
(iii) Linkage isomerism
(iv) Hydrate isomerism
(v) Ligand isomerism

stereoisomerism

(i) Geometrical or cis-trans isomerism
(ii) optical isomerism

Structural isomerism :

This type of isomerism due to the difference in structures of coordination compounds.

(i) **Ionization isomerism :** Complexes that have the same empirical formula and are produced by the interchange of the position of the ligands inside the complex zone and outside the complex zone are called ionisation isomers. They give different ions on ionization. For example

$$[Co(NH_3)_4Cl_2]NO_2 \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + NO_2^-$$

$$[Co(NH_3)_4Cl(NO_2)] \rightleftharpoons [Co(NH_3)_4Cl(NO_2)]^+ + Cl^-$$

(ii) **Coordination isomerism :**

Ionic coordination compounds that contain complex cations and anions can exist as isomers if the ligands associated with the two metal atoms are exchanged. For example :

(1) $[Pt(NH_3)_4]\ [PtCl_6]$ and $[PtCl_2(NH_3)_4]\ [PtCl_4]$
(2) $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Cr(NH_3)_6]\ [Co(CN)_6]$

(iii) **Linkage isomerism :** Isomerism which results when a given ligand is joined to the central atom through different atoms of the ligand. For example

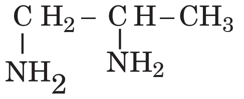
$[Co(NH_3)_5(NO_2)]Cl_2$
and $[Co(NH_3)_5(ONO)]Cl_2$

Here, the ligand NO_2^- may attach with the central ion either through O-atom or through N-atom.

(iv) **Hydrate isomerism :** This type of isomerism arises due to the different position of water molecules inside and outside the coordination sphere. For example

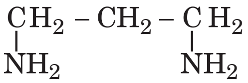
$[Cr(H_2O)_6]Cl_3$ and	$[Cr(H_2O)_5Cl]Cl_2.H_2O$
Violet colour	Blue green colour

(v) **Ligand isomerism :** Some ligands themselves are capable of existing as isomers, for example diaminopropane can exist both as i.e.


$CH_2(NH_2)-CH(NH_2)-CH_3$

1,2–diaminopropane

and


$CH_2(NH_2)-CH_2-CH_2(NH_2)$

1, 3-diaminopropane

when these ligands are associated to form complexes, these complexes are isomers of each other.

e.g. $[Co\ (1,\ 2\text{-diaminopropane})_2Cl_2]^+$ and

$[Co\ (1,\ 3\text{-diaminopropane})_2Cl_2]^+$

Stereo isomerism

Stereo isomerism in coordination compounds arises due to different spatial arrangement of ligands around the central metal ion.

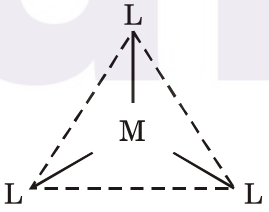
Geometrical isomerism

In complexes ligands may occupy different sites. When the ligands in question occupy adjacent positions it is called ‘Cis’ (Cis, Latin, meaning “On this side”) and when they occupy opposite sites, it is called ‘trans’ (trans, Latin meaning “across”). Therefore, geometrical isomerism is also called ‘Cis – Trans ‘isomerism. This type of isomerism is not possible for complexes of CN 2 or 3 or for CN 4, tetrahedral complexes.

L — M — L

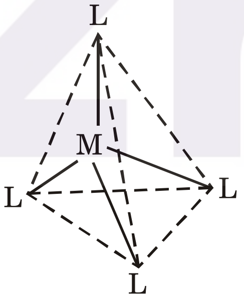
CN2

(Linear)



CN3

(Δr PL)

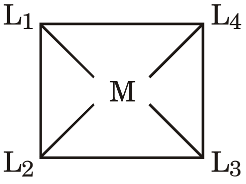


CN4

(Td)

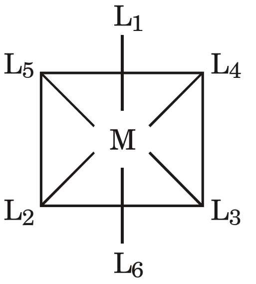
In this complexes all ligand positions are adjacent not opposite. However, cis-trans isomerism is common in square planar and octahedral complexes.

(a) Square planar



	L_1, L_2
L_1, L_3	L_2, L_3
L_2, L_4	L_3, L_4
	L_1, L_4
opposite (trans)	adjacent (Cis)

(b) Octahedral



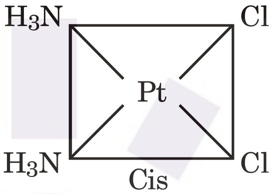
	L_1, L_2	L_6, L_3
L_1, L_6	L_1, L_3	L_6, L_2
L_2, L_4	L_1, L_4	L_6, L_5
L_3, L_5	L_1, L_5	L_6, L_4
opposite (trans)	adjacent (Cis)	

(1) CN–4 Sq planar complexes

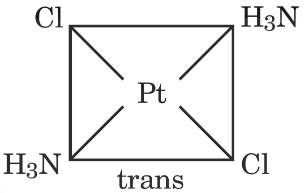
The following types of four coordinated sq. planar complexes show cis-trans isomerism.

(i) MA_2B_2

$[Pt(NH_3)_2Cl_2]$ diammine dichloro Pt (II)



Cis



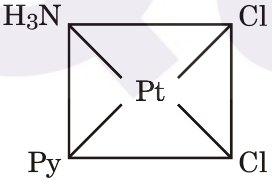
trans

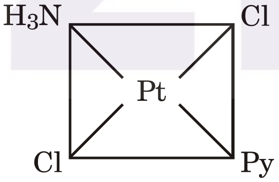
(Cl^- and NH_3 ligands are adjacent) (Cl^- and NH_3 ligands are opposite)

Cis and trans isomers may be distinguished by dipole moment measurement

(ii) $MABX_2$

$[Pt(NH_3)PyCl_2]$ (Py = pyridine C_5H_5N)



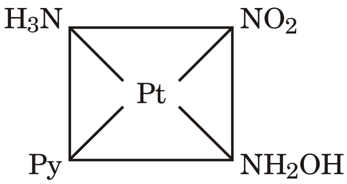


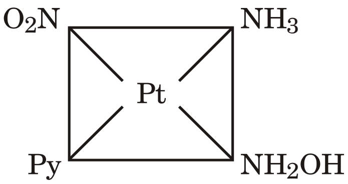
Cis trans

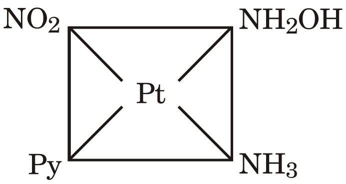
(iii) [MABCD]

$[PtNH_3(NH_2OH)Py\ NO_2]^+$ Ammine hydroxylamine pyridine nitro Pt (II)

In such complexes three of the ligands (B, C or D) may be trans to A.

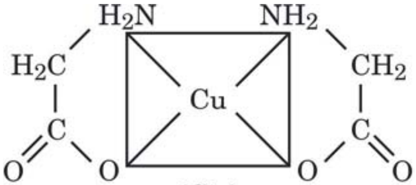






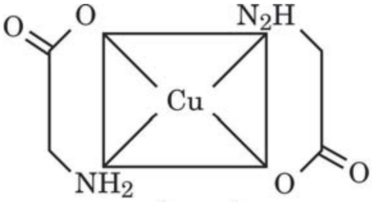
Such complexes are best denoted as [M < AB > CD], the ligands in the angular brackets are trans to each other.

(v) Geometrical isomerism is also found in square planar complexes containing unsymmetrical bidentate ligands e.g. $[M(AB)_2]$, gly = $NH_2 - CH_2 - COO^-$



(Cis)

[Cis – biglycinato Cu (II)]



(trans)

[trans – biglycinato Cu (II)]

(2) CN – 6 (Octahedral complexes)

Geometrical isomerism in octahedral complexes is also very common. The familiar examples include compounds of the type :

(i) $[MA_4X_2]$
(ii) $[MA_4XY]$
(iii) $[M(AA)_2X_2]$
(iv) $[M(AA)_2XY]$
(v) $[MA_2X_2Y_2]$

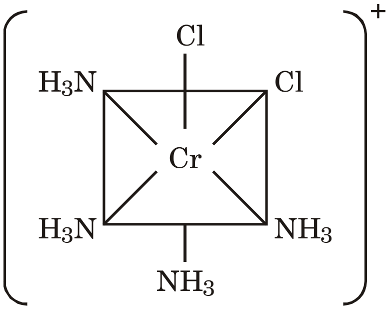
Where M = Co (III), Cr (III), Rh (III), Pt (IV) etc.

A – A = Symmetrical bidentate ligands

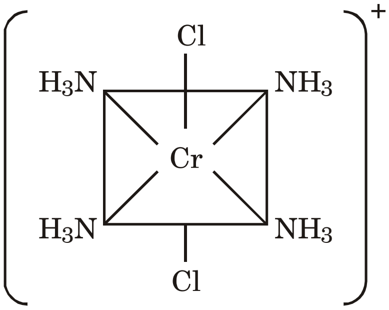
X & Y = – ive ligands.

For example

(i) $[Cr(NH_3)_4Cl_2]^+$

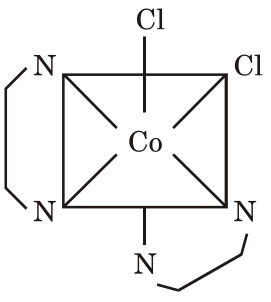


Cis

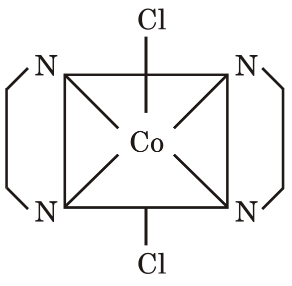


trans

(ii) $[Co(en)_2Cl_2]^+$

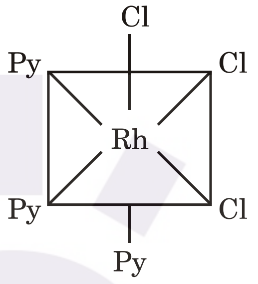


Cis

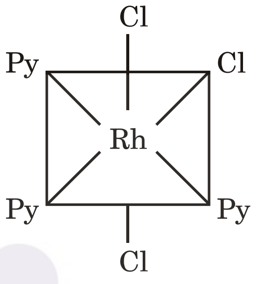


trans

A few complexes of the type $[MA_3X_3]$ are also known e.g. $[Rh(Py)_3Cl_3]$



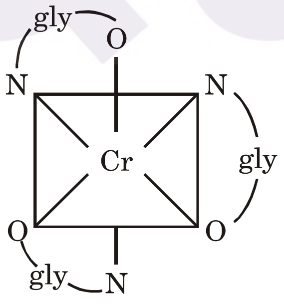
Facial (fac)



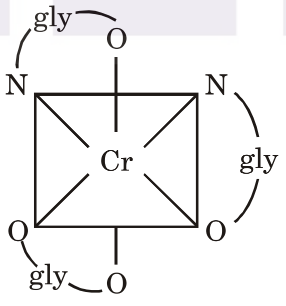
Meridional (mer)

Largest numbers of geometrical isomers are found for complex of the type [MABCDEF] where each ligand is different e.g. $[Pt (Py) (NH_3) (NO_2) ClBrI]$.

Unsymmetrical bidentate ligands also produce cis-trans isomers, e.g. $[Cr(gly)_3]$.



cis



trans

Preparations of complex compounds

Complex compounds are generally prepared by the following methods :

(i) **Substitution reaction in aq. solutions**

This method involves a reaction between a metal salt in aq solution and a coordinating agent, e.g. aq. solution of $CuSO_4$ and excess NH_3 forms a Cu^{2+} ammine.

$$\underset{\text{(Blue)}}{[Cu(H_2O)_6]SO_4} + 4NH_3 \longrightarrow \underset{\text{(Deep Blue)}}{[Cu(NH_3)_4]SO_4} + 6H_2O$$

(ii) **Substitution reactions in the absence of solvent**

Direct reaction between anhydrous metal salt and liquid NH_3 produces metal ammines, e.g.

$$\underset{\text{Yellow}}{NiCl_2 + 6NH_{3(l)}} \longrightarrow \underset{\text{Violet}}{[Ni(NH_3)_6]Cl_2}$$

(iii) **Redox reactions**

Co(II) salt forms a Co(III) complex

$$4[Co(H_2O)_6]Cl_2 + 4NH_4Cl + 20NH_3 + O_2 \longrightarrow 4[Co(NH_3)_6]Cl_3 + 26H_2O$$

Stability of complex compound in solution

Complex formation can be seen as a Lewis acid – base reaction. The M^{n+} is Lewis acid and the ligands are Lewis bases. If the interaction between M^{n+} and the ligands is strong, the complex is thermodynamically stable. The reaction between M^{n+} and the ligands can be written as

$$M^{n+} + xL^{m-} \rightleftharpoons [ML_X)^{p+}, \text{ where } (n+) + (m\ -) = (p+)$$

The equilibrium constant k is stability constant and it is defined as

$$k = \frac{[ML_X]^{p+}}{[M^{n+}][L^{m-}]^X}$$

The numerical value of k gives an indication of thermodynamic stability. Some stability constants are given below :

	K
$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6 10^7
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	5.3 10^{33}
$Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN_4)^{2-}]^+$	2.0 10^{27}
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	4.5 10^{11}

The value of k for Cu^{2+} complexes with NH_3 and CN^- show that cyanocomplex is more stable than NH_3 complex.

Effective atomic number (EAN) rule

Sidwick proposed effective atomic number (EAN) to explain the stability of metal in a complex. EAN is defined as the total number of electrons on the metal atom or ion after the complex formation which should be equal to that of the next higher noble gas.

If Z is the atomic number, (O.N). is the oxidation number and (C.N.) is the co-ordination number of the central metal atom or ion in the complex then

$$EAN = Z - (O.N.) + 2 \quad (C.N.)$$

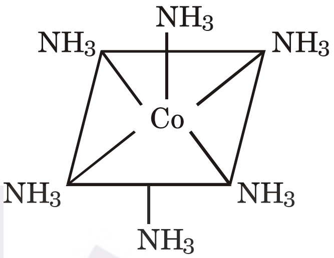
If EAN of an element in a complex is equal to atomic number of a noble gas. The complex is considered to be more stable.

Example 13

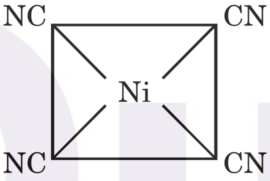
Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case.

Solution :

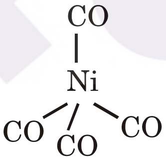
Hybridization of Co^{+3} is d^2sp^3, shape is octahedral.



Hybridization of Ni^{+2} is dsp^2 so shape is square planar.



Hybridisation of Ni is sp^3 so shape is tetrahedral.



Colour of Transition metal compounds

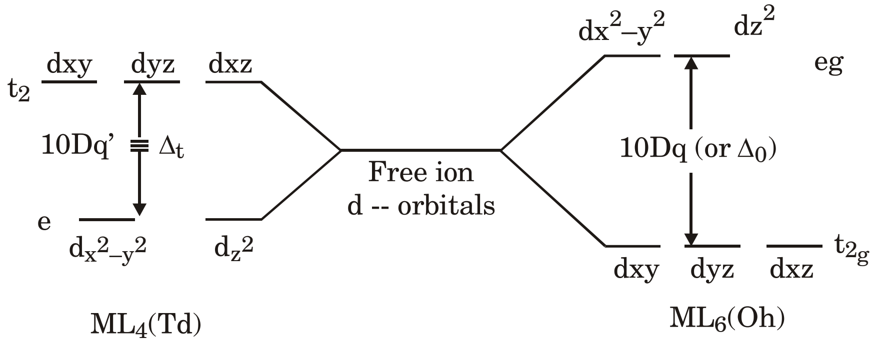
A chemical substance looks coloured if it absorbs a portion of visible light (λ – 3800 – 7800 Å) and transmits the rest. For example, if a compound absorbs the yellow-red (6000 – 7500 A) it appears green (i.e. transmitted light) i.e. the colour is complementary colour. Absorption of radiation excite electron to higher energy state. Therefore, when a substance looks coloured, it means that absorption of visible light and transition of electron must have taken place. Most of the transition metal compounds are coloured. It arises due to the following reasons :

(i) d-d transition

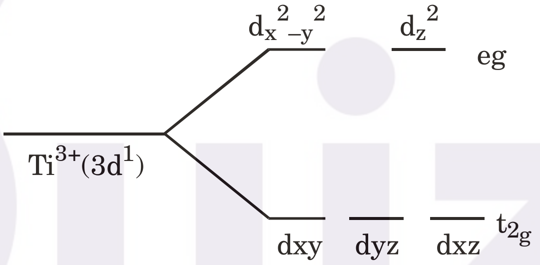
(ii) Charge transfer

The d–d transition

The five d–orbitals of a free ion are degenerate i.e. have equal energy. But in the presence of ligands (H_2O, NH_3, CN^-, F^- etc.) the d–orbitals split. It depends on structure of the complex (Oh, Td, Sq, Pl etc.).

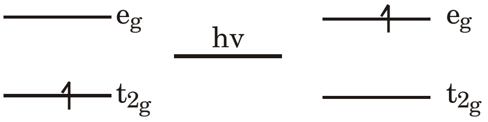


Let us consider $Ti(H_2O)_6^{3+}$. It is an Oh complex. The d–orbitals split as,



and single electron occupies t_{2g} level. When light falls on the complex t_{2g} electron is excited to e_g level.

$(t^{1}_{2g}\ e^{0}_{g} \rightarrow t^{0}_{2g}\ e^{1}_{g}$ i.e.



This excitation takes place when the compound absorbs radiation corresponding to λ ≈ 5000 Å, (grenish-yellow light). Therefore, transmitted wavelength corresponds violet light and the complex looks violet. As electron transition takes place from one group of d orbitals to the other, it is called d–d transition. The d–d transition is shown by transition metal ions of electron configurations, d^1, d^2, d^3, d^4, d^6, d^7, d^8, and d^9.

Colour of aqua complexes

Aquo ion	d–electrons	Colour
$[Sc(H_2O)_6]^{3+}$	O	Colourless
$[Ti(H_2O)_6]^{3+}$	d^1	Violet
$[V(H_2O)_6]^{3+}$	d^2	Blue
$[V(H_2O)_6]^{2+}$	d^3	Violet
$[Cr(H_2O)_6]^{2+}$	d^4	sky-blue
$[Fe(H_2O)_6]^{3+}$	d^5	Colourless
$[Fe(H_2O)_6]^{2+}$	d^6	Pale-green
$[Co(H_2O)_6]^{2+}$	d^7	Pink
$[Ni(H_2O)_6]^{2+}$	d^8	Green
$[Cu(H_2O)_6]^{2+}$	d^9	Blue
$[Zn(H_2O)_6]^{2+}$	d^{10}	Colourless

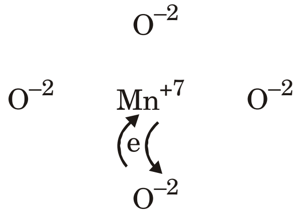
Colours due to d–d transition are faint. Metal ions which have d^0, d^5 and d^{10} configurations are colourless, if at all coloured not due to d–d transition.

Colour and charge transfer

Many transition metal ions or compounds such as MnO_4^-, CrO_4^{-2}, Cu_2O, CdS etc are coloured. They have their d–orbitals either vacant or fully filled.

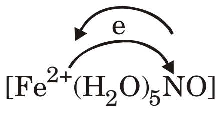
Ion or Compound	Oxidation state of transition metal	d–electrons	Colour
MnO_4^-	Mn^{+7}	$3d^0$	Purple
CrO_4^{-2}	Cr^{+6}	$3d^0$	Yellow
Cu_2O	Cd^+	$3d^{10}$	Red
CdS	Cd^{+2}	$4d^{10}$	Yellow

Colour in such compounds is explained by charge transfer mechanism. In MnO_4^-, Mn^{+7} is oxidizing agent and O^{-2} is reducing agent. As oxidizing agent picks up electrons and reducing agent gives up electrons, electrons moves from O^{-2} to Mn^{+7}.



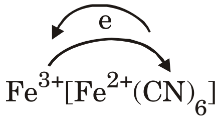
Due to such movement of electrons the ion is coloured.

The colour of brown ring compound $[Fe(H_2O)_5NO]^{2+}$, and $Fe^{3+}[Fe^{2+}(CN)_6]$ are also due to charge transfer.



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

(deep brown)



$Fe^{3+}[Fe^{2+}(CN)_6]$

(deep blue)

Colours due to charge transfer are intense (deep).

Hydrolysis of Transition metal compounds

Splitting of water molecules by ions is known as hydrolysis. Cation hydrolysis takes place when charge density on the cation is high.

$$\text{Charge density} = \frac{\text{Charge}}{\text{Ionic radius}}$$

Transition metal ions on the average are small in size and the common oxidation states are + 2, + 3 etc. Therefore, their charge density is high and they under go hydrolysis.

$$M^{n+} \leftarrow :O\begin{matrix}H\\H\end{matrix} = [M(OH)]^{n-1} + H^+$$

Thus, soluble salts of transition metals from slightly acidic solution.

$FeCl_3$ + Water $\longrightarrow$ Solution, slightly acidic.

$FeCl_3 \xrightarrow{\text{Water}} Fe^{3+} + 3Cl^-$

$$Fe^{3+} \leftarrow :O\begin{matrix}H\\H\end{matrix} \longrightarrow Fe(OH)^{2+} + H^+$$

$$Cr^{3+} \leftarrow :O\begin{matrix}H\\H\end{matrix} \longrightarrow Cr(OH)^{2+} + H^+$$

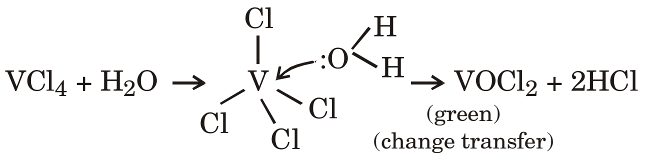
$$Cu^{2+} \leftarrow :O\begin{matrix}H\\H\end{matrix} \longrightarrow Cu(OH)^{2+} + H^+$$

Due to such hydrolytic reaction, cations, such as Mn^{+7}, Cr^{+6}, etc. are not stable in water

$Mn^{+7} + 4H_2O \longrightarrow MnO_4^- + 8H^+$

$Cr^{+6} + 4H_2O \longrightarrow CrO_4^{-2} + 8H^+$

Covalent transition metal compounds, such as $TiCl_4$, VCl_4 etc are hydrolysed due to ability of transition metal ion to expand coordination number by the use of empty d–orbitals.



ORGANOMETALLIC COMPOUNDS

These compounds constitute a broad class of substances in which carbon atom is directly bonded to a metal. Thus organic compounds in which metal atom is directly linked to carbon atom are known as organometallic compounds.

For example, NaC ≡ CNa is an organometallic compound as sodium is directly linked to carbon whereas C_2H_5ONa, $Ti(OC_2H_5)_4$ are not organometallic compounds since the metal atom is linked to carbon through oxygen. Some representative organometallic compounds are

C_2H_5MgBr–	Ethyl magnesium bromide
$(C_2H_5)_2Zn$ –	Diethyl zinc
$(CH_3)_2Cd$ –	Dimethyl cadmium
C_6H_5Li –	Phenyl lithium
$(C_2H_5)_4Pb$ –	Tetraethyl lead

Alkyl or aryl magnesium halides (RMgX or ArMgX) are also called as Grignard reagents.

Classification of Organometallic Compounds

(i) Ionic compounds of electropositive metals :

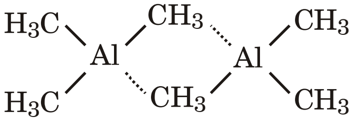
These compounds are mostly formed between the electropositive metals and the carbon compounds which are mostly acidic in nature. Thus organometallic compounds of alkali metals and alkaline earth metals consist of ions or ion pairs.

$R^- Na^+$ Alkyl sodium	$R^-Mg^{2+} X^-$ Alkyl magnesium halide
$R^- C \equiv C– Na^+$ Sodium alkynide	$R^- Zn^{2+} R^-$ dialkyl zinc

These compounds are normally soluble in hydrocarbon solvent. They are very reactive towards air and water. The stability of these compounds depends upon the structure of the carbon containing part of the compound.

(ii) σ–bonded complexes :

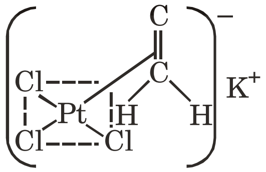
In a σ–bonded complex, a metal and a carbon atom of the ligand are joined together with a sigma bond. This means that the ligand contributes 1 electron and is therefore called one electron donor. Tetramethyl tin, $(CH_3)_4$ Sn and trimethyl aluminium, $(CH_3)_3Al$ are σ–bonded oroganometallic compounds. $(CH_3)_3Al$ exists as dimer and has structure analogous to diborane. Two methyl groups act as bridges between two aluminium atoms.



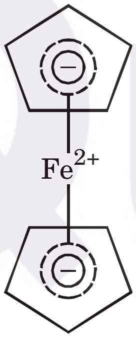
Trimethyl aluminium

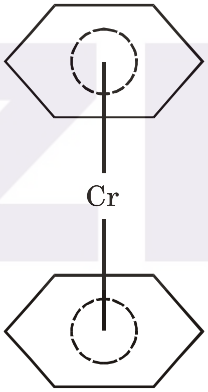
(iii) π–complexes :

These are organometallic compounds which involve the use of π–bonds present in organic compounds. For example, Zeise's salt, ferrocene and dibenzene chromium are organometallic compounds of this type. In all these compounds the π–electrons of the organic compound interact with the metal ion and thus occupy one of the coordination sites. For example in ferrocene and dibenzene chromium, the iron and chromium atoms are sandwiched between two aromatic rings.



Zeise's salt K [Pt Cl_3 (n^2 – C_2H_4)]





Ferrocene Fe (η^5 – $C_5H_5)_2$

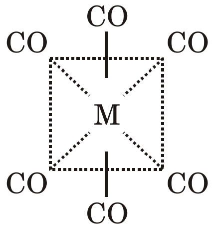
[bis cyclopentadienyl iron]

dibenzene chromium Cr (η^6 – $C_6H_6)_2$

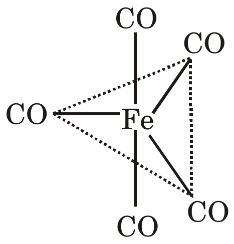
The number of carbon atoms involved in the formation of π–complexes with metals is indicated by the power of η^x (eta). For example, ferrocene is represented as Fe[$\eta^5(C_6H_6)_7$] indicating that 5–carbon atoms or cyclo pentadienyl anion are involved in π–complexation with the metal. Similarly one can write dibenzene chromium as [$Cr(\eta^6–C_6H_6)_2$] indicating that all the six carbons of benzene are involved in π–complexation with chromium.

(iv) Metal Carbonyls :

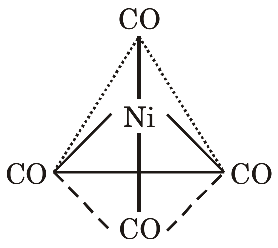
These are the complexes where carbon of carbon monoxide donates a pair of electrons to the metal. Nickel carbonyl and iron carbonyl are the common examples.



$[M(CO)_6]$
(M = Cr, Mo, W)



$[Fe(CO)_5]$



$[Ni(CO)_4]$

In metal carbonyl the oxidation state of the metal is zero. These metal carbonyls may be monomeric bridged or polynuclear.

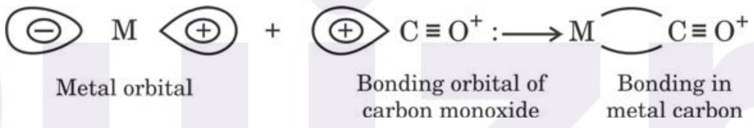
Bonding in Organometallic Compounds

(a) Bonding in metal carbonyls :

The metal-carbon bond in metal carbonyls has σ as well as π character.

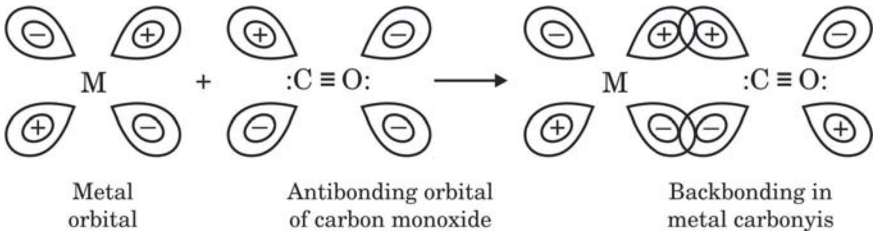
(i) σ–overlap

In a sigma bonded complex, the lone pair of electrons is present on the bonding orbital of carbon monoxide. This bonding orbital containing lone pair interacts with the empty d–orbital of the metal to form a metal-carbon bond as shown below :



(ii) π–overlap :

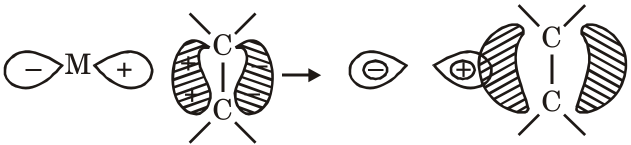
In addition to this, the antibonding orbitals of CO can also overlap with the filled d–orbitals of the metal resulting in back bonding as explained earlier. Thus metal carbonyls become much more stable compounds due to multiple bonding in them.



It is important to note here that σ-bond is in the nodal plane of the σ-electrons whereas π-overlap is perpendicular to the nodal plane.

(b) Bonding of alkenes to a transition metal

The bonding of alkenes to a transition metal to form complexes has two components. First, the π–electron density of the alkene overlaps with a σ-type vacant orbital on the metal atom. Second is the back bonding formed by the flow of electron density from a filled d–orbital on the metal into the vacant π^x–antibonding molecular orbital on the carbon atom as shown.



σ – overlap