Table 3.2. Electronic configuration of elements of second transition series in ground state and their oxidation states

Element	Atomic Number	Electronic configuration	Oxidation state
Y	39	$[Kr]4d^1 5s^2$	(+3)
Zr	40	$[Kr]4d^2 5s^2$	+2, +3, (+4)
Nb	41	$[Kr]4d^4 5s^1$	+3, (+5)
Mo	42	$[Kr]4d^5 5s^1$	+1, +3, +4, +5, (+6)
Tc	43	$[Kr]4d^5 5s^2$	(+4), +5, (+6)
Ru	44	$[Kr]4d^7 5s^1$	+2, (+3), +4, +6
Rh	45	$[Kr]4d^8 5s^1$	+2, (+3), +4
Pd	46	$[Kr]4d^{10} 5s^0$	(+2), +4
Ag	47	$[Kr]4d^{10} 5s^1$	(+1), +2, +3
Cd	48	$[Kr]4d^{10} 5s^2$	(+2)

Note: Stable Oxidation state is shown in parenthesis.

On the basis of the table 3.2, it can be said that in this transition series the electronic configuration of Pd, Ag and Cd in ground state have $4d^{10}$ that is 4d-orbital is completely filled with electrons; but in +2 of Pd and +2 of Ag, oxidation states, the electronic configurations, 4d-orbital is incompletely filled and so they are considered as transition elements but in the electronic configuration of Cd^{2+}, 4d-orbital is completely filled ($4d^{10}$). Hence **Cd is not considered as a transition element.** The electronic configuration of elements of third transition series in ground state and their oxidation states are shown in table 3.3.

Table 3.3. Electronic configuration of third transition elements in ground state and their oxidation states

Element	Atomic Number	Electronic configuration	Oxidation state
La	57	$[Xe]5d^1 6s^2$	(+3)
Hf	72	$[Xe]4f^{14} 5d^2 6s^2$	+2, +3, (+4)
Ta	73	$[Xe]4f^{14} 5d^3 6s^2$	+3, (+5)
W	74	$[Xe]4f^{14} 5d^4 6s^2$	+1, +4, +5, (+6)
Re	75	$[Xe]4f^{14} 5d^5 6s^2$	(+3), (+4), +5, (+6)
Os	76	$[Xe]4f^{14} 5d^6 6s^2$	(+4), +5, +6
Ir	77	$[Xe]4f^{14} 5d^7 6s^2$	(+3), (+4)
Pt	78	$[Xe]4f^{14} 5d^9 6s^1$	(+2), (+4)
Au	79	$[Xe]4f^{14} 5d^{10} 6s^1$	+1, (+3), +5
Hg	80	$[Xe]4f^{14} 5d^{10} 6s^2$	+1, (+2)

Note: Stable oxidation state is shown in parenthesis.

On the basis of table 3.3, it can be said that in the electronic configuration of Au and Hg in ground state there is $5d^{10}$ that is 5d-orbital is completely filled but in the electronic configuration of Au^{3+}, 5d-orbital is incompletely filled ($5d^8$) and so Au is considered transition element while in electronic configuration of Hg, 5d orbital is completely filled ($5d^{10}$) and so **Hg is not considered transition element.**

3.2.3 Occurrence of Transition Elements :

Definite transition metal is obtained from its definite mineral and a definite method is used for obtaining pure metal from the mineral. You have studied in unit 4 of semester III about the methods for the extraction of Cu, Fe and Zn from their minerals.

3.2.4 General Characteristics of Transition Elements :

- All the transition elements are metallic elements.
- These elements are hard and strong.
- Their melting points are high.
- These elements can form alloys with each other.
- Most of these elements dissolve in acid, but acid has no effect on certain noble elements.
- These elements possess various valencies.
- They possess property of malleability and ductility.
- They are good conductors of electricity and heat.
- Some of their ions possess paramagnetic property.

3.3 Periodic Trends in Properties of Elements of First Transition Series

(1) Metallic property : All the elements of first transition series possess metallic property. This point can be understood from the study of general characteristics of transition elements (see point 3.2.4)

(2) Atomic radii and Ionic radii : Generally in the periodic table, moving from left to right, there is decrease in atomic radii. This trend is observed in the transition elements, but this decrease in atomic radii is less. The tendency of ionic radii in transition elements is found to be similar to atomic radii. The atomic radii and ionic radii of first transition series elements are shown in tables 3.4 and 3.5 respectively.

Table 3.4 Atomic radii of first transition series elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radius (pm)	144	132	122	117	117	117	116	115	117	125

Table 3.5 Ionic radii of first transition series elements

Element	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic Radius (pm)	-	90	79	82	82	77	74	70	73	75

As shown in table 3.4, the atomic radius decreases from Sc to V while the atomic radii from Cr to Cu is almost similar. In addition to this, instead of decreasing the atomic radius of Zn is found to be increasing. The reason for this is that, as we move from left side to right side in period, the positive electric charge of nucleus increases and the entering electron is added to 3d-orbital. This electron, increases the shielding effect for attraction of electron present in 4s-orbital due to increase in positive electric charge in the nucleus. As a result, the electrons present in 4s-orbital are not attracted more towards the nucleus (Relative to neighbouring transition element). Thus, the orbit does not contract hence the atomic radii remain same. 3d-orbital of Zn atom is completely filled. Hence, it decreases the attraction towards electron of 4s-orbital of positive electric charge of nucleus due to its shielding effect. Also repulsion between electron-electron in 3d orbital increases more than the value of attraction of electrons of 4s-orbital and nucleus. Hence, there is expansion of orbit; so the value of atomic radius of Zn is seen to be increasing.

(3) Ionisation enthalpy : Moving from left side to right side in first transition series elements, the nuclear electric charge increases and so the value of ionization enthalpy increases but the increase in this value, is not equal to the increase in enthalpy in the elements of the main group. Thus, there is not much change in the first ionization enthalpies of two neighbouring transition elements (table 3.6). The values of first, second and third ionization enthalpies are shown in table 3.6.

Table 3.6 First, second and third ionization enthalpies (kJ mol^{-1}) of first transition series elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta_i H_1$	631	656	650	653	717	762	758	736	745	906
$\Delta_i H_2$	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H_3$	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

As shown in table 3.6, there is not much difference seen in the values of second ionization enthalpies like the changes in the first ionization enthalpies of first transition series elements. But chromium and copper are found to be exceptions. The values of second ionization enthalpy of these two elements are more than those of their neighbouring elements, because both these elements attain the electronic configuration Cr^+ : $[Ar]3d^5$ and Cu^+ : $[Ar]3d^{10}$ after loss of one-one electron from these two elements. From Cr and Cu, the second electron is removed from half filled or completely fill 3d orbitals respectively having more stability. It is natural that more energy will be required for removal of such electrons.

(4) Electrode potential : Thermodynamic stability of transition metals depends on their magnitude of ionization enthalpy. The compounds of metals having less ionization enthalpy are more stable, while the stability of compounds in solution is more dependent on relative electrode potentials.

The value of electrode potential is determined on the basis of the sum of the enthalpy changes (ΔH_T) of different reactions. The stabilities of different oxidation states of transition metal ions are determined on the basis of the electrode potentials. More negative the values of standard reduction poitentials more will be the stabillity of ions in aqueous medium.

3.4 Characteristic Properties of Elements of First Transition Series

(1) Colour : Most of the ionic and covalent compounds of transition elements are coloured. It is due to the presence of incompletely filled d-orbitals. When visible light falls on transition metal ions, they absorb light of definite wavelength and emit the remaining light. Our eye catches the colour of this emitted light as the colour of those ions. Hence, ions appear coloured. For example, when visible light passes through the aqueous solution of $[Ni(H_2O)_6]^{2+}$, green colour is emitted and other colours are absorbed. Hence, the colour of this aqueous solution appears to be green. In the similar, when visible light passes through aqueous solution of $[Co(NH_3)_6]^{3+}$, then red and green colours are emitted and other colours are absorbed. Because of the mixing of the emitted red and green colour, the colour of this solution appears to be yellowish orange. During absorption of light the electrons in d-orbital of ions receive energy and go to the d-orbital having higher energy. This transition of electrons is called **d-d transition.** It is necessary to note here, that generally the energy of all five d-orbitals is equal but according to crystal field theory, there is splitting of d-orbitals in different energy levels. The splitting of d-orbitals of different energy levels in transition compounds having tetrahedral and octahedral geometry are shown in figure 3.1.

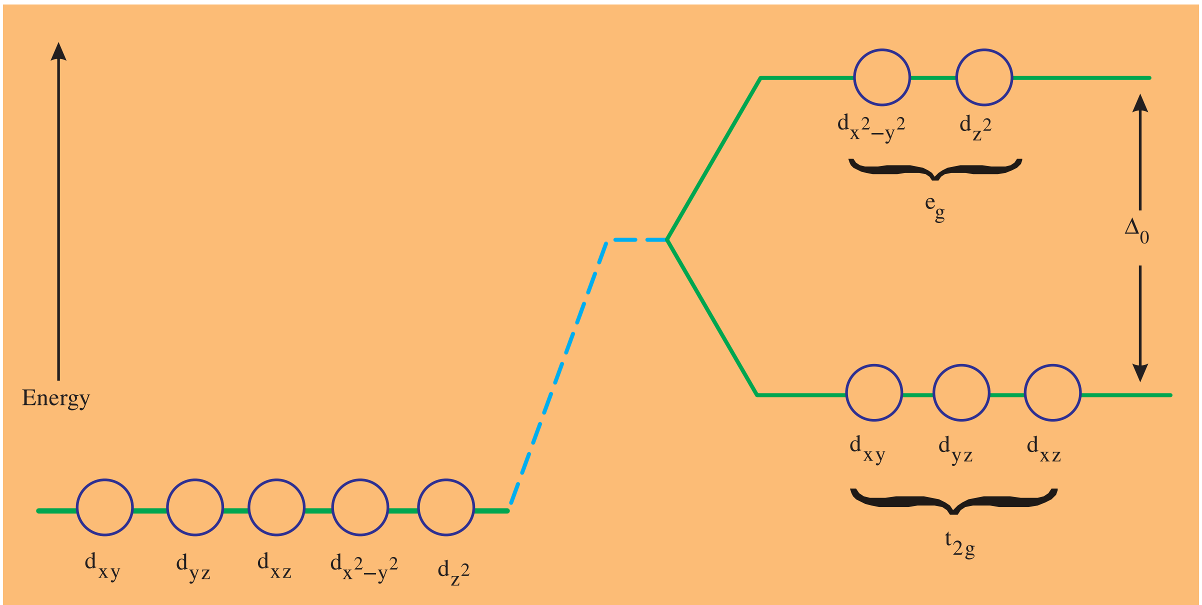


Fig.3.1(a) Splitting of d-orbitals in octahedral complex compounds

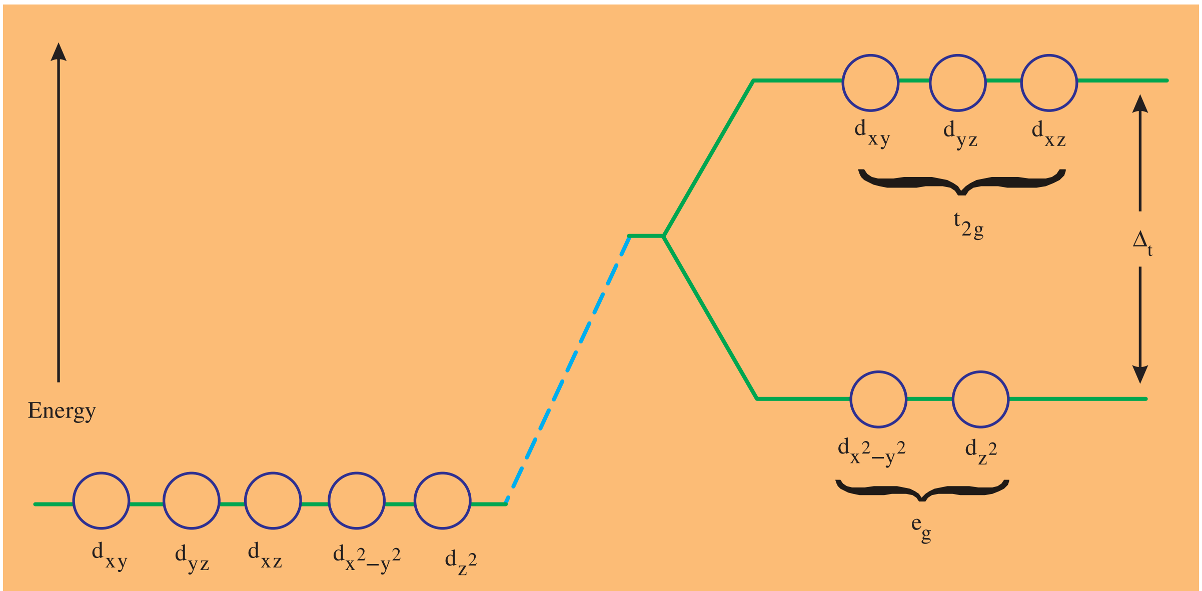


Fig.3.1(b) Splitting of d-orbitals in tetrahedral complex compounds

The colours of some metal ions are mentioned in table 3.7

Table 3.7 Colours of some of the hydrated metal ions of first transition series

Metal ions	Colour
Cu^{2+}, Cr^{2+}, Co^{3+}, V^{4+}	Blue
Ni^{2+}, Fe^{2+}, V^{3+}	Green
V^{2+}, Cr^{3+}, Mn^{3+}	Violet
Co^{2+}, Mn^{2+}	Pink
Fe^{3+}	Yellow
Ti^{3+}	Purple
Zn^{2+}, Sc^{3+}, Ti^{4+}, Cu^{+}	Colourless

Student friends, the verfication of colour of certain metal ions mentioned in table 3.7 can be done in chemistry laboratory by observing easily the colours from the chemicals available- $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_3$ and $ZnCl_2$.

(2) Catalytic property : Transition metals and their certain compounds increase the rate of chemical reaction. Hence, they are useful catalysts. These substances used as catalyst are in solid state. The random and pointed peak points on the surface at the ends of the edges of their particles are responsible centres for catalysis work. The molecule-atom in the depth in the matter of solid substance are surrounded by similar other atoms. Hence, the magnetic field of their unpaired electrons is destroyed by the effect on each other, while atoms of the ends of the edges or the peak points, get affected by the magnetic field which are active centres for catalysis. The molecules of reactant are attracted by the magnetic field and so the required activation energy of the reaction decreases. As a result, the reaction rate increases viz. Ni in hydrogenation of vegetable oil, Fe in industrial production of NH_3 by Haber process, V_2O_5 catalyst is used in obtaining SO_3 from SO_2 in contact process for manufacturing of H_2SO_4. You have studied in detail the point on catalysis in unit 2 : Surface Chemistry.

(3) Magnetic property : When a substance is placed in the magnetic field, then they possess two types of magnetic properties (i) Paramagnetism and (ii) Diamagnetism.

The molecule, atom or ion of a substances in which there are unpaired electrons, such substances possess paramagnetism, so they are called **paramagnetic substances;** while molecule, atom or ion in which all the electrons are paired, possesses diamagnetism. Hence, they are called **diamagnetic substances.** In the electronic configuration of transition elements, the (n–1)d-orbitals are incompletely filled; hence they possess unpaired electrons and so the atoms of these elements are paramagnetic. Because of paramagnetism they possess magnetic moment. Magnetic moment is produced due to rotation of unpaired electron on its axis and orbital rotation. In transition metal ions the unpaired electrons are present in the outermost orbit. Hence, in such cases axial rotation contribution is much more important than the orbit contribution. The value of magnetic moment based on only rotation on axis, can be calculated with the help of following formula :

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

where μ = Magnetic moment, n = Number of unpaired electrons, BM = Bohr Magneton (unit)

The value of magnetic moment increases with increase in number of unpaired electrons. Thus, through the measurement of magnetic moment we come to know about the number of unpaired electrons in atom, molecule or ion. Maximum five unpaired electrons can be in d-orbitals, so the theoretical values of magnetic moments are shown in table 3.8.

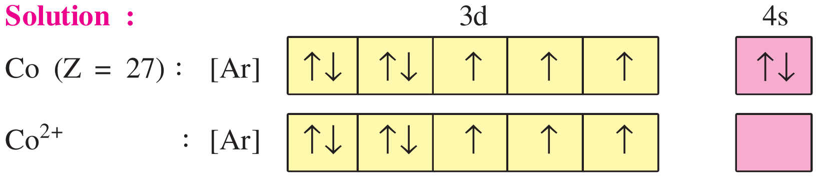
Table 3.8 Theoretical Value of Magnetic Moment

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

The magnetic moments of ions of transion elements or their compounds, are based on the axial rotation; so sometimes their values obtained experimentally are slightly more or less than the theoretical values. The reason for this is the rotation-orbital combination. This type of combination being directional, the value obtained is slightly more or less i.e. it depends on how these directional combinations occur. Earlier you have studied about diamagnetic or paramagnetic properties in semester III in unit 1 on Solid State.

Example : 1 Calculate magnetic moment of $Co^{2+}(aq)$

Solution :



Here number of unpaired electrons n=3

Now, magnetic moment $\mu = \sqrt{n\,(n+2)}$ BM

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

$$= \sqrt{15} \text{ BM} = 3.87 \text{ BM}$$

Thus, the value of magnetic moment of $Co^{2+}(aq)$ will be 3.87 BM

(4) Capacity of transition metal ions to form complex compounds : Transition metal ions combine with one or more anion or neutral molecule (ligand) and form complex species by co-ordinate covalent bond having definite characteristics which are called complex compounds. In depth, study of such **complex compounds** will be done in Unit 4 : complex compounds. The capacity of transition elements to form complex compounds is more than that with other elements; the reason of which is the below mentioned characteristics of transition metal ions.

- The size of transition metal ions is small.
- The nuclear electric charge and ionic electric charge of transition metal ions is comparatively more.
- The electronic configurations of transition metal ions is favourable for formation of complexes. In these metal ions, d-orbitals are vacant and so the electron pairs coming from the ligand can be accommodated.

- As very less difference is there between energy values of 3d, 4s, 4p or 4d orbitals, hybridization of different types can be possible with these orbitals. Thus, the different hybrid orbitals produced are helpful in formation of complex compounds.
- Due to formation of various types of hybridization and because of co-ordinate covalent bonds are directional, different types of geometrical shapes containing complex compound can be formed.
- Transition metal ions exhibit various oxidation states. Thus, varieties of complex compounds can be formed.

3.5 Interstitial Compounds

The atoms in solid state of transition metals are arranged in definite crystal structure. There are definite voids between atoms in such an arrangement. Hence, non-metallic atoms of smaller size viz. H, C, N and B can be easily arranged in the voids of crystal structure. The compounds formed in such a manner are called **interstitial compounds;** in which chemical bond is not formed between non-metal elements of smaller size arranged in the voids and the metal atom, hence the proportion of components in such compound is not definite. So interstitial compounds are not detinite. In fact interstitial compounds are nonstoichiometric or non-proportionate compounds, e.g., $TiH_{1.7}$, $VH_{0.56}$ etc. On the basis of the non-metal arranged in the interstitial void, they can be classified as hydrides, carbides, nitrides and borides, because elements like hydrogen, carbon, nitrogen and boron can be arranged in interstitial positions.

A notable change is observed in the characteristic properties of metals due to presence of non-metal elements like H,C,N and B in the voids of crystal structure. The small size of non-metal atoms present here in the void attract free electrons of metallic bond, hence free electrons of metallic bond are localised and so the strength of the bond increases. Hence, the properties of the metals like hardness, melting point resistance to wear, resistance to corrosion etc. are notably increased. Therefore, interstitial compounds are used in preparation of tools, machinery parts, vehicles etc. This type of compounds have not definite molecular formula. VN, Fe_3N, Fe_3C, Cr_3C_2, Mn_3C, TiC, VB, CrB_2 etc. are interstitial compounds.

3.6 Alloys

The characteristic properties like hardness, conductance, malleability, resistance to corrosion are essential for machineries, tools, vehicles and vessels of house-hold usages. There is no combination of all these properties and is not together found in any pure metal. Hence, instead of using pure metals in practice, alloys prepared from two or more metal-elements are used frequently..

Scientists **Hume** and **Rothery** presented rules as follows to obtain alloys of combination of useful properties :

(1) The atomic size of two metals forming the alloy must be the same. There must not be more than 15 % difference in their atomic radii.

(2) The chemical properties of the metals used for preparation of alloys must be same, that is, their electronic configurations of valence shell must be the same.

(3) The crystal structures of pure metallic elements used for alloys must be similar.

22 carat gold ornaments is the best example of alloy. It is the alloy of Au and Cu. The difference between atomic size of Au (atomic size = 134 pm) and Cu (atomic size = 117 pm) is about 14.5 %. Both of them possess cubic close pack structure. Both of them being members of group-11 the electronic configuration of their valence shells is same. Thus best alloy can be prepared according to laws

suggested by Hume and Rothery. The difference in atomic sizes between Cr, Mn, Fe, Co, Ni, Cu metals, is less than 2%. There is much less difference in the electronic configuration of valence shell of these elements. Hence, these elements form number of alloys having different proportions which are very useful in practice. Certain important alloys, their components, properties and uses are shown in table 3.9.

Table 3.9 Alloys, their components, properties and uses

Alloy	Components	Properties	Uses
Stainless steel	Fe (70%), Cr (20%) Ni (10%)	No effect of air, water and alkali and does not get rusted	In preparation of utensils, blades, surgical instruments.
Brass	Cu (70%), Zn (30%)	Ductile, hard, corrosion resistant and can be shaped easily	In preparation of cooking vessels, parts of machine and musical instruments.
Bronze	Cu (90%), Sn (10%)	Very strong and possessing more corrosion resistance	In preparation of statues, currency coins and medals.
Nitinol	Ti (45%), Ni (55%)	Light in weight and strong and resists corrosion. It has marvellous property of memory.	Rivetting and useful in space research.
Cupronickel	Cu (75-85%), Ni (15-25%)	Strong and corrosion resistant.	In preparation of currency coins.
	Cu (50-55%), Ni (45-50%)	Electrical resistance is more.	In preparation of electric resistant wires.
German-silver	Ni (40-50%), Zn (25-30%) Cu (25-30%)	Possesses shining as silver	In preparation of household vessels,art models and resistant wires.
Nichrome	Ni (60%), Cr (40%)	Electrical resistance is very high	As electric resistant wire in electric furnaces and electric heaters.

In addition, amalgam with mercury - alloy is also well known. In this alloy there are Hg (50%), Ag (35%), Sn (12%), Cu (3%) and Zn (0.2%). This alloy is, used in filling the cavity in the tooth. When this alloy is to be filled in cavity in the tooth, all these metals are mixed, some time before filling. This alloy is soft. By the time the dentist can fill in the cavity of tooth, it remains soft so that it becomes convenient for dentist to fill in the cavity. After filling in this alloy in cavity, it becomes hard and it does not expand.

3.7 Some Important Compounds of 3d-Transition Elements

Many compounds of 3d-transition elements are familiar. We shall study here, preparation, properties and uses of only potassium dichromate $(K_2Cr_2O_7)$ and potassium permanganate $(KMnO_4)$.

(1) Potassium dichromate $(K_2Cr_2O_7)$:

Perparation : Sodium chromate (Na_2CrO_4) and ferric oxide (Fe_2O_3) are formed by fusion of chromite mineral ($FeCr_2O_4$) with sodium carbonate and quick lime in presence of air. After the reaction, the roasted mass is extracted with water when Na_2CrO_4 is completely dissolved while Fe_2O_3 is left insoluble in presence of air.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Filtering the yellow coloured solution of sodium chromate, it is acidified with H_2SO_4; so that sodium dichromate $(Na_2Cr_2O_7)$ is formed, which reacts with potassium chloride and forms potassium dichromate and sodium chloride. $K_2Cr_2O_7$ being much less soluble than NaCl it crystallizes out on cooling.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Properties :

- Potassium dichromate is orange coloured crystalline substance.
- It is soluble in water.
- It acts as a strong oxidizing agent in acidic medium.
- When an alkali is added to an orange coloured solution of potassium dicromate a yellow coloured solution results due to the formation of potassium chromate and on acidifying it, the colour again changes to orange due to the reformation of potassium dichromate.

Chromate and dichromate ions are interconvertible in aqueous solution; which depends on the pH of the aqueous solution; because the oxidation state of chromium in chromate and dichromate is the same.

$$\underset{\text{Yellow colour}}{2CrO_4^{2-}} + 2H^+ \rightarrow \underset{\text{Orange colour}}{Cr_2O_7^{2-}} + H_2O$$

$$\underset{\text{Orange colour}}{Cr_2O_7^{2-}} + 2OH^- \rightarrow \underset{\text{Yellow colour}}{2CrO_4^{2-}} + H_2O$$

Uses :

- Potassium dichromate is mainly useful in leather industry and formation of azo compounds.
- As oxidizing agent used in synthesis of organic compounds, used as a reagent in chemical oxygen demand (COD) measurement in polluted water. In addition, the mixture of potassium dichromate with concentrated sulphuric acid which is known as chromic acid, is used for cleaning of glasswares in laboratory. It is corrosion inhibitant.
- It is used as titrant in redox titrations to determine the amount of metal ions like iron (II).

(2) Potassium permanganate $(KMnO_4)$:

Preparation : Dark green coloured potassium manganate (K_2MnO_4) is formed by fusion of manganese dioxide (MnO_2) with KOH in presence of air or oxidizing agent like KNO_3. Potassium permanganate is formed when sulphuric acid is added to this solution and made acidic.

$$2MnO_2 + 4KOH + O_2 \rightarrow \underset{\text{(Green colour)}}{2K_2MnO_4} + 2H_2O$$

$$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O$$

Properties :

- Potassium permanganate is dark purple coloured crystalline substance.
- It is soluble in water.
- It acts as oxidising agent in acidic, basic and neutral medium.

Uses :

- Potassium permanganate is used as strong oxdising agent in synthesis of organic compounds.
- It is used as bleaching agent for cotton cloth, silk and wood and in textile industries.
- An aqueous solution of potassium permanganate is used for gargling to keep mouth germfree as it is antiseptic.
- It is useful as titrant in redox titrations to know the proportion of metal ions like iron (II) and organic compounds like oxalic acid.

3.8 Applications of d-Block Elements

- The alloys-stainless steel, brass, bronze, nitinol, cupronickel, german silver and nichrome prepared from elements of d-block elements are used for preparation of household utensils, currency coins, statues, and machinery.
- Some elements and compounds of these elements act as catalyst in chemical reaction e.g., Ni in hydrogenation of vegetable oil, Fe in Haber process of industrial production of NH_3, V_2O_5 catalyst for obtaining SO_3 from SO_2 in contact process for production of H_2SO_4.
- Alloy like mercury-amalgam is useful for filling in tooth cavity.
- Alloy of gold and copper is more appropriate for preparation of ornaments.
- Mercury is used in thermometer.
- The use of inert metal like platinum is made as electrodes in the experiments of electro-chemistry.
- Some compounds like $KMnO_4$ and $K_2Cr_2O_7$, of d-block elements act as strong oxidizing agents in synthesis of organic compounds. They are used as titrant in redox titrations.
- MnO_2 is used in dry cell.
- To prevent water pipes and the roof on the house from corrosion they are changed in to galvanized form with the help of zinc metal.

3.9 Innertransition Elements (Elements of f-Block)

The f-block elements are distributed into two series : (A) Lanthanide series and (B) Actinide series. The series of fourteen elements immediately after lanthanum- Ce(Z = 58) to Lu (Z = 71) is called **lanthanide series.** The elements of this series are known as **lanthanoids.** Lanthanoids are expressed by general symbol Ln. As lanthanum has more similarity with lanthanoids, it is included in the lanthanide series, during discussion. In the periodic table, series of fourteen elements immediately after actinium-Th (Z = 90) to Lr (Z = 103) is called **actinide series.** The elements of this series are known as **actinoids.** As actinium possesses more similarity with actinoids, it is included in the discussion of actinide series. **The general electronic structure of outermost electrons of elements of f-block is $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$.**

3.10 Lanthanide Series

To understand the lanthanide series, we shall study here, its electronic configuration, oxidation state, atomic size, chemical reactivity and lanthanide contraction.

3.10.1 Electronic Configuration and Oxidation State :

In the electronic configuration of elements of lanthanide series, $6s^2$ is common in all the elements but the electrons in 4f-orbital keep changing. **All the lanthanoids and lanthanum element possess stable oxidation state + 3.** The electronic configuration and oxidation states of lanthanum and lanthanoids are shown in table 3.10.

Table 3.10 Electronic configuration and oxidation states of lanthanum and lanthanoids

Element	Atomic Number	Electronic configuration	Oxidation state
La	57	$[Xe]5d^16s^2$	(+3)
Ce	58	$[Xe]4f^15d^16s^2$	(+3), +4
Pr	59	$[Xe]4f^36s^2$	(+3)
Nd	60	$[Xe]4f^46s^2$	+2, (+3)
Pm	61	$[Xe]4f^56s^2$	(+3)
Sm	62	$[Xe]4f^66s^2$	+2, (+3)
Eu	63	$[Xe]4f^76s^2$	+2, (+3)
Gd	64	$[Xe]4f^75d^16s^2$	(+3)
Tb	65	$[Xe]4f^96s^2$	(+3), +4
Dy	66	$[Xe]4f^{10}6s^2$	(+3), +4
Ho	67	$[Xe]4f^{11}6s^2$	(+3)
Er	68	$[Xe]4f^{12}6s^2$	(+3)
Tm	69	$[Xe]4f^{13}6s^2$	+2, (+3)
Yb	70	$[Xe]4f^{14}6s^2$	+2, (+3)
Lu	71	$[Xe]4f^{14}5d^16s^2$	(+3)

Note : Stable oxidation state is shown in parenthesis

It is apparent from the study of electronic configuration shown in table 3.10, that only in the lanthanoids like Ce, Gd and Lu electrons are filled in 5d orbital. In Gd, because of half filled orbital like $4f^7$, stability may be obtained and so newly added electron enters into 5d orbital, while in Lu, 4f orbital being completely filled, the added new electron enters into the 5d orbital. The filling of electron of Ce in 5d-orbital is accepted at present as an exception. Thus, **the general electronic configuration of lanthanoids is [Xe]$4f^{1-14}5d^{0-1}6s^2$.** Amongst lanthanoids, promethium (Pm) is a radioactive element.

3.10.2 Atomic Size and Lanthanide Contraction :

Like the elements in any period of periodic table, in elements of lanthanide series going from cerium(Ce) to lutetium (Lu), the atomic radii and ionic radii go on decreasing, In the elements of this series, with the increase in atomic number the addition of new electron is in inner orbit 4f(n = 4) instead of last orbit (n = 6). Hence, with the increase in positive electric charge, the electrons in 4f-orbital possess more attraction towards it. Hence, there is contraction of atom. i.e. atomic radius decreases. This contraction occurring in lanthanide elements, is called **lanthanide contraction.** The effect of this lanthanide contraction is observed on the atomic radii of the elements after lanthanide series. The atomic radii of some of the elements of third transition series after lanthanide series are equal to the atomic radii of some elements of second transition series earlier to this, which can be understood from table 3.11.

Table 3.11 Atomic radii (pm) of elements of second and third transition series

Second Transition Series	Y 162	Zr 145	Nb 134	Mo 129	Tc -	Ru 124	Rh 125	Pd 128
Third Transition Series	Lanthanoids	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 126	Pt 129

3.10.3 Chemical Reactivity :

As lanthanoids possess (+3) oxidation state they form hydroxides of the type $Ln(OH)_3$. These hydroxides are less basic than $Ca(OH)_2$ but more basic than $Al(OH)_3$. The carbonates and nitrates of these elements decompose faster into their oxide by heating. The size of ion decreases on going from Ce^{3+} to Lu^{3+}, hence their basicity decreases, that is $Ce(OH)_3$ is most basic and $Lu(OH)_3$ is least basic. These elements possess similarity in physical and chemical properties so their separation is carried out on the basis of the difference in their basicity. Ln_2O_3 type oxides of these elements are ionic and basic. The property of basicity decreases with ionic size. Some ions of these elements possess paramagnetic property because of unpaired electrons in f-orbital. Their certain ions are coloured and give coloured solution. The general chemical reactions of lanthanoids are shown below :

$$Ln \xrightarrow{H_2O} Ln(OH)_3 + H_2$$

$$Ln \xrightarrow{C / 2773\ K} LnC_2$$

$$Ln \xrightarrow[\Delta]{N} LnN$$

$$Ln \xrightarrow[\Delta]{S} Ln_2S_3$$

$$Ln \xrightarrow{\text{Combusting in } O_2} Ln_2O_3$$

$$Ln \xrightarrow{\text{Acid}} Ln^{3+} + H_2$$

$$Ln \xrightarrow{X_2} LnX_3$$

3.11 Actinide Series

We shall study electronic configuration and oxidation states to understand the actinide series.

3.11.1 Electronic Configuration and Oxidation State :

In the electronic configuration of elements of actinide series, $7s^2$ is common in all the elements but electrons keep on changing in 5f orbital. Irregularity is found more in the electronic configuration of actinoids. Actinoids possess more than one oxidation states. The electronic configuration and the oxidation states of actinium and actinoids are shown in table 3.12.

Table 3.12 Electronic configuration and oxidation states of actinium and actinoids

Element	Atomic Number	Electronic configuration	Oxidation state
Ac	89	$[Rn]6d^{1}7s^{2}$	(+3)
Th	90	$[Rn]6d^{2}7s^{2}$	(+4)
Pa	91	$[Rn]5f^{2}6d^{1}7s^{2}$	+3, +4, (+5)
U	92	$[Rn]5f^{3}6d^{1}7s^{2}$	+3, +4, +5, (+6)
Np	93	$[Rn]5f^{4}6d^{1}7s^{2}$	+3, +4, (+5), +6, +7
Pu	94	$[Rn]5f^{6}7s^{2}$	+3, (+4), +5, +6, +7
Am	95	$[Rn]5f^{7}7s^{2}$	(+3), +4, +5, +6
Cm	96	$[Rn]5f^{7}6d^{1}7s^{2}$	(+3), +4
Bk	97	$[Rn]5f^{9}7s^{2}$	(+3), +4
Cf	98	$[Rn]5f^{10}7s^{2}$	(+3)
Es	99	$[Rn]5f^{11}7s^{2}$	(+3)
Fm	100	$[Rn]5f^{12}7s^{2}$	(+3)
Md	101	$[Rn]5f^{13}7s^{2}$	(+3)
No	102	$[Rn]5f^{14}7s^{2}$	(+2), +3
Lr	103	$[Rn]5f^{14}6d^{1}7s^{2}$	(+3)

Note : Stable oxidation state is shown in parenthesis

In the electronic configuration of elements Th to Np as shown in table 3.12, irregularity is found to be more in comparison to other elements which is at present accepted as an exception, while in Cm and Lr, the half filled 5f-orbital and completely filled 5f-orbitals respectively, to attain stability, the new added electron is filled in 6d-orbital.

Thus **general electronic configuration is $[Rn]5f^{0-14}6d^{0-2}7s^{2}$.** All the actinoids are radioactive.

3.12 Comparison of Actinoids with Lanthanoids

- Actinoids are like silver in appearance. More irregularity is observed in the metallic radii in actinoids than lanthanoids. Hence, diversity is found in the structures of actinoids.
- As the outermost orbit in actinoids is far from the nucleus in comparison to lanthanoids, their electron can be easily removed. Hence, the values of ionization enthalpy of actinoids are less than the values of ionisation enthalpies of lanthanoids.

- The stable oxidation state of all the lathanoids is (+3). In actinoids, oxidation states (+2) to (+6) are seen.
- In lanthanoids only promethium is radioactive but all the actinoids are radioactive.

3.13 Applications of f-Block Elements

- Pyrophoric Misch metal (50 % Ce +40 % La + 7 % Fe + 3 % other metals) is used as reducing agent and as stones in gas lighters.
- CeO_2 is useful in pigments.
- Ceric compounds are used as oxidizing agent in volumetric analysis.
- Oxides of lanthanoids are useful in preparation of optical glass of camera having high refractive index.
- Gadolinium sulphate is used to produce very low temperature by magnetic effect.
- Metals like, uranium, plutonium, and thorium are useful in production of atomic energy. Electrical energy can be obtained from nuclear energy.

SUMMARY

Position in periodic table	Block
Groups 1 to 2	s-Block
Groups 13 to 18	p-Block
Groups 3 to 12	d-Block
Two horizontal rows at the bottom of the periodic table	f-Block

- d-block elements are in periods 4 to 7.
- f-block elements are in periods 6 and 7.

Elements of d-block (Transition metal elements)

- The elements which in their ground state or any one of their oxidation states, d-orbital is incompletely filled are called transition elements.
- Amongst the d-block elements Zn, Cd and Hg do not act as transition elements.
- All the transition elements are metallic elements.
- In the first transition series, atomic radii decrease from Sc to V, while atomic radius remains same in elements Cr to Cu and the atomic radius of Zn is found increasing instead of decreasing.
- Not much difference is observed in first and second ionization enthalpies of two neighbouring transition elements but the value of second ionization enthalpy of Cr and Cu are more than those of their neighbouring elements.
- Most of the ionic and covalent compounds of transition elements are coloured.

- Compounds of transition elements act as catalysts in certain chemical reactions.
- The magnetic moment of transition element compounds,

  $\mu = \sqrt{n\,(n+2)}$ where μ = magnetic moment. n = number of unpaired element

  The unit of magnetic moment is BM (Bohr Magneton)
- The capacity to form complex compounds is much more than other elements because of definite characteristics of transition elements.
- In the formation of crystals of transition metals, the voids are there in which non-metal elements (H, C, N, B) arrange and form interstitial compounds.
- Scientists Hume and Rothery suggested the rules for the alloys and accordingly alloys having useful properties are obtained from transition metal elements.
- The compounds of transition element- $KMnO_4$ and $K_2Cr_2O_7$ are very useful in laboratory and in synthesis of organic compounds.

f-Block elements (Innertransition elements)

- f-Block elements are divided in to (1) Lanthanide series and (2) Actinide series.

Lanthanide series

- Lanthanide series : In period-6 Ce (Z = 58) to Lu (Z = 71)
- Elements of lanthanide series are called lanthanoids which are shown by symbol Ln.
- All the lanthanoids possess stable oxidation state (+3).
- The general electronic configuration of lanthanoids : $[Xe]4f^{1-14}5d^{0-1}6s^2$
- Amongst lanthanoids, promethium (Pm) is radioactive.

Actinide series

- Actinide series : In period-7 Th (Z = 90) to Lr (Z = 103).
- Elements of actinide series are called actinoids.
- The stable oxidation state in actioids is found to be from (+2) to (+6).
- The general electronic configuration of actinoids is : $[Rn]5f^{0-14}6d^{0-2}7s^2$
- All the actinoids are radioactive.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Elements of which groups are called d-block elements ?

(A) Groups 1 to 2 (B) Groups 3 to 12

(C) Groups 13 to 18 (D) Groups 13 to 17

(2) Which of the following elements is of d-block even then it is not transition element ?

(A) Cu (b) Ca (C) Fe (D) Hg

(3) The aqueous solution of which of the following ions is green coloured ?

(A) Co^{2+} (B) Zn^{2+} (C) Ni^{2+} (D) Cr^{2+}

(4) What will be the order of energy of d-orbitals during their division in tetrahedral complex compounds ?

(A) $d_{xy} \cong d_{yz} \cong d_{xz} < d_{x^2-y^2} \cong d_{z^2}$ (B) $d_{x^2-y^2} \cong d_{z^2} < d_{xy} \cong d_{yz} \cong d_{xz}$

(C) $d_{xy} \cong d_{z^2} < d_{yz} \cong d_{xz} \cong d_{x^2-y^2}$ (D) $d_{x^2-y^2} \cong d_{xz} < d_{xy} \cong d_{yz} \cong d_{z^2}$

(5) Which of the following ions in its aqueous solution possesses the value of magnetic moment as 3.87 ?

(A) Cu^{2+} (B) Cr^{3+} (C) Co^{3+} (D) Fe^{3+}

(6) Which of the following is the alloy of iron ?

(A) Stainless steel (B) Brass (C) Bronze (D) Nichrome

(7) Which of the following compounds of transition elements is used in dry cell ?

(A) V_2O_5 (B) $KMnO_4$ (C) $K_2Cr_2O_7$ (D) MnO_2

(8) Which of the following elements is radioactive ?

(A) Pr (B) Pm (c) Gd (D) Tm

(9) What is the general electronic configuration of actinide series ?

(A) $[Xe]\ 4f^{0-14}\ 5d^{0-1}\ 6s^2$ (B) $[Xe]\ 4f^{0-14}\ 5d^{0-10}\ 6s^2$

(C) $[Rn]\ 5f^{0-14}\ 5d^{0-2}\ 6s^2$ (D) $[Rn]\ 5f^{0-14}\ 6d^{0-2}\ 7s^2$

(10) Which of the following statements is incorrect ?

(A) Atoms of all the transition elements are paramagnetic.

(B) All the transition elements are metal elements.

(C) All the elements of d-block are transition elements.

(D) The position of d-block is between s and p-block element in the periodic table.

2. Answer the following questions in brief :

(1) Innertransition elements are the members of which period ?

(2) Elements of which block are called innertransition elements ?

(3) Which of the elements of the first transition series (Sc to Zn) do not act as transition element ?

(4) Which are the elements of first transition series elements having d^5 and d^{10} electronic configurations ?

(5) Aqueous solutions of which ions of first transition elements are blue coloured ?

(6) Write unit of magnetic moment.

(7) Which non-metal elements form interstitial compounds with elements of first transition series ?

(8) Which centres are responsible for catalytic function of catalyst ?

(9) Which alloy is filled in tooth cavity ?

(10) Which alloy is used for preparation of electric resistant wire ?

(11) Cupronickel is the alloy of which metals ?

(12) Which compound of transition elements acts as strong oxidizing agent in acidic and basic media ?

(13) By which common symbol, the elements of lanthanide series are shown ?

(14) Write general electronic configuration of lanthanide series elements.

(15) Which compound of f-block elements is useful in pigment ?

(16) Give definitions :

(i) Transition elements (ii) d-d transition (iii) Interstitial compounds (iv) Alloy (v) Lanthanide series (vi) Actinide series

3. Write answers of following questions :

(1) Write electronic configuration of Cr and Cu.

(2) Write formula to determine magnetic moment and give identification of symbols in it.

(3) Write two properties and two uses of $KMnO_4$.

(4) Write two properties and two uses of $K_2Cr_2O_7$.

(5) Write four applications of f-block elements.

(6) Write three laws presented by scientists Hume and Rothery for preparation of alloys.

(7) Explain giving reason :

(i) The values of second ionization enthalpy of Cr and Cu are found to be more than their neighbouring elements.

(ii) The atomic radius of Zn in first transition series increases instead of decreasing.

(iii) The atomic radii of elements Cr to Cu in first transition series are almost same.

(iv) In electronic configuration of Pd, Ag and Cd, d^{10} electrons are present even then Pd and Ag are considered transition elements, while Cd is not considered transition element.

(8) Calculate magnetic moments : Sc^{3+}, Ti^{4+}, V^{4+}, Cr^{3+}, Cr^{6+}, Mn^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

4. Answer the following questions in detail :

(1) Mention the general properties of transition elements.

(2) Discuss catalytic and magnetic properties of transition elements.

(3) Describe the characteristic capacity of transition metal ions to form complex compounds.

(4) Mention the preparation of potassium dichromate and potassium permanganate.

(5) Describe applications of d-block elements.

(6) Compare actinide elements with lanthanide elements.

(7) Write short notes :

(i) Interstitial compounds (ii) Alloys

(iii) Chemical reactivity of lanthanide elements (iv) Lanthanide contraction

●

Unit

4

Complex Salts or Co-ordination Compounds

4.1 Introduction

The salt that is obtained according to the laws of chemical combination by combination of two or more salts (compounds) having independent existence and maintains the properties of the original salts is called double salt, e.g., if saturated aqueous solution of K_2SO_4 and $Al_2(SO_4)_3$ are mixed and crystallized, then crystals of alum- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ are obtained, which is called double salt. On qualitative analysis of solution of this alum, yellow precipitate with picric acid are obtained. This indicates presence of K^+, with NaOH gum-like gelatinous precipitates are obtained which indicates presence of Al^{3+} and with $BaCl_2$ gives white precipitates which indicates presence of SO_4^{2-} and thus K_2SO_4 and $Al_2(SO_4)_3$ maintain their properties. Hence it is a double salt In addition, $FeSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$ ferrous ammonium sulphate and carnalite are also double salts whose equations are shown below :

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow \underset{\text{Potassium alum}}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}$$

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow \underset{\text{Ferrous ammonium sulphate}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

$$KCl + MgCl_2 + 6H_2O \rightarrow \underset{\text{Carnalite}}{KCl \cdot MgCl_2 \cdot 6H_2O}$$

Similarly, by combination of two or more compounds of independent existence, according to the laws of chemical combination, compounds obtained with new properties are called complex salts or co-ordination compounds, viz. when KCN is added to ferrous cyanide $Fe(CN)_2$, and ferric cyanide $Fe(CN)_3$ are formed and then both of them become soluble. The crystals having formula

$Fe(CN)_2 \cdot 4KCN$ and $Fe(CN)_3 \cdot 3KCN$ are obtanined. They are known as potassium ferrocyanide $K_4[Fe(CN)_6]$ and potassium ferricyanide $K_3[Fe(CN)_6]$ respectively. In these two, the qualitative analysis of Fe^{2+}, Fe^{3+} or CN^- ions cannot be carried out but new ions $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$ are obtained. In electrolysis; they move towards anode. Equations for preparing some complex salts are given below :

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

$$Fe(CN)_3 + 3KCN \rightarrow K_3[Fe(CN)_6]$$

$$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$$

$$CoCl_3 + 6NH_3 \rightarrow [Co(NH_3)_6]Cl_3$$

$$PtCl_4 + 2KCl \rightarrow K_2[PtCl_6]$$

From the equation of $CuSO_4$ and NH_3 as shown above, it appears that the valency of Cu^{2+} and SO_4^{2-} ions is satisfied even then $CuSO_4$ combines with four molecules of ammonia and gives complex salt.

The elements in the d-block of modern periodic table, are called transition elements. Among these transition elements, Scandium to Zinc (Z = 21 to 30), Yttrium to Cadmium (Z = 39 to 48) and Lanthanum to Mercury (Z = 57 to 80). That is the elements of fourth, fifth and sixth periods are very important in modern inorganic chemistry. Some of the properties of these elements are same. There is change in their valency and the aqueous solution of their salts are coloured. In the electronic configuration of these transition elements, electrons are arranged successively in d-orbitals. **When (n–1)d, ns and np or ns, np and nd orbitals of the atoms or ions of transition elements are vacant, these transition elements accept electron pairs from negative ions or neutral molecules, which are called complex (co-ordination) compounds.** The bond that is formed between metal ions of metallic elements in this type of compound and the negative ions or neutral molecules is called co-ordinate covalent bond. In these compounds, around the metal ion in the centre of the molecules are arranged negative ions or neutral molecules by co-ordinate covalent bond. Mostly the transition elements have more tendency to form complex compounds.

4.2 Werner's Theory

The question that why the other compounds combine with stable compounds after satisfaction of valency; had become the subject of discussion in the beginning of the nineteenth century. In 1905, Swiss scientist Alfred Werner prepared many new compounds by mixtures of cobalt chloride and ammonia, studied them thoroughly and gave a new theory, which is known as Werner's co-ordination theory. By the Werner's theory many clarifications were made in this field. **Werner obtained different compounds of $CoCl_3$ and NH_3 viz. $[Co(NH_3)_6]Cl_3$ (yellow), $[Co(NH_3)_5Cl]Cl_2$ (purple, $[Co(NH_3)_4Cl_2]Cl$ (violet / green) and $[Co(NH_3)_3Cl_3]$, (bluish green).** Werner received nobel prize for this work in 1913.

The theory given by Werner for the formulas and structures of complex salt is "Certain metals have secondary valency in addition to primary valency. With this it combines strongly with the metal ions, neutral molecules or negative ions in its first attraction sphere [ ]."

According to Werner, metal ion possesses two types of valency. Primary valency or ionizing valency and Secondary valency or non-ionisable valency.

(i) The primary valency is similar to positive electric charge of positive ion of metal or oxidation number of metal. It forms ionic bond. The other ion combined by this valency becomes free by ionization of compound.

(ii) Secondary valency is non-ionized. The negative ions or neutral molecules contained with secondary valency are not ionized.

(iii) Primary valency is satisfied by only negative ions, while secondary valency is satisfied by negative ions or neutral molecules (ligand).

(iv) The secondary valency of metal ion or metal elements form co-ordinate covalent bond, so the secondary valency is called co-ordination number of metal.

(v) The co-ordination number of metal ion is definite which is independent of primary valency.

(vi) Secondary valency being directional, different types of geometrical structures are obtained.

Note : (1) In some complex compounds, the positively charged ligand like ^{+}NO, $^{+}NO_2$ are also seen.

(2) Now it is proved that the some metal ions of transition elements possess more than one co-ordination number.

(3) To understand these geometrical structures, it is important to know the magnetic properties of complex compounds.

The bond between metal ion combined through secondary valency, and ligand is called co-ordinate covalent bond. This is indicated by → which indicates the co-ordination site. The electron pair present between metal ion and ligand are given by negative ion or neutral molecule.

The complex ion in complex compounds is shown by [ ] bracket (first attraction sphere) whereas outside the bracket, on the left side, the positive ion combined by ionic bond is shown viz. In $K_3[Fe(CN)_6]$ complex compound $[Fe(CN)_6]^{3-}$ complex negative ion is combined by ionic bond with positive ion K^+. Similarly in $[Cr(NH_3)_6]Cl_3$ complex compound $[Cr(NH_3)_6]^{3+}$ complex positive ion is combined with negative ion Cl^- by ionic bond.

4.3 Clasification of Ligands

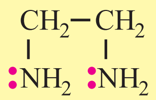
Generally the ligand has a negative electric change or is a neutral molecule. The classification of ligands is made on the basis of the number of electron pair donating atoms.

(I) Unidentate ligand : If only one atom of ligand of negative ion or neutral molecule donates one atom to metal ion by giving one electron pair and form one co-ordinate covalent bond, then it is called unidentate ligand. Neutral molecules like H_2O, NH_3, CO and negative ions like Cl^-, CN^-, F^- which combine with metal ion by giving one electron pair; viz. In $[Cr(NH_3)_6]Cl_3$ complex compound, nitrogen atom of each ammonia combine by giving one electron pair to chromium metal ion, it is called unidentate ligand. In $[Cr(H_2O)_6]Cl_3$ complex compounds each molecule of water co-ordinates with chromium metal ion by giving one electron pair, so it is unidentate ligand. In these unidentate ligands, nitrogen atom in ammonia molecule and oxygen atom in water molecule donate one electron pair to metal ion. Hence, the **atom present in negative ion or neutral molecule gives electron pair to metal-ion which is called the co-ordinate site of ligand** and it is shown as $M \leftarrow L$, where M is metal ion and L is ligand.

(II) Didentate ligand : The ligand which can donate two electron pairs and forms two co-ordinate covalent bonds, is called didentate ligand. In this type of ligand two atoms combine with metal ion by giving two electron pairs and form two co-ordinate covalent bonds. Thus, only one ligand satisfies two secondary valencies of metal ion viz. In ethane 1-2 diamine (ethylene diamine–en), its one molecule forms two co-ordinate covalent bonds by giving two electron pairs on two nitrogen atoms, to metal ion.

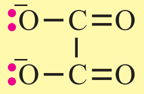
In oxalate $(OX)^{2-}$ negative ion, two electron pairs on two oxygen atoms are given to metal-ion and two co-ordinate covalent bonds are formed.

e.g.,



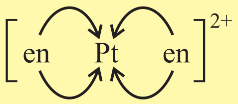
Ethane 1,2-diamine

$C_2O_4^{2-}$ OR $(OX)^{2-}$ OR



Oxalate

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



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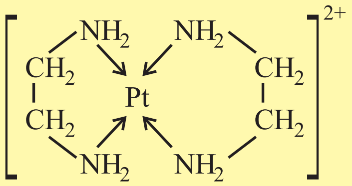
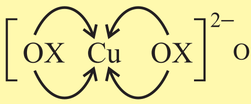
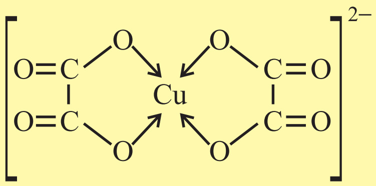


$[Cu(OX)_2]^{2-}$

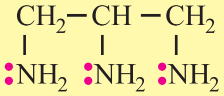


OR



(III) Tridentate ligand : The ligand in which there are three co-ordination sites is called tridentate ligand. In this type of ligand, three atoms form three co-ordinate covalent bonds by giving three electron pairs. Thus only one ligand satisfies three secondary valencies of metal ion viz. Propane 1-2-3 triamine (Propylene triamine-ptn) one neutral molecule form three co-ordinate covalent bonds by giving three electron pairs on its three nitrogen atoms. Similary, PO_4^{3-} is a negative ion tridentale ligand.

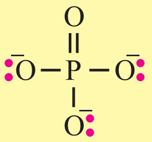
e.g.



Propane 1, 2, 3-triamine

(propylene triamine (ptn))

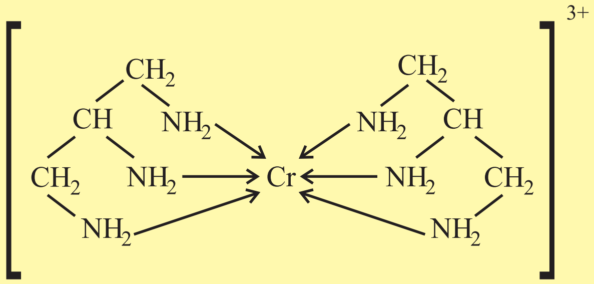
PO_4^{3-} OR

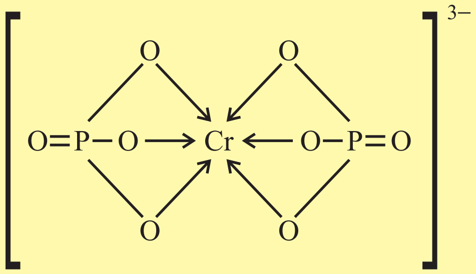


Phosphate

$[Cr\ (ptn)_2]^{3+}$

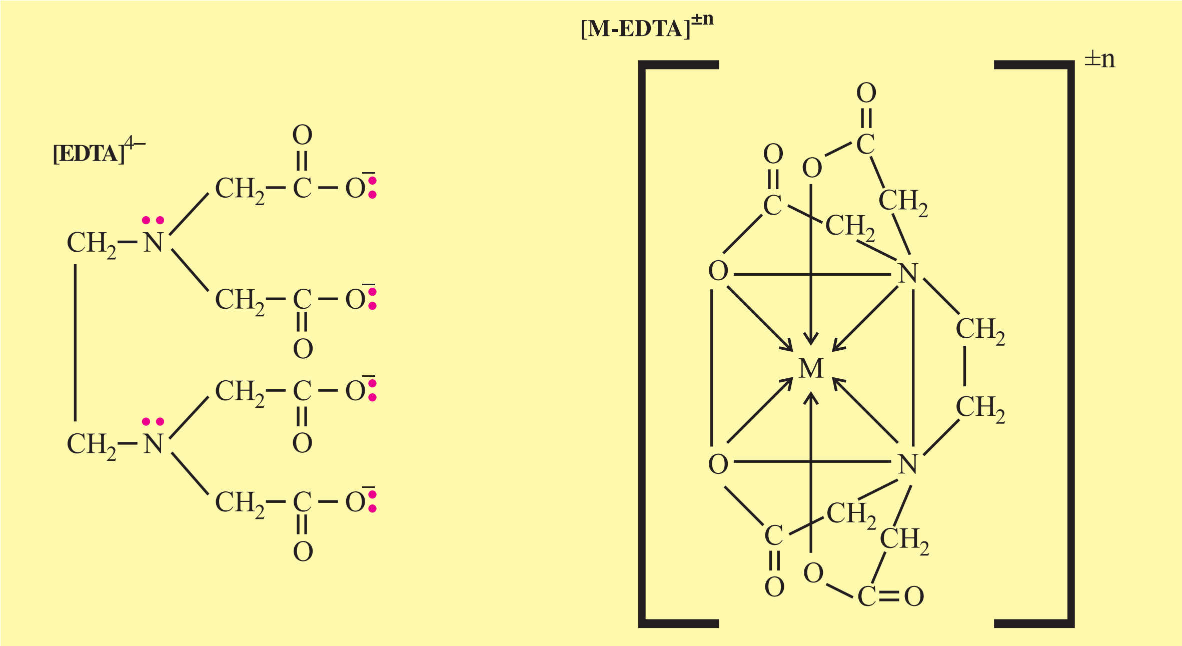
$[Cr\ (PO_4)_2]^{3-}$





(IV) Hexadentate ligand : The ligand in which there are six co-ordination sites is called hexadentate ligand. Six atoms of this type of ligand give six electron pairs to metal ion and form six co-ordinate covalent bonds. Thus, only one ligand satisfies six secondary valencies of metal ion viz. In ethylene diamine tetraacetate $(EDTA)^{4-}$, four oxygen atoms and two nitrogen atoms give four electron pairs and two electron pairs respectively to metal ion and form six co-ordinate covalent bonds.

e.g. $[M\ EDTA]^{\pm n}$

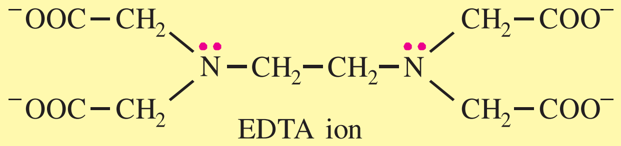


Generally, the ligand in which two or more co-ordination sites are there or the ligand in which two or more atoms donate electron pairs to metal ion and form co-ordinate covalent bond, is called multidentate ligand.

Some ligands and their types are shown in table 4.1

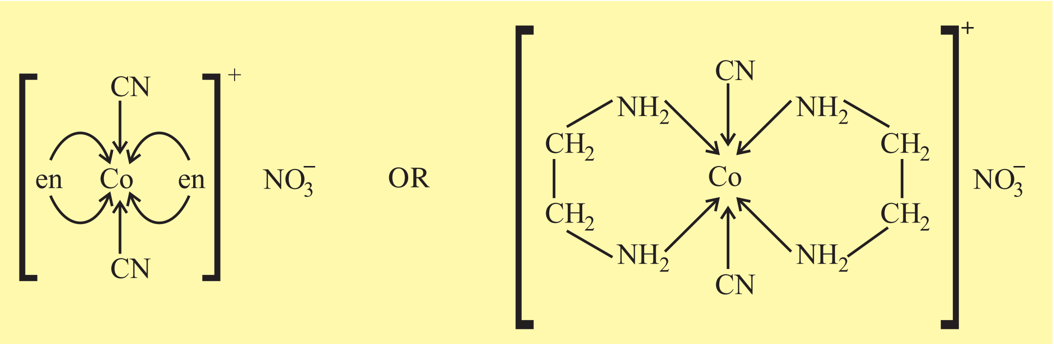
Table 4.1 Some ligands and their types

Type	Ligand	Electric charge
Unidentate Neutral ligand	$H_2\ddot{O}\!:$, $:NH_3$, $:CO$, $:NO$, $CH_3\ddot{N}H_2$, $C_5H_5\ddot{N}$ (py)	0
Unidentate Negative ion ligand	^-OH, F^-, Cl^-, Br^-, I^-, ^-CN, $^-NH_2$, NO_3^-, NO_2^-, $CH_3COO^-(AcO^-)$, O^{2-}, S^{2-}, N^{3-}	– 1
Unidentate Positive ion ligand	^+NO, $^+NO_2$,	+ 1
Didentate Neutral ligand	$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ (en), $\begin{array}{ccccc} CH_2 & - & CH_2 & - & CH_2 \\ \vert & & & & \vert \\ :NH_2 & & & & :NH_2 \end{array}$ (pn)	0
Didentate Negative ion ligand	CO_3^{2-}, SO_4^{2-}, $\begin{array}{c} COO^- \\ \vert \\ COO^- \end{array}$ $(OX)^{2-}$	– 2
Tridentate Neutral ligand	$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ \vert & & \vert & & \vert \\ :NH_2 & & :NH_2 & & :NH_2 \end{array}$ (ptn)	0

Tridantate Negative ion ligand	PO_4^{3-}, AsO_4^{3-}	– 3
Hexadentate Negative ion ligand	 EDTA ion	– 4

When multidentate ligands like en, OX^{2-}, pn, ptn, $(EDTA)^{4-}$ form co-ordinate covalent bond with metal ion, it results into cyclic structure involving central metal ion. **Thus, the complex compound formed by ligand and metal ion having cyclic structure is called chelate.** The stability of such chelate compounds is more than the stability of simple complex compounds (formed by monodentate ligand).

e.g. $[Co(CN)_2(en)_2]^+ NO_3^-$



4.4 Requirements for Formation of Complex Compounds

Some basic requirements are necessary for formation of complex compound. The capacity of transition element metal ions of formation of complex compounds is more than that of other elements.

Basic requirements :

(i) The ligand must have electron pair which can be easily donated.

(ii) There must be vacant orbitals in the metal ion to receive electron pairs.

(iii) The metal ions should have the symmetry of vacant orbitals same as the symmetry of orbitals of ligand having electron pairs. Hence, co-ordinate covalent bond can be formed by overlapping of orbitals having electron pair in ligand.

These basic requirements are satisfied by metal ions and so complex salts are easily formed. Even then, it is not necessary that each transition element forms complex compounds with equal ease. There is change in capacity of formation of complex compounds according to different oxidation states of metal ions. In addition, there is difference in the stability of the compounds that are formed.

4.5 Stability of Complex Compounds and Strength of Ligand

As the strength of different ligands to form co-ordinate covalent bond varies, stronger ligand possesses more attraction with metal ion. As a result, complexes having stronger ligands possess more stability and the complexes having weak ligand possess less stability. Hence, it can be said that the strength of the complexes is determined on the basis of strength of ligand. The basis of strength of ligand can be determined by same metal ion combined with different ligands. The order of strength of some complex compounds is as follows : **$Cl^- < F^- < OH^- < H_2O < NH_3 < CN^-$**

$[NiCl_4]^{2-} < [NiF_4]^{2-} < [Ni(OH)_4]^{2-} < [Ni(H_2O)_4]^{2-} < [Ni(NH_3)_4]^{2-} < [Ni(CN)_4]^{2-}$

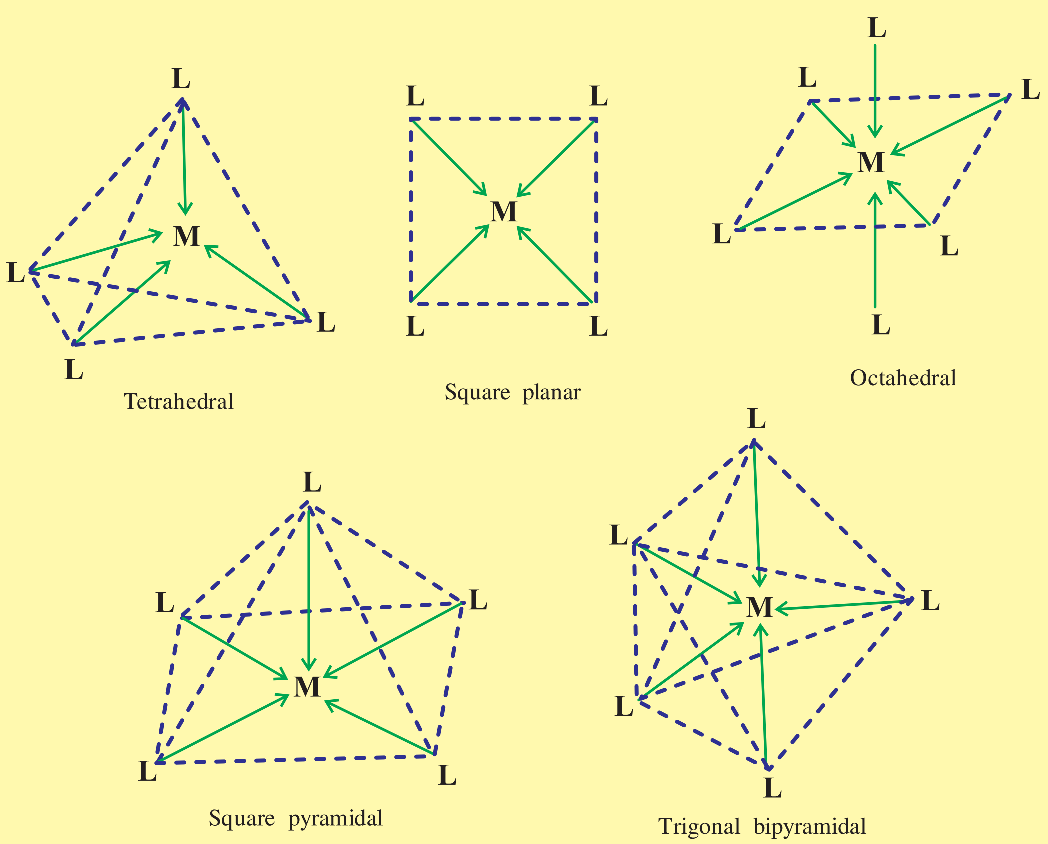
$[CuCl_4]^{2-} < [CuF_4]^{2-} < [Cu(OH)_4]^{2-} < [Cu(H_2O]^{2+} < [Cu(NH_3)_4]^{2+} < [Cu(CN)_4]^{2-}$

Hence, change in the capacity is seen in the formation of complex ions of metal ions of transition elements according to different conditions.

It is not necessary that any metal ion form only one type of complex salt with ligand. Sometimes different types of ligands form complex compounds with metal ion. This type of complex compounds are called mixed ligand complex compounds. viz. In the complex $[Cr(NH_3)_4(CN)_2]NO_3$, four ammonia molecules and two cyanide ions, total six unidentate ligands are combined. If ligand is of only one type, the complex salts are called simple complex compounds.

As in mixed ligand complex compounds two or more types of ligands combine and form complex compound, similary if only one metal ion is present in any complex compound, then it is called unicentred complex compound, e.g. $K[MnO_4]$. **If more than one metal ions are present in the complex compound then it is called polycentred complex compound.** e.g. $K_2[Cr_2O_7]$.

In unicentred or polycentred complex compounds, the three dimensional arrangement of ligand combined to metal ion are directional, so different geometrical structures formed accordingly are called co-ordination polyhedral. Mostly, the shape of this geometrical structure is tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal.



Tetrahedral

Square planar

Octahedral

Square pyramidal

Trigonal bipyramidal

Fig. 4.1

4.6 Geometry of Complex Ions

The co-ordination number of metal ion and the geometrical structures of ions can be known from the studies of magnetic properties and crystal field theory. It is not necessary that metal ion should possess same co-ordination number and one definite type of geometrical structure containing complex ions. Sometimes, it may happen that the metal ion possesses more than one co-ordination number and even if the co-ordination number remains the same, it can form complex ions having different types of geometrical structures. In most of the metal complex ions, the co-ordination number 4 and 6 are very common and the complex ions showing these co-ordination numbers are found comparatively in larger number.

Co-ordination number 4 : The metal ions possessing co-ordination number 4 form complexes having two types of geometrical structures :

(i) Tetrahedral structure containing complex ions and (ii) square planar structure containing complex ions.

(i) Tetrahedral complex ions : Metal ions form tetrahedral complex ions and they are stable in special conditions. Most of the tetrahedral complex ions are obtained in negative ion form viz. MnO_4^- . While, tetrahedral complex like $[Ni(CO)_4]$ is obtained in form of neutral molecule.

(ii) Square planar complex ions : Metal ions of only some of the transition elements form square planar complexes. Square planar complexes are formed by combination of Ni^{2+} metal ion with negative ion and / or neutral molecule ligand viz. $K_2[Ni(CN)_4]$ and $[Ni(NH_3)_2Cl_2]$.

In table 4.2 some examples of tetrahedral and square planar complexes possessing co-ordination number 4 of some transition elements in the fourth period are shown.

Table 4.2 Some complexes of transition elements possessing co-ordination number-4

Transition Element	Oxidation state	Electrons of 3d-orbital	Complex compound	Geometrical structure
Mn	+7	$3d^0$	$K[MnO_4]$	Tetrahedral
Co	+2	$3d^7$	$K_2[CoCl_4]$	Tetrahedral
Ni	0	$3d^{10}$	$K_4[Ni(CN)_4]$	Tetrahedral
	+2	$3d^8$	$K_2[NiCl_4]$	Tetrahedral
	+2	$3d^8$	$K_2[Ni(CN)_4]$	Square planar
	+2	$3d^8$	$[Ni(NH_3)_2Cl_2]$	Square planar

Co-ordination number 6 : The complex compounds of metal ions possessing co-ordination number 6 are easily available. The geometrical structures of these complexes are octahedral due to which different ligands deformations are also found viz. $[CrCl_2(en)_2]NO_3$ and $[Co(NH_3)_4CO_3]Cl$.

In table 4.3, some examples of octahedral complexes possessing co-ordination number 6 of elements of some transition elements of fourth period are given.

Table 4.3 Some complexes possessing co-ordination number 6 of transition elements

Transition Element	Oxidation state	Electrons of 3d-orbital	Complex compound (Octahedral structure)
Cr	0	$3d^6$	$[Cr(CO)_6]$
	+1	$3d^5$	$K_4[Cr(CN)_5(NO)]$
	+3	$3d^3$	$K[Cr(NH_3)_2(CO_3)_2]$
	+4	$3d^2$	$K_2[CrF_6]$
Mn	+2	$3d^5$	$[Mn(H_2O)_6]Cl_2$
	+3	$3d^4$	$[Mn(en)_3]Cl_3$
Fe	+2	$3d^6$	$K_4[Fe(CN)_6]$
	+3	$3d^5$	$Na_3[Fe(OX)_3]$
Co	+2	$3d^7$	$Na_4[Co(NO_2)_6]$
	+3	$3d^6$	$[Co(NH_3)_6]Cl_3$
	+4	$3d^5$	$K_2[CoF_6]$
Ni	+2	$3d^8$	$[Ni(H_2O)_6]Cl_2$
	+3	$3d^7$	$K_3[Ni(CN)_6]$
	+4	$3d^6$	$K_2[NiF_6]$

4.7 Hybridization of Orbitals of Metal Ions of Complex Compounds and Magnetic Properties

Most of the metal ions have geometrical structures- tetrahedral, square planar or octahedral. To understand this geometrical structures, hybridization of metal-ion orbitals and magnetic property are very useful.

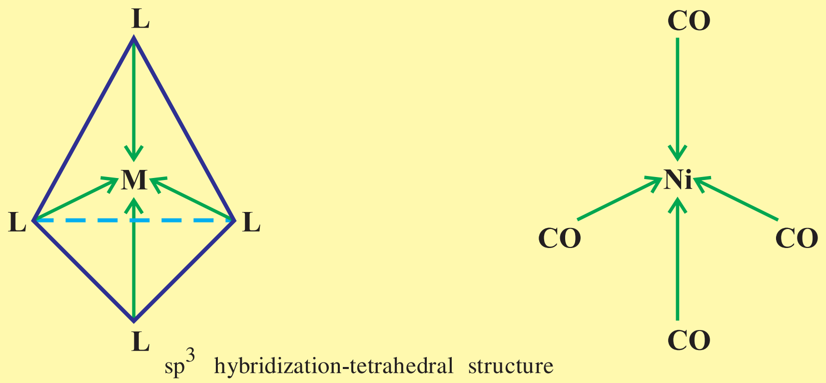
sp^3 hybridization : When one 4s-orbital and three $4p_x$, $4p_y$, $4p_z$ orbitals overlap with one another and get hybridised, then new four hybrid orbitals are produced. These four orbitals are called sp^3 hybrid orhitals. The energy value of these four hybrid orbitals are same and are extended towards the four corners from the centre of the tetrahedral. Also, the angle between any two sp^3 hybrid orbitals is $109^0 28'$. Hence, if the metal ion orbitals in complex ion hybridization of sp^3 type, then the geometrical structure of complex compounds is tetrahedral.

dsp^2 hybridization : When one 3d-orbital, one 4s-orbital and two $4p_x$, $4p_y$ orbitals of metal ion overlap with one another and get hybridized, new four hybrid orbitals are produced. These four hybrid orbitals are called dsp^2 hybrid orbitals. The value of energy of these four hybrid orbitals is same and are extended towards four corners from the centre of the plane square. Also, the angle between any two nearby dsp^2 orbital is 90^0. Hence, if the hybridization of metal ion orbitals in compound, is of dsp^2 type then, the geometrical structure of metal in the compound becomes of dsp^2 type; then the geometrical structure of complex compounds is square planar.

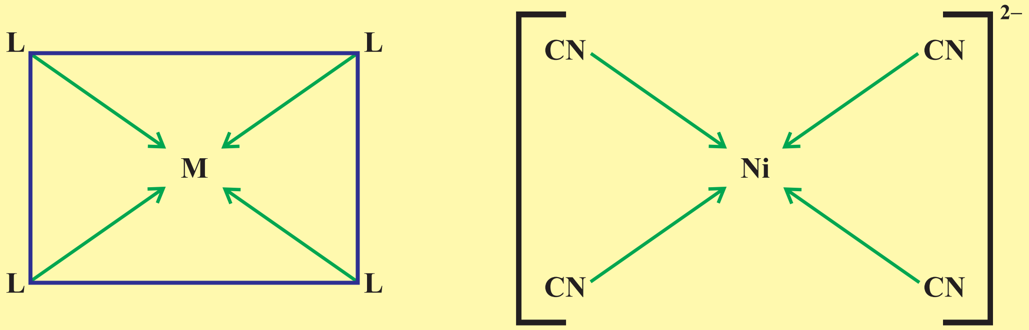
d^2sp^3 hybridization : When two 3d-orbitals, one 4s-orbital and three $4p_x$, $4p_y$, $4p_z$ orbitals overlap with one another and get hybridized, then new six hybrid orbitals are produced. These hybrid orbitals are called d^2sp^3 hybrid orbitals. The value of energy of these six hybrid orbitals is same and it is extended to six corners of octahedral from the centre of that octagon. Also, all these hybrid orbitals are on X-axis, Y-axis and Z-axis to one another. So the angle between any two nearby d^2sp^3 orbitals is 90^0. Hence, the complex compounds in which the hybridization of metal ion in complex compound is of d^2sp^3 type, the geometrical structure of this complex compound is octahedral.

sp^3d^2 hybridization : Sometimes, sp^3d^2 hybridisation can occur to produce octahedral structure when 3d-orbitals of metal ion are not available, then one 4s-orbital, three $4p_x$, $4p_y$, and $4p_z$ orbitals and two 4d-orbitals overlap with one another and sp^3d^2 hybridization occurs. Here also, in sp^3d^2 hybridization the geometrical structure is octahedral.

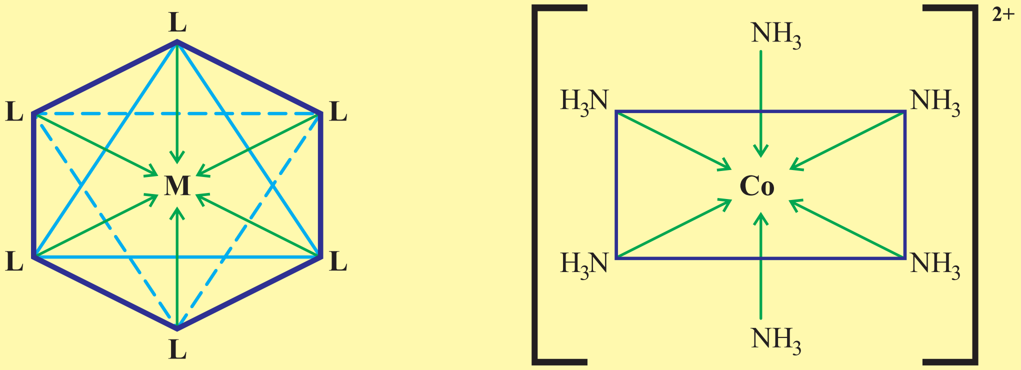
Hence, it can be said that in octahedral structure d^2sp^3 or sp^3d^2 hybridization occurs. To determine which type of hybridization is possessed by study of magnetic properties becomes very essential. In fig. 4.2 the geometrical structures of complex molecules or ions on the basis of sp^3, dsp^2, d^2sp^3 or sp^3d^2 hybridization are shown.



sp^3 hybridization-tetrahedral structure



dsp^2 hybridization-square planar structure



d^2sp^3 Or sp^3d^2 hybridization-octahedral structure

Fig. 4.2 Geometrical structures of complex ions

Magnetic properties : If the electrons of 3d-orbital of the metal ion are paired in transition element in any complex then the complex is called diamagnetic. If there are unpaired electrons then the complex is called paramagnetic. The theoretical value of magnetic moment can be found out by the equation $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons. The unit of this value is BM (Bohr magneton).

The magnetic moment of complex compounds of metal ions of transition elements is dependent on geometrical structure, type of ligand etc. In the detailed study of complex compounds, the calculation of magnetic moment is very helpful. In table 4.1, the theoretical and experimental values of magnetic moment of Sc^{2+} to Zn^{2+} (d^1 to d^{10}) ions are given.

Table 4.4 Unpaired electrons and magnetic moment of M^{2+} ions of transition elements

Ion	$3d^n$	Unpaired Electrons	Magnetic moment (μ) BM	
			Theoretical value	Experimental value
Sc^{2+}	d^1	1	1.73	1.73 – 1.74
Ti^{2+}	d^2	2	2.83	2.76
V^{2+}	d^3	3	3.87	3.86
Cr^{2+}	d^4	4	4.90	4.80
Mn^{2+}	d^5	5	5.92	5.96
Fe^{2+}	d^6	4	4.90	5.00 – 5.50
Co^{2+}	d^7	3	3.87	4.40 – 5.20
Ni^{2+}	d^8	2	2.83	2.90 – 3.40
Cu^{2+}	d^9	1	1.73	1.80 – 2.20
Zn^{2+}	d^{10}	0	0	0

4.8 IUPAC Nomenclature of Complex Compounds

There are different types of ligand for variety of complex compounds with various metal elements. Also many complex compounds possessing mixed ligands are prepared. In the earlier times, the names of the complex compounds were given on the basis of metal ion and their colours. Werner had named the complexes obtained from cobalt chloride and ammonia on the basis of their colours viz. greenio cobaltic ammonium chloride, violetio cobaltic ammonium chloride, purpleo cobaltic ammonium chloride etc. As many complexes were being formed, the accurate names of complex compounds could not be given. Hence to have accuracy in the names of the complex compounds, IUPAC method was used. The IUPAC nomenclature of monocentric complex compounds is done according to the definite rules as shown below :

(i) In showing name of ionic complex compound, the positive ion is written first and then the name of negative ion, is mentioned.

(ii) In complex compound co-ordination sphere [ ] in naming is done according to the rules.

  (a) In nomenclature in co-ordination sphere the name of ligand according to English alphabates is first shown and then the name of the metal is written.

(b) For the ligands having negative electric charge, the suffix 'O' is joined with the name of the ligand viz OH^- hydroxo, CN^- cyano, NH_2^- amido, NO_2^- nitro, ONO^- nitrito, NO_3^- nitratato, SCN^- thiocyanato, CNO^- cyanato, CO_3^{2-} carbonato, O^{2-} oxo, OX^{2-} oxalato, PO_4^{3-} phosphato, AsO_4^{3-} arsenato etc. As per IUPAC rules, 2004, Cl^- is written as chlorido instead of chloro and Br^- as bromido instead of bromo.

(c) The neutral ligand is shown according to its original name viz. $CH_3 \cdot NH_2$ methyl amine, $H_2N–CH_2–CH_2–NH_2$ ethane 1-2 diamine, $NH_2–CH_2–CH(NH_2)–CH_2–NH_2$ propane-1,2,3-triamine $H_2N–CH_2–CH_2–CH_2–NH_2$ propane 1,2-diamine but as exception H_2O aqua, NH_3 ammine, CO carbonyl, NO nitrosyl etc. are written.

(d) If the number of ligand of only one type is more than 1, then according to the number of ligands 2, 3, 4, 5, 6, the words di, tri, tetra, penta, hexa etc are used as prefix respectively. If organic ligand is there, and the prefix is a number, then ligand is placed in bracket and for numbers 2, 3, 4 etc. corresponding bis, tris, tetrakis prefix are added.

(e) If there is monocentred complex ion, in which only one metal ion, then there is definite order of showing its name.

(i) If the complex is negative ion, then write names of ligand successively. The suffix 'ate' is joined with metal ion and then its oxidation state is shown in ( ) bracket in Roman numbers viz. ferrate (II), ferrate (III), chromate (III), manganate (VII), cobaltate (III), nickelate (II), molybdate (VI).

(ii) If the complex is positive ion or neutral molecule, then first writing the name of ligand successively, the name of metal is added at the end and its oxidation state is shown in ( ) bracket, in Roman numbers. The whole part of complex positive ion, negative ion and neutral molecule is placed in the square bracket [ ].

The formulae and IUPAC names of some complex compounds on the basis of these rules are given below :

Formula	**IUPAC**
$K[MnO_4]$	Potassium tetraoxomanganate(VII)
$Na_2[CoCl_4]$	Sodium tetrachloridocobaltate(II)
$[Ni(CO)_4]$	Tetracarbonylnickel(0)
$K_2[NiCl_4]$	Potassium tetrachloridenickelate(II)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II)ion
$[Cu(NH_3)_4]Cl_2$	Tetraamminecopper(II)chloride
$[Cr(CO)_6]$	Hexacarbonylchromium(0)

$[Ni(H_2O)_2(NH_3)_4]SO_4$	Tetraamminediaquanickel(II)sulphate
$[Cr(OX)_3]^{3-}$	Trioxalatochromate(III)ion.
$[Co(en)_2(CN)_2]Cl$	Dicyanobis(ethane-1,2-diamine)cobalt(III)chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$(NH_4)_2[MoO_4]$	Ammonium tetraoxomolybdate(VI)
$K_2[CrF_6]$	Potassium hexafluoridoochromate(IV)
$Na_2[Fe(NO)(CN)_5]$ (Sodium introprusside)	Sodium pentacyanonitrosoniumferrate(II)
$Na_4[Co(NO_2)_6]$	Sodium hexanitrocobaltate(II)
$NH_4[Co(NH_3)_2(OX)_2]$	Ammonium diamminedioxalatocobaltate(III)
$[Pt(Pn)_2CO_3]SO_4$	Carbonatobis(propane-1,3-diammine)platinum(II)sulphate
$[Ag(NH_3)_2][Ag(CN)_2]$	Diammineargentinun(I) dicyanoargentate(I)
$[Cr(en)_3][Cr(OX)_3]$	Tris(ethane-1,2-diamine)chromium(III)trioxalatochromate(III)
$[Pt(NH_3)_2ClNO_2]$	Diamminechloridonitroplatinum(II)
$[Co(NH_3)_4CO_3]Cl$	Tetramminecarbonatocobalt(III)chloride.
$[Cr(NH_3)_4(ONO)Cl]NO_3$	Tetraamminechloridonitritochromium(III)nitrate
$Na_2[Ni(EDTA)]$	Sodium ethylenediamminetetraacetatonickelate(II)
$[Pt(Py)_4][PtBr_4]$	Tetrapyridineplatinum(II)tetrabromidoplatinate(II)
$[CuCl_2(CH_3NH_2)_2]$	Dichloridodi(methanamine)copper(II)
$[Cr(NH_3)_6][Cr(SCN)_6]$	Hexaamminechromium(III)hexathiocyanatochromate(III)

Formula from the IUPAC name of the complex

(a) Tetrammineaquachloridocobalt(III)chloride

$[Co(NH_3)_4(H_2O)Cl]Cl_2$

(b) Potassium tetrahydroxozincate(II)

$K_2[Zn(OH)_4]$

(c) Sodium trioxalatoaluminate(III)

$Na_3[Al(C_2O_4)_3]$

(d) Dichloridobis(ethane-1-2-diamine)cobalt(III)ion.

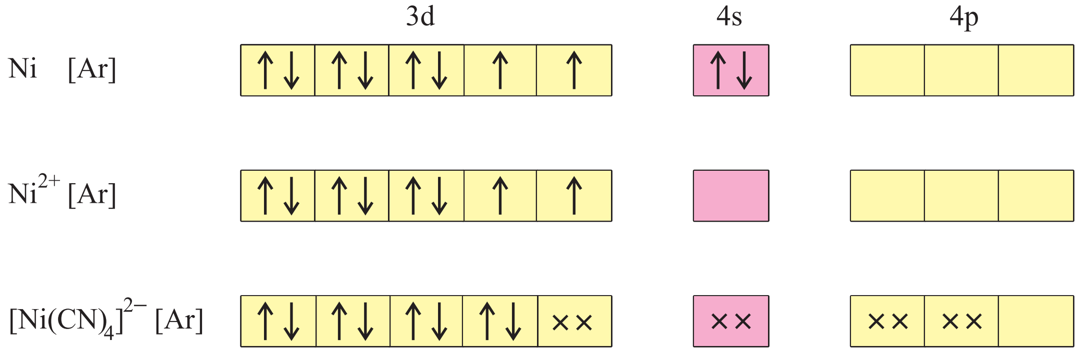
$[Co(en)_2Cl_2]^+$

(e) Pentacarbonyliron(0)

$[Fe(CO)_5]$

4.9 Geometrical Structures and The Magnetic Properties of Complex Compounds

$[Ni(CN)_4]^{2-}$ complex ion : In tetracyano nickelate (II) four CN^- strong ligands are combined with Ni^{2+} metal ion. In this compound, four ligands are joined and so possesses square planar or tetrahedral structure. Here the electronic configuration of Ni metal and Ni^{2+} ion are $[Ar]3d^8 4s^2$ and $[Ar]3d^8$ respectively. The arrangement of eight electrons in 3d-orbitals is shown in the following figure. The orbitals are shown by square blocks and the electrons by vertical arrow sign ↑ or ↓.



Unpaired electrons n = 0

dsp^2 hybridization.

Hence $\mu = 0$ BM

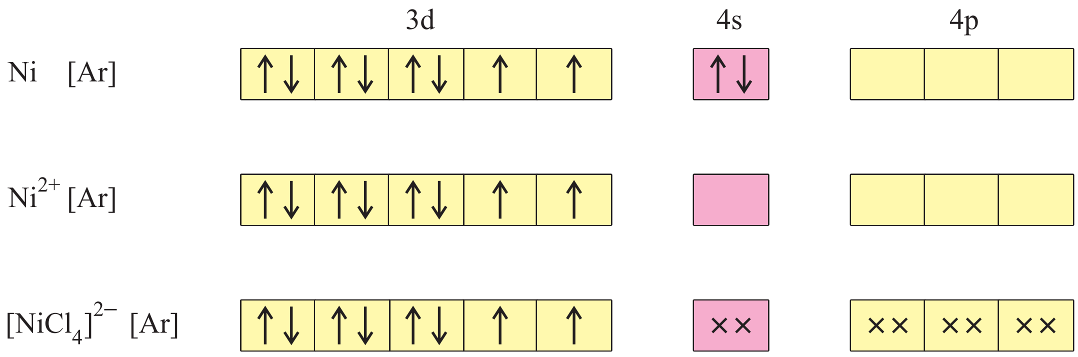
In one square block, the vertical arrows in opposite directions show electron pairs in which the rotation of both the electrons is in opposite directions. Here Ni^{2+} metal ion combines with four CN^- strong ligand and forms complex ion. Each CN^- strong ligand gives one electron pair to Ni^{2+} metal ion Hence Ni^{2+} metal ion receives four electron pairs from four ligands.

If the structure of $[Ni(CN)_4]^{2-}$ is square planar, then dsp^2 type hybridization occurs in Ni^{2+} metal ion. For this, one 3d-orbital, one 4s-orbital and two 4p-orbitals take part in hybridization of dsp^2, orbitals having equal energy are produced. For this, the arrangement of eight electrons in 3d-orbitals of Ni^{2+} metal ion, the charge is necessary because of the strong ligand like CN^-. In this two unpaired electrons in 3d-orbital, one unpaired electron of 3d-orbital enters into the other 3d-orbital having unpaired electron and forms a pair. As a result one 3d-orbital becomes vacant.

[Note : Because of strong ligands like CN^-, NH_3 and CO, the unpaired electrons get paired in rearrangement of electrons.]

This vacant one 3d-orbital, one 4s-orbital and two 4p-orbitals overlap and form dsp^2 four hybrid orbitals and arrange at 90^0 angle in square planar form. In the four dsp^2 orbitals produced, this four electrons pairs coming from four strong ligand CN^-, get arranged, which are shown by $\boxed{\times\times}$ sign. **Here $[Ni(CN)_4]^{2-}$ complex possesses dsp^2 hybridization and its all 3d-orbitals have paired electrons and so it becomes diamagnetic and its geometric structure is square planar.**

$[NiCl_4]^{2-}$ complex ion : In tetrachlorido nickelate (II) complex ion, Ni^{2+} metal ion is combined with four weak Cl^- ligands. As CN^- strong ligand comes nearer to the metal ion because it possesses more attraction, while weak Cl^- ligand does not come near to metal ion because it possesses less attraction. Hence, the 3d-orbital of Ni^{2+} ion is not capable of forming co-ordinate covalent bond with four Cl^- weak ligand. Hence, the rearrangement of electrons in 3d-orbitals if Ni^{2+} metal ion is not required. Here, one 4s, and three 4p-orbitals take part in hybridization and form sp^3 hybrid orbitals having same energy, which is arranged at the angle of $109^0 28'$ tetrahedrally in which the four electron pairs coming from four weak Cl^- ligand are arranged.

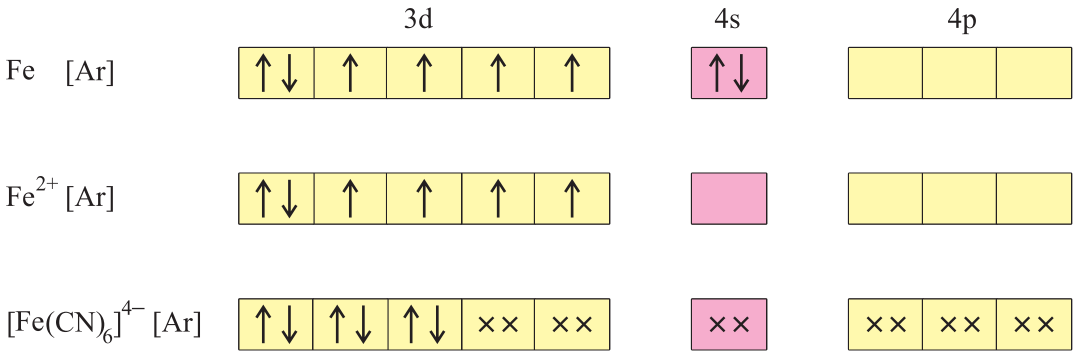


Unpaired electrons n = 2 sp^3 hybridization

Hence, μ = 2.83 BM

Because of this $[Ni(Cl)_4]^{2-}$ complex ion has sp^3 type of hybridization and its geometrical structure becomes tetrahedral. As there are two unpaired electrons in two 3d-orbitals, the theoretical value of its magnetic moment becomes 2.83 BM and the value of experimental magnetic moment is 2.90 BM. So it becomes paramagnetic.

$[Fe(CN)_6]^{4-}$ complex ion (Ferrocyanide ion) : In hexacyano ferrate (II) complex ion Fe^{2+} metal ion has combined with six CN^- strong ligand and so it possesses octahedral structure. Here, the electronic configuration of Fe metal and Fe^{2+} ion are [Ar] $3d^6 4s^2$ and [Ar]$3d^6$ respectively. The arrangement of six electrons in 3d-orbitals is shown below :



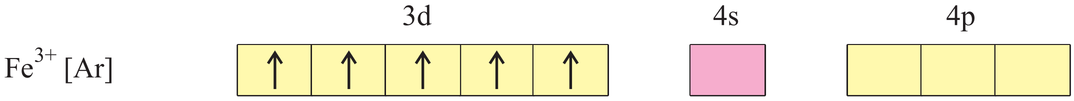
Number of unpaired electrons n = 0 d^2sp^3 hybridization

Hence, μ = 0 BM

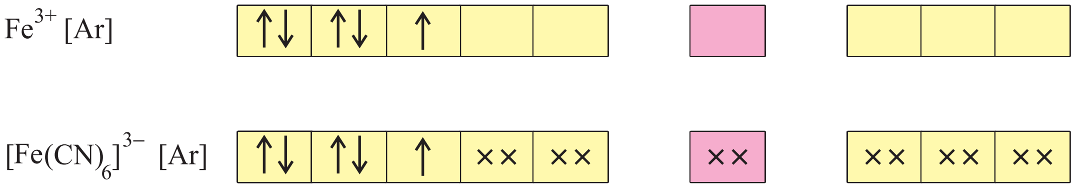
In Fe^{2+} ion d^2sp^3 type hybridization occurs. Octahedral structure is obtained in this hybridization. In d^2sp^3 hybridization, the inner 3d-orbital takes part.

For d^2sp^3 hybridisation there must be two 3d-orbitals vacant in Fe^{2+} metal ion. For this, the rearrangement of six electrons in 3d-orbitals is necessary i.e. as the CN^- ion is a strong ligand, total six electrons form three electron pairs and get arranged in 3d-orbitals. As a result the vacated two 3d-orbitals, one 4s-orbital and three 4p-orbitals overlap and form d^2sp^3 hybridization; six d^2sp^3 hybrid orbitals having same energy, produced in the above are arranged octahedrally. In d^2sp^3 hybrid orbitals six electron pairs coming from six CN^- strong ligand are arranged. **Here, $[Fe(CN)_6]^{4-}$ complex ion possesses d^2sp^3 type hybrid orbitals and its geometrical structure is octahedral. In the 3d-orbitals of this complex only paired electrons are there and so it becomes diamagnetic.**

$[Fe(CN)_6]^{3-}$ Hexacyanoferrate (III) ion (Ferricyanide ion) : In hexacyanoferrate (III) complex ion, the oxidation state of Fe is +3 and its coordination number is 6. The electronic configuration of Fe^{3+} metal ion in this complex compound is [Ar] $3d^5$. As CN^- is a strong ligand, rearrangement of electrons in 3d-orbitals is necessary. On rearrangement of five electrons in 3d-orbitals, two orbitals become paired and one electron remains unpaired in 3d-orbital. Hence, two 3d-orbitals, one 4s-orbitals and three 4p orbitals overlap and form d^2sp^3 type hybridization. Six electron pairs coming from strong ligand CN^- are arranged in six d^2sp^3 hybrid orbitals having same energy. Here, $[Fe(CN)_6]^{3-}$ complex ion possesses d^2sp^3 hybridization.



On rearrangement of electrons because of strong ligand like CN^-



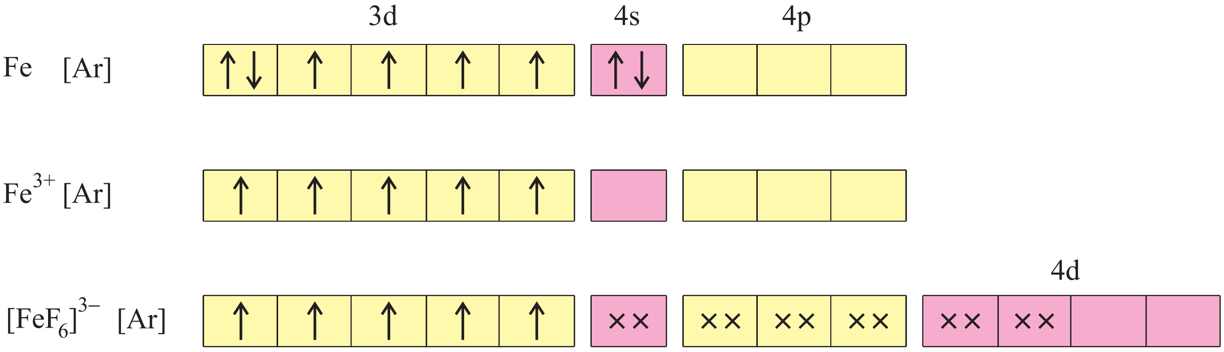
Unpaired electron n = 1

d^2sp^3 hybridization

Hence μ = 1.73 BM

$[Fe(CN)_6]^{3-}$ complex ion possesses d^2sp^3 hybridization whose geometrical structure is octahedral. As there is one unpaired electron in its 3d-orbit it becomes paramagnetic and the theoretical value of magnetic moment becomes 1.73 B.M. and the experimental value is about 1.8 BM.

$[FeF_6]^{3-}$ complex ion : In hexafluorido ferrate (III) ion, six weak F^- ligands combine with Fe^{3+} metal ion. As six F^- weak ligands are combined with Fe^{3+} metal ion, this complex compound possesses sp^3d^2 hybridisation and octahedral structure. In this complex ion in 3d-orbitals, five unpaired electrons are there and so it becomes paramagnetic. Its theoretical value of magnetic moment is 5.92 B.M.



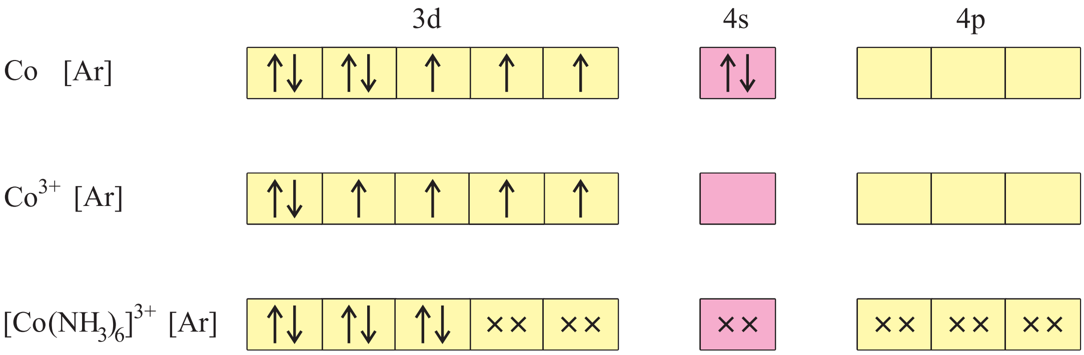
Unpaired electrons n = 5

sp^3d^2 hybridization

Hence μ = 5.92 BM

If ligand had been strong, the electrons present in 3d-orbitals would have rearranged but as F^- is a weak ligand, the rearrangement of five electrons in 3d-orbital does not take place. So one 4s-orbital, three 4p-orbitals and two 4d-orbitals, aggregating six orbitals overlap and sp^3d^2 hybridization occurs. In this six sp^3d^2 hybrid orbitals having same energy, six electron pairs coming from six weak F^- ligand are arranged. **Here, $[FeF_6]^{3-}$ complex ion possesses sp^3d^2 hybridization. So, its geometrical structure is octahedral and complex is paramagnetic.** Generally, the basis of d^2sp^3 hybridisation or sp^3d^2 hybridisation is dependent on the strength of ligand.

$[Co(NH_3)_6]^{3+}$ complex ion : In hexaamminecobalt (III) complex ion the oxidation state of cobalt is +3. The electronic configuration of Co metal and Co^{3+} metal ion are $[Ar]3d^7 4s^2$ and $[Ar]3d^6$ respectively. Here, in Co^{3+} metal ion, the six electrons- one in 3d-orbital are paired and in four other 3d-orbitals unpaired electrons are present. When the strong ligand NH_3 gives six electron pairs to Co^{3+} metal ion, it forms six co-ordinate covalent bonds, the hybridization of Co^{3+} ion, is of d^2sp^3 and six electron pairs of six NH_3 strong ligand are arranged in six hybrid orbitals. Here, to have d^2sp^3 hybridization, two 3d-orbitals must be vacated. NH_3 being a strong ligand, there is rearrangement of six electrons in 3d-orbitals and become paired and two 3d-orbitals remain vacant. Two 3d-orbitals, one 4s-orbital and three 4p-orbitals overlap and d^2sp^3 hybridization occurs so that six hybrid orbitals having same energy get arranged octahedrally.



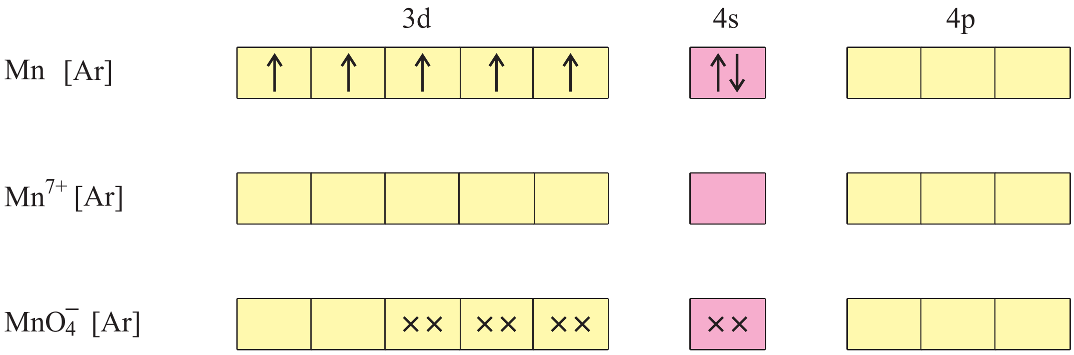
Unpaired electrons n = 0

d^2sp^3 hybridization

Hence diamagnetic $\mu = 0$ BM

Here, $[Co(NH_3)_6]^{3+}$ complex possesses d^2sp^3 hybridization and the complex becomes octahedral. As there is no unpaired electron in 3d-orbitals, the complex becomes diamagnetic.

$[MnO_4]^-$ complex ion : In tetraoxomanganate (VII) complex, four O^{2-} weak ligands are combined with Mn^{7+} metal ion, so it possesses tetrahedral structure. The electronic configuration of Mn metal and Mn^{7+} metal ion are $[Ar]3d^5 4s^2$ and $[Ar]3d^0$ respectively. Here 3d and 4s-orbitals are vacant. In Mn^{7+} metal ion, one 4s and three 3d-orbitals overlap and d^3s type hybridization occurs. In d^3s hybridisation, four hybrid orbitals having same energy are arranged on the four corners of tetrahedral. Four electron pairs of oxygen ions from co-ordination covalent bonds in hybrid orbitals.



d^3s hybridization.

In $[MnO_4]^-$ complex ion there is d^3s hybridization. The co-ordinate bonds formed by O^{2-} weak ligand electrons undergo d-d transition in d-orbital, so that eventhough there is no unpaired electron in Mn^{7+} of MnO_4^-, it gives coloured ion.

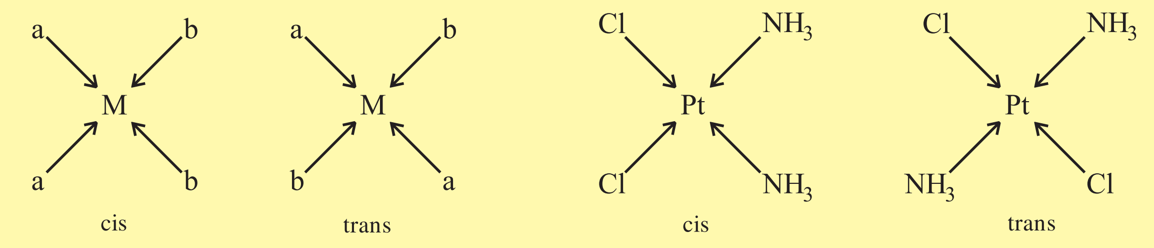
4.10 Isomerism in Complex Compounds

The complex compounds whose molecular formulae are same but the structural formulae are different, are called isomers of each other. Complex compounds possess geometrical isomerism, optical isomerism and structural isomerism.

Geometrical isomerism : Geometrical isomerism is generally observed in square planar and octahedral complex ions. If the two same ligands combined to metal ion are in nearby position to each other, then that isomer is called cis isomer and if they are in opposite positions then the isomer is called trans isomer.

In the square planar structure if there are M metal ion and two different types of two ligands a and b combine then two geometrical isomerism cis and trans are produced

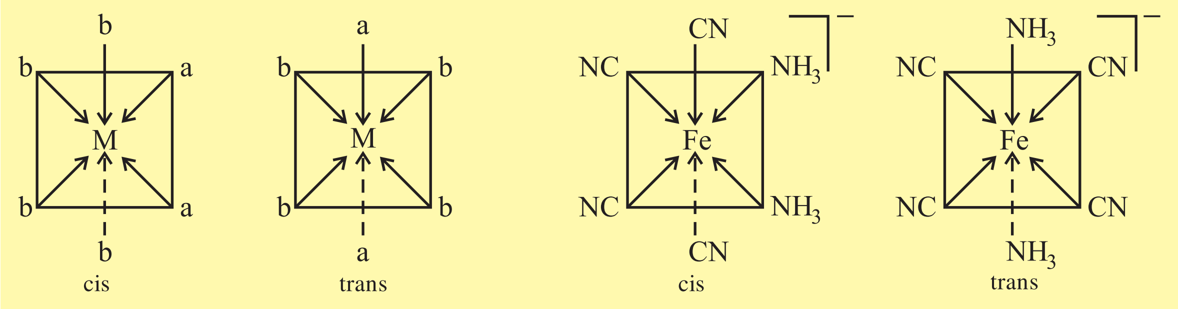
e.g. $[Pt(NH_3)_2Cl_2]$



cis trans cis trans

In octahedral structure, if M is metal ion and two ligands of type a and four ligands of type b are there, then two types of geometrical isomerism cis and trans are produced

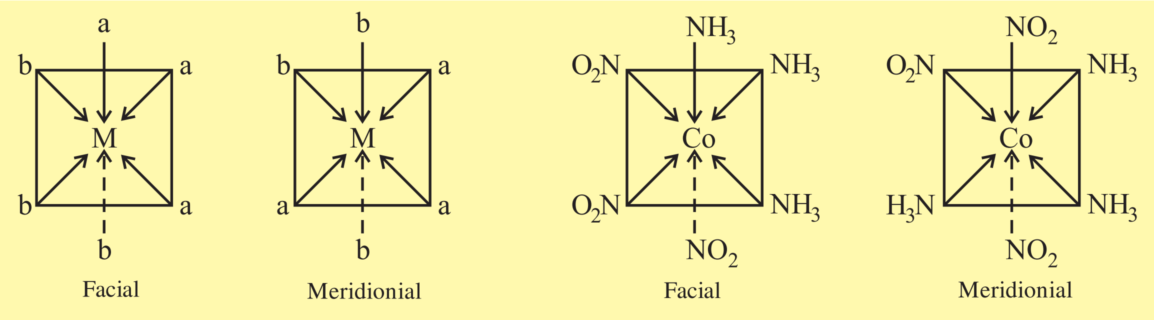
e.g. $[Fe(NH_3)_2(CN)_4]^-$



cis trans cis trans

In octahedral structure, if M is metal ion and three ligands of two types a and b are present then two types geometrical isomerism-facial and meridional- are produced

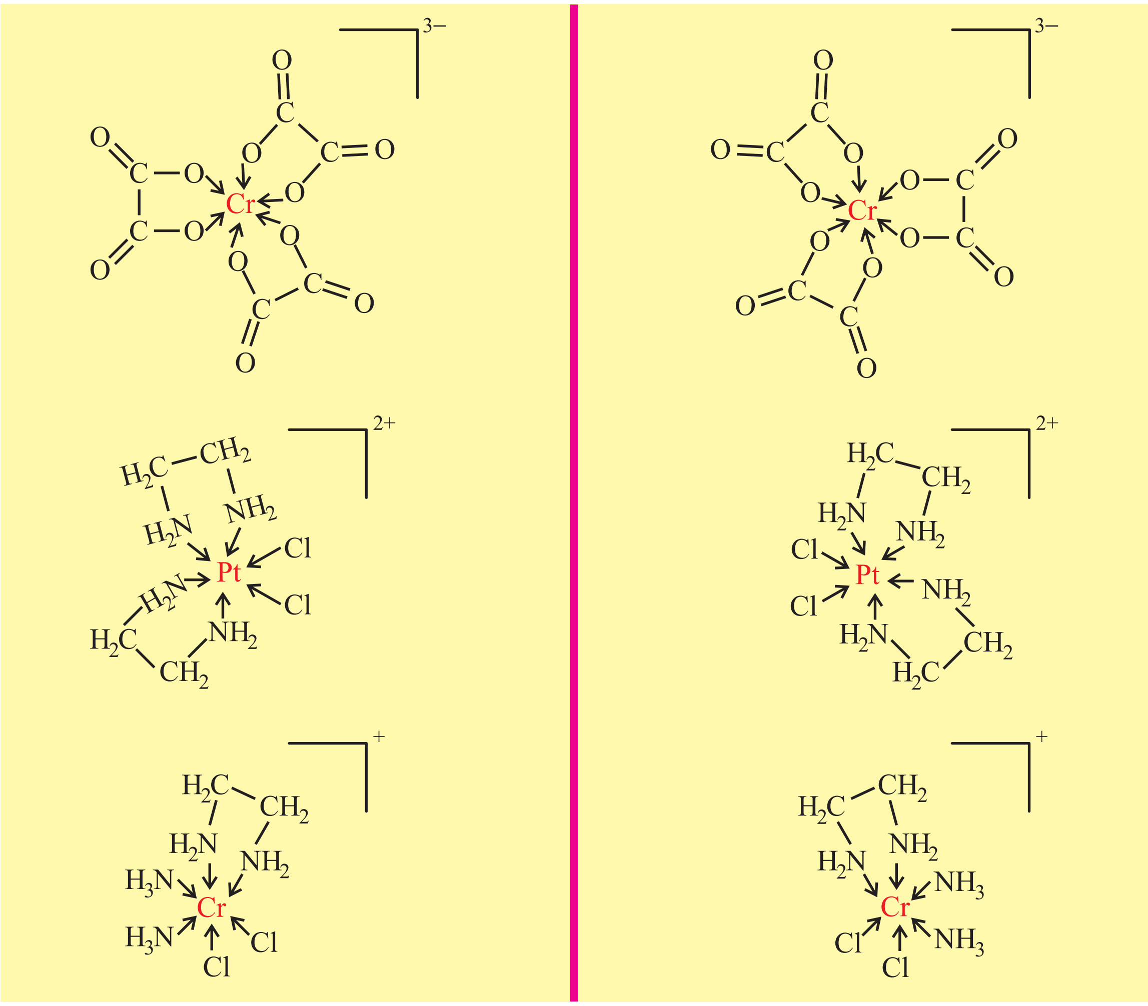
e.g. $[Co(NH_3)_3(NO_2)_3]$



Facial Meridionial Facial Meridionial

Optical isomerism : Optical isomerism is generally observed in octahedral complex-chelate ions. There are certain complex compounds in which molecular formula and structural formulas are same, but the two isomers produced, because of directional arrangement of ligands in it. They are mirror images to each other and the superimposition of two isomers on each other is not possible. This type of complex ions possess property of chirality and they are called optical isomers. **The main difference between these two isomers is that both the isomers rotate the plane polarized light to left or right in directions opposite to each other.** If it rotates angle of rotation on left side, then that isomer is called *l* (levo) or (–) and one which rotates angle of rotation on right side, than that isomer is called *d* (dextro) or (+). The equal proportion mixture of dextro and levo isomers is called racemic, *dl* or (±) mixture.

e.g. $[Cr(C_2O_4)_3]^{3-}$, cis $[PtCl_2(en)_2]^{2+}$, $[CrCl_2(NH_3)_2(en)]^+$



Structural isomerism : Various types of isomerism as compared to organic chemistry are observed because of different geometrical arrangements and different types of bonds in structural isomerism co-ordination. (i) Linkage isomerism (ii) Co-ordination isomerism (iii) Ionic isomerism (iv) Hydration isomerism.

(i) Linkage isomerism : NO_2^- ion combines with metal ion with nitrogen atom through co-ordination and acts as nitro ($-NO_2$) ligand or through any one of the oxygen by co-ordination and act as nitrito (ONO^-) ligand. Thus one ligand forms isomers by bonding of different atoms. Some of the examples are given below :