13. TRANSITION ELEMENTS AND LANTHANIDES

Synopsis :

The elements in which the differentiating electron enters the d-orbital of the penultimate shell are called d - block element.

- d-block elements are present in between electropositive s-block elements and electronegative p-block elements in the periodic table.
- There are 4 series of d-block elements.
- First 3 series conation 10 elements each and fourth series is incomplete.
- 3d series – present in IV period starting from Sc(21) to Zn (30)
- 4d series – present in V period starting from Y(39) to Cd (48)
- 5d series – present in VI period starting from La(57) to Hg (80)
- 6d series – starts from Ac(89) and in complete. Present in VII period.
- d- block elements are also called transition elements, as they bring about the change from electropositive to electronegative in a gradual manner by being present in between s-block and p-blocks.
- All d-block element are not transition elements but all transition element are d-block elements.
- Zn, Cd and Hg are not transition elements as they contain completely filled (n –1)d orbitals.
- Cu, Ag and Au are called typical transition elements though they contain completely filled (n-1) d-orbitals because they show some similarities with other transition elements.
- A true transition element has partly filled d-sub level either in elemental state or in stable oxidation state of it's ion.
- d-block elements occupy III B – VII B, VIII, I B, II B groups of periodic table in 4^{th}, 5^{th}, 6^{th} and 7^{th} periods. VIII group has 3 elements. i.e transition triad.
- The outer electronic configuration of d-block elements is $ns^{1 \text{ or } 2}$ $(n-1)\, d^{1-10}$.
- Some d-block elements have exceptional configuration, to acquire the extra stability having half filled and completely filled d-orbtials, due to greater exchange energy.
- The following elements violate aufbau principle.

Ex : 1) Chromium - $4s^1\ 3d^5$
2) Copper - $4s^1\ 3d^{10}$
3) Molybdenum - $5s^1\ 4d^5$
4) Palladium - $5s^0\ 4d^{10}$
5) Silver - $5s^1\ 4d^{10}$
6) Platinum - $6s^0 3d^{10}$ or $6s^1 5d^9$
7) Gold - $6s^1\ 5d^{10}$

Transition of electrons between ns and (n –1) d levels takes place easily because the energy difference between these two levels is small.

Typical characteristic properties :

- The transition elements exhibit the following typical characteristic properties due to small size, large nuclear charge and presence of d-electrons.

i) Variable oxidation states
ii) Para and ferromagnetic properties
iii) Formation of coloured hydrated ions and salts
iv) Alloy formation
v) Catalytic properties

vi) Complex formation.

Variable oxidation states :

- They show variable oxidation states and variable valency due to the involvement of (n–1)d electrons along with ns electrons.
- Smaller energy difference between (n–1)d and ns electrons permit the (n–1)d electrons to participate in bonding.
- Cr and Cu can exhibit +1 oxidation state. Highest oxidation state is exhibited by Mn i.e. +7 in 3d series.
- The number of oxidation states increases from left to middle and then decreases.
- The stability of oxidation state is related to stable electronic configuration.
  Fe^{3+} ($3d^5$) is more stable than Fe^{2+} ($3d^6$)
  Mn^{2+} ($3d^5$) is more stable than all it's other oxidation state.
  Cu^{2+}($3d^9$) is more stable than Cu^{+1} ($3d^{10}$) due to greater hydration energy.
- The maximum oxidation state of these elements is the sum of ns electrons and unpaired (n–1)d electrons.
- Co $\rightarrow$ **+ 2, + 3,** + 4
- Cr $\rightarrow$ + 1,+2,**+3**,+5,**+6** oxidation state are possible
- Sc $\rightarrow$ + 3 ; Ni $\rightarrow$ **+ 2**, + 4
- Mn$\rightarrow$ **+2**, +3, +4, + 5, +6, +7.oxidation states are possible.
- Ti $\rightarrow$ + 2, + 3, **+ 4**
- Cu$\rightarrow$ +1, **+ 2** oxidation states are possible
- V $\rightarrow$ + 2, + 3, **+ 4, + 5**
- Fe $\rightarrow$ **+ 2, + 3,** + 4, + 5, + 6
  Oxidation states which are underlined are stable.

Magnetic properties:

- A substance through which the magnetic lines of force of an external magnetic field pass is paramagnetic.
- A substance becomes paramagnetic when it possesses unpaired electrons. Ex. Sc^{++}, Cr^{++}
- Para magnetism increases with increase in number of unpaired electrons.
- A substance through which magnetic lines of force do not pass and repelled is called diamagnetic.
- A substance which contains only paired electrons and no unpaired electrons is diamagnetic.
  Ex . KCl, Ti^{4+}, V^{5+}
- Ferromagnetism is a special case of paramagnetism
- A substance which contains unpaired electrons and which are aligned in the same direction is ferromagnetic. Ex. Fe, Co, Ni.
- Ferromagnetism disappears in the solution of substance.
- In paramagnetic substance, the field strength (B) in the substance is greater than the applied field (H). i. e B > H .
- In ferromagnetic substance, the field strength (B) in the substance is much greater than (H) i.e. B>>H the applied field.
- In diamagnetic substance, the field strength (B) is less than the applied field. i.e B < H.
- Paramagnetic substance moves from a weaker part of the field to stronger part of the field.
- Diamagnetic substance moves from a stronger part of the field to weaker part of the field.

- In 3d –series for some metal ions like Co^{2+}, Fe^{2+} the experimental value of μ is slightly more than calculated value of μ due to contribution of orbital motion.
- Both spin and orbital motions of unpaired electrons will contribute to the net magnetic moment.
- Magnetic moment, $m_{S+L} = \sqrt{4S(S+1)+L(L+1)}BM$

  S →Sum of the electron spin quantum numbers of all the unpaired electrons.
  L → Sum of the Azimuthal quantum number of all the unpaired electrons.
- B.M = Bohr magneton.

  $1BM=\frac{eh}{4\pi mc}=9.273\times10^{-24}$Joules $Tesla^{-1}$ in S.I units

  e = Charge of the electron
  h = Planck's constant
  m = Mass of an electron
  T = Tesla
- Angular momentum due to orbital motion of unpaired electrons is small and ignored in 3d series.
- There fore the magnetic moment is due to spin of unpaired electron only.
- The following spin only formula gives spin only magnetic moment.

  $m_s = \sqrt{4S(S+1)}BM = \sqrt{n(n+2)}BM$

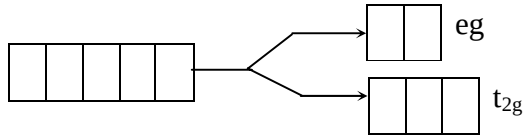
  n = number of unpaired electrons
  S = sum of spin quantum number values
- For I 3d series of metal ions, the spin only magnetic moments are given below

Metal Ion	3d configuration	No.of Unpaired electron	Magnetic moment
Sc^{+++}			
Ti^{+++}	$3d^0$	0	0
Ti^{++}	$3d^1$	1	1.7 – 1.8
V^{++}	$3d^2$	2	2.8 – 3.1
Cr^{++} or	$3d^3$	3	3.7 – 3.9
Mn^{++}	$3d^4$	4	4.8 – 4.9
Mn^{++}or	$3d^5$	5	5.7 – 6
Fe^{+++}	$3d^6$	6	5 – 5.6
Fe^{++}			

- In II and III series transition elements, L must be included in the formula for m_{S+L}. Thus it is significant.
- **Colour of hydrated transition metal ions and their compounds :**
- A substance is coloured, if it absorbs a part of white light and transmit the remaining light.
- The colour of a substance is the complementary colour of that part of visible light which is absorbed by the substance.
- Colour is due to the presence of partly filled d-orbtials, with unpaired electrons.
- The metal ion possessing completely filled d-orbitals or completely vacant d-orbtials is colourless. Ex TiO_2, CuCl.
- d-orbitals are degenerate in isolated gaseous metal ions.
- d-orbitals of the metal ion in compounds or hydrated ions or complexes posses slightly different energies.
- Under the influence of the anion of the compound or the water molecule in hydrated state these

d-orbitals of the metal ions split into 2 sets. It is known as d-orbital splitting.

- One set consists of two orbitals - $d_{x^2-y^2}, d_{z^2}$ of higher energy and the other set consists three orbitals - d_{xy}, d_{yz}, d_{zx} of lower energy.



- Electron in the lower energy d-orbital is promoted to higher energy d-orbital with in the same energy level.
- Thus, the colour of transition metal ions involve d–d transitions.
- This excitation is possible in visible region (1 = 400 – 750 nm) as the energy difference between the two sets is less.
- $[Ti(H_2O)_6]^{3+}$ absorbs green and yellow lights and transmits pink colour.
- The same metal ion may exhibit different colours in different oxidation states.
- Fe^{++} - green ; Fe^{+++} - yellow
- Cr^{2+} - blue Cr^{3+} - green Cr^{6+} - yellow
- Mn^{2+} - pink Mn^{3+} - blue Mn^{6+} - green
- Sc^{3+}, Ti^{4+}, Mn^{7+}- are colourless as all the d-orbitals in these ions are vacant
- Cr^{6+} and Mn^{7+} posses vacant d orbitals but their oxyanions like $Cr_2O_7^{2-}$, CrO_4^{2-} and MnO_4^- are coloured due to charge transfer phenomenon.
- Zn^{++} and Cu^{+} are colour less as all the d orbitals are completely filled.

Alloys :

- Homogenous mixture of a metal with other metal or metalloid or non metal having metallic properties is known as an alloy.
- Transition metals form alloys easily because they have similar atomic radii and similar crystal structures.
- Alloys are prepared to modify certain properties like malleability, ductility, toughness, resistance to corrosion to suit the needs in the industry.
- Alloys are classified as
  Ferrous alloys (contain iron) Ex. Cast Iron. Stainless steel,
  Non Ferrous alloys (no iron) ex. Brass, German silver.
- Alloys are prepared, by mixing the metals or components in proper composition in molten state and solidifying.
- By simultaneous electrolytic deposition of metals under the same conditions to get alloys

Alloy	Composition	Uses
Invar	64% Fe, 35% Ni. Mn and C in trace amounts.	To make pendulum rods, due to low temperature coefficient
Nichrome	60% Ni, 25% Fe 15% Cr.	To manufacture heating elements of stoves and Furnaces
Non – Ferrous alloys		

Type metal	60–80 % Pb, 13–30% Sb, 3–10% Sn.	Used for sharply defined castings
Wood's metal	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd,	In automatic alarams. Sprinklers systems
Devarda's Alloy	50% Cu, 45% Al, 5% Zn	To reduce nitrites and nitrates to NH_3
Solder metal	50% Sn, 47.5% Pb, 2.5 % Sb	Electrical appliances
Duralumin	95% Al, 4% Cu, 0.5% Mn, 0.5 %Mg.	Aircraft
Magnalium	85-99% Al, 1–15% Mg	Balance beams, aircraft parts, motor spares
Aluminium Bronze	88–90% Cu, 10–12% Al	Ornaments, Photoframes, coins
German silver	50–60% Cu, 10–30 % Ni, 20–30% Zn	Spoons, forks, Utencils
Bell metal	80% Cu, 20% Sn	Bells
Bronze	75 – 90% Cu, 10 –25% Sn	Utensils, Coins and statues
Gun metal	88% Cu, 10% Sn, 2% Zn	Bearings, guns
Brass	60–80% Cu, 20–40 % Zn	Machine parts

STEELS :

Name of the steel	**% of the element present**	**Uses**
Nickel steel	2.5 – 5 % Ni, Fe, C	Cable wires, guns
Manganese steel	10– 14% Mn, Fe, C	Ball mills, Helmets
Chromium steel	5 – 15% Cr, Fe, C	Kitchen ware, Razorblades
Tungsten steel	6–8% W; 14–20% Fe, C	Magnets, Electric motors

- Alloys are used in nuclear engineering, dental fillings, to manufacture magnetic materials.

Complex compounds :

- Two or more different compounds combine and exhibits the properties of all the components present in it, called double salt. Ex. Alums, Carnalite.
- Double salt ionises completely and respond positively to all the tests of constituent ions.
- Carnalite is formed by combining KCl and $MgCl_2$. It exhibits the properties of K^+, Mg^{++}, and Cl^-.
- K_2SO_4, $Al_2 (SO_4)_3$ 24 H_2O is formed by mixing K_2SO_4, $Al_2(SO_4)_3$.
- It exhibits the properties of K^+, Al^{+++}, SO_4^{-2}.
- In molecular compound two compounds combine and does not exhibit the properties of all the ions present in it is, called complex compound.

  $K_4Fe(CN)_6$ Potassium ferrocyanide it is formed by mixing KCN, $Fe(CN)_2$. It does not exhibit the properties of Fe^{++} or CN^-. It is complex compound.
- A complex compound is also known as coordination compound with coordinate covalent bonds.
- A complex compound doesn't ionise completely and retains it identity even in aqueous state.
- Cuprous-ammonium sulphate, $CuSO_4$, $4NH_3$ is another complex compound.

Important characters of complex compounds:

- They are formed by combining stable compounds or species :
- They contain a new species different from the parent compounds from which it is formed.
- $K_4Fe(CN)_6$ contains $[Fe(CN)_6]^{-4}$ which is not present either in KCN or in Fe $(CN)_2$ from which it is formed.
- Complex species do not dissociate in solution.
- The properties of complex species formed are different from those of the parent compounds.
- Ex. $[Cu(NH_3)_4]SO_4$ is dark blue, where as $CuSO_4$ is pale blue and NH_3 is colorless.
- The physical properties like color, conductivity etc. of the complexes are different from the substances from which it is formed.
- Alfred Werner explained how complexes are formed.

Werner's theory :

- Every complex compound has a central metal ion or atom.
- The metal in a complex exhibits two types of valencies
  a) Primary valency
  b) Secondary valency
- Central metal ion/ atom forms dative bonds with electron pair donors or ligands.

Primary valency or Ionisable valency :

- It is equal to oxidation state of metal ion
- It is satisfied by negative ions. The groups bound by primary valency will ionise.
- These are held by electrostatic attraction by the metal ion, like ionic bond.
- These group are connected to the metal- ions, shown by broken line in the formula, or shown outside the square bracket.
- These are non directional.

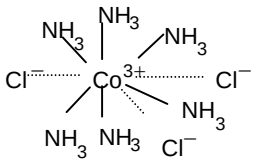
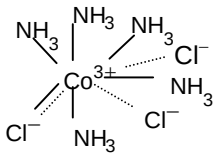
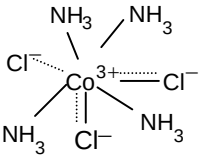
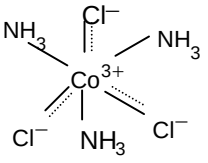
Secondary valency or non ionisable valency :

- Secondary valency is equal to co-ordination number or number of coordinate covalent bonds.
- Secondary valency may be satisfied by neutral groups NH_3, H_2O or negative ions. CN^-, Cl^- or even positive ion like NO^+.
- The groups satisfying secondary valency are called ligands.
- The number of unidentate ligands around the metal is known as coordination number.
- Ligands donate lone pairs to the metal atom or ion and form coordinate covalent bonds.
- Ligands act as Lewis bases and metal ion/atom acts as Lewis acid.
- Ligands are connected to the metal by thick line or shown inside the square bracket.
- Some liqands may satisfy both primary and secondary valencies and they don't ionise.
- Lignads are directed in space around the metal in a symmetric order, and acquired a specific shape. Secondary valency is directional in nature and it determines the shape of the complex.

No of lignads	Shape of complex
2	Linear
3	Trigonal planar
4	Tetrahedral (or) Square planar
5	Square pyramidal (or) Trigonal bipyramidal
6	Octahedral

7 Pentagonal bipyramidal

Example :

Complex	**No of ligands (or) Coordination no.**	**Werner Structure**	
1. $CoCl_3$ $6NH_3$	6	Octahedral – Three Cl^- ions satisfy pimary valency – Six NH_3 molecules satisfy secondary valency – No.of ions in solution = 4 – AgCl molecules precipitated on adding excess of $AgNO_3$ = 3AgCl	
2. $CoCl_3$ $5NH_3$	6	Octahedral – $2Cl^-$ satisfy primary valency – One Cl^- satisfies both primary and secondary valency – $5NH_3$ molecules satisfy secondary valency – No.of ions in solution = 3 – AgCl molecules precipitated on adding excess of $AgNO_3$ = 2	
3. $CoCl_3$ $4NH_3$	6	Octahedral – 2 Cl^- & $4NH_3$ molecules satisfy both primary and secondary valency – One Cl^- satisifies only primary valency – No.of ions in solution =2 – AgCl molecules precipitated = 1	
4. $CoCl_3$ $3NH_3$	6	Octahedral – The three Cl^- ions satisfy both primary and secondary valencies and $3NH_3$ molecules satisfy secondary valency – No.of species in solution = 1 – AgCl molecules precipitated by adding excess of $AgNO_3$ is zero.	

Defects in Werner's theory :

- This theory does not explain the role of the electronic configuration of metal in forming complexes.
- It is known now in through coordinate bond formation that the metal tries to acquire the nearest inert gas configuration during the formation of complex.
- This theory does not explain the reason for the colour of the complex.
- This theory does not explain the magnetic behaviour of complex.

Nomenclature of complex compounds :

- The naming of complex compounds is done according to the guidelines given by IUPAC. In this system the complexes are divided into 2 types.
  1) Neutral or molecular complexes.
     Ex. $CoCl_3.3NH_3$; $Ni(CO)_4$; $PtCl_4.2NH_3$
  2) Ionic complexes. These ionic complexes may be cationic or anionic depending on whether the cation constitutes the complex group or the anion is the complex group in the compound.

  Ex: $CuSO_4.4NH_3$; $TiCl_3.6H_2O$ are cationic complexes. Potassium ferrocyanide, cryolite, sodium argento thiosulphate are anionic complexes.

  IUPAC rules : The main principles to be followed are as follows :

  i) Complex part of the compound is written in square brackets.
     Ex:$[Co(NH_3)_3\ Cl_3]$; $[Cu(NH_3)_4]SO_4$; $K_4[Fe(CN)_6]$
  ii) The names of the ligands H_2O, and ammonia are written as 'aquo' (or aqua) and 'ammine' respectively. Other neutral ligands are named as they are CO (carbonyl) ; $H_2N - NH_2$ (hydrazine) ; $H_2NCH_2 - CH_2NH_2$ (ethylene diamine) etc.
  iii) The names of negative ligands terminate in –O
     Ex: Cl^- (chloro); CN^-(cyano); SO_4^{2-} (sulphato) ; $S_2O_3^{2-}$ (thiosulphato) etc.
  iv) In case a large number of simple ligands of the same type is present, the name of the ligand is prefixed with di, tri, tetra etc corresponding to the presence of two, three or four ligands in the complex.
  v) The ligands are written in alphabetical order of their names irrespective of the complexity of the groups.
  vi) In neutral and cationic complexes, the name of the central metal will not change. But in anionic complexes the suffix –ate is added to the name of the meta.
     Ex : cobalt $\rightarrow$ cobaltate ; nickel $\rightarrow$nickelate
     Copper changes to cuprate; Iron changes to ferrate etc.
  vii) The oxidation number (or the primary valency) of the metal is represented in roman numerals and is always written, immediately after the name of the metal, in paranthesis.
  viii) The name of the non – ionic complexes are given a one word name.
     Ex: $[Co(NH_3)_3Cl_3]$. Triammine trichloro cobalt (III)
  ix) The sequence in writing the name of a complex part of a compound is name(s) of ligands, name of the metal in proper form and the oxidation state of the metal.

- In the case of ionic complexes, the order is name of the cation first, and then the name of the anion.

Examples :

i) $[Cu(NH_3)_4]SO_4$: Tetrammine copper (II) sulphate.

ii) $[Ti(H_2O)_6]Cl_3$: Hexa aquo titanium (III) chloride

iii) $K_2[PtCl_6]$: Potassium hexachloroplatinate (IV)
iv) $K_4[Fe(CN)_6]$: Potassium hexacyano ferrate (II)
v) $Na_2[Ni(CN)_4]$: Sodium tetracyano nickelate (II)
vi) $[Ag(NH_3)_2]Cl$: Diammine argentinum(I) chloride
vii) $[Cr(NH_3)_4Cl_2]Cl$: Dichloro tetraammine chromium (III) chloride

- **Hume – Rothery Rules :** alloys (homogenous mixtures) of the metals are formed according to the Hume-Rothery rules. They are simplified as
  i) for metals to form the alloys, they must haves similar or same atomic radii valuses i.e. sizes. (should not differ by more than 15%)
  ii) The metals must have similar chemical properties, especially the number of valency electrons.
  iii) The metals must have same crystal structures.
  When one or more of these conditions are satisfied alloys are formed
- **Double salts :** Double salts are those compounds which exist only in crystal lattice and lose their identity when dissolved in water. Ex: Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$.
- **Coordination or Complex compounds :**
  Coordination compounds are those molecular compounds which retain their identities when dissolved in water or any other solvent and their properties are different from those of the constituents. Ex: $K_4[Fe(CN)_6]$.
  $Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + Fe(CN)_6^{4-}$
- **Complex ion (or) Coordination entity :**
  It may be defined as an electrically charged (cationic or anionic) or even a neutral species which is formed by the combination of a simple cation with more than one neutral molecule or negative ion.
  Ex: $[Ag(NH_3)_2]^+$
- The central metal cation is generally a transition metal and has a positive oxidation state.
- In some coordination compound (carbonyls), the metal is in zero oxidation state.
- Coordination entities or complex ions may be classified as
- a) Mononuclear compounds:
  Ex : $K_4[Fe(CN)_6]$, $K_3[Co(CN)_6]$, $[Co(NH_3)_6]Cl_3$ etc.
- b) Poly nuclear compounds :
  Ex: $[Co_2(NH_3)_6(OH)_3]Cl_3$, $[(CO)_3Fe(CO)_3Fe(CO)_3]$ etc.
- Mononuclear compounds are divided into three types. They are
- a) Neutral complex compounds :
  Ex: $[Ni(CO)_4]$; $[Co(NH_3)_3Cl_3]$ etc.
- b) Cationic complex compounds :
  Ex:$[Cu(NH_3)_4]SO_4$,$[Co(NH_3)_6]Cl_3$, $[Co(H_2O)_6]Cl_3$ etc.
- c) Anionic complex compounds :
  Ex: $K_4[Fe(CN)_6]$, $K_3[CoCl_6]$ etc.
- **Ligand :** An ion or a molecule that can have an independent existence and can donate a pair of electrons.
  Ligand can be negative, neutral or positive.

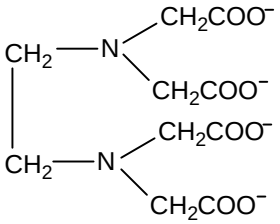
Formula and names of some ligands.

Neutral ligands	Negative ligands	Positive Ligands
H_2O aqua	OH^- hydroxo	$NO_2^{\oplus}$ nitronium
CO carbonyl	F^- Fluoro	$NO^{\oplus}$ Nitrosonium
NH_3 ammine	Br^- Bromo	$(NH_2NH_3)^+$ hydrazinium
NO Nitrosyl	CN^- Cyano	
C_6H_5 Phenyl	NCS^- Isothiocyanato	
C_6H_5N Pyridine	SO_4^{2-} Sulphato	
PH_3 Phosphine	NO_2^- Nitro	
$P(C_6H_5)_3$ Triphenyl phosphine	CO_3^{2-} Carbanato	
$H_2N.CS.NH_2$ Thiourea	O^{2-} Oxo	
$H_2N.CH_2.CH_2.NH_2$ Ethylene diammine	Cl^- Chloro	
	I^- Iodo	
	O_2^{2-} Peroxo	
	$C_2O_4^{2-}$ Oxalato	
	CH_3COO^- Acetato	

- **Coordination number :** Number of electron pairs arising from ligand donor atoms to which the metal is directly bonded (or) the number of coordinate bonds around the central metal atom in a complex compound is called as co-ordination number of the metal.
- Coordination number range from 1 to 12. (For some f –block elements it is greater than 12 also).

Types of ligands :

- **a) Unidentate :** Ligand which binds to a metal through a single point of attachment.
  Ex : $NH_3, H_2O,\ X^-\left(Cl^-, Br^-, I^-\right), O_2^{2-}$ etc.
- **Bidentate :** Ligand which binds to a metal through two points.
  Ex: : Ethylene diammine $(H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2)$
  $C_2O_4^{2-}$ (oxalato) etc.
- **Polydentate :** Several donor atoms are present in one molecule.
  Ex :



(EDTA)

  Ethylene diamminetetra acetate
- **Chelate complex :** The complex formed when a bi- or polydentate ligand uses two or more donor atoms to bind to one metal atom.

- **Co-ordination sphere :** The combination of central metal atom and ligands written in 'square bracket' is called the co-ordination sphere.
- **Ionisation sphere :** The portion present outside the square bracket is called ionisation sphere.
- Species present in the in the co-ordination sphere are non-ionisable and species present in the ionisation sphere are ionisable.

  Ex: $[Co(NH_3)_6]Cl_3$

  [ ] $\rightarrow$ Co-ordination sphere

  Co $\rightarrow$ Central metal atom

  NH_3 $\rightarrow$ Ligand

  $3Cl^-$ $\rightarrow$ Ionisation sphere

Rules of writing the formulae of mononuclear coordination compounds :

- Central meal atom is symbolised first.
- The ligands may be anionic, neutral or cationic in nature. Sequence of writing ligands in the formula is
  a) Anionic ligands are listed in the alphabetic order of their first letter.
  b) Next to anionic ligands neutral ligands are written in the alphabetical order of their first letter.
  c) After anionic and neutral ligands cationic ligands are written in the alphabetical order of their first letters.
  d) Formulae of polyatomic ligands are enclosed in parentheses.
- The formula of complete complex ion is enclosed in square brackets.
- All the species present in the formula are written continuously without leaving any space between them.
- If the complex entity is an ion then the charge of ion is indicated outside the square brackets as a right superscript and the number of charges put before the sign.

Examples :

- Hexamine cobalt (III) chloride. $[Co(NH_3)_6]Cl_3$
- Pentammine chloroplatinum (IV) chloride $[PtCl(NH_3)_5]Cl_3$.
- Tetrammine chloronitro chromium (III) nitrate $[CrCl(NO_2)(NH_3)_4]NO_3$
- Tetracyano nickelate (II) chloride $[Ni(CN)_4]Cl_2$

Anionic complexes :

- Potassium tetra chloroplatinate (II) $K_2[PtCl_4]$
- Potassium hexacyano ferrate (II) $K_4[Fe(CN)_6]$
- Sodium tetrachlorozincate (II) $Na_2[ZnCl_4]$
- Potassium pentacyanonitrosyl ferrate (II) $K_3[Fe(CN)_5NO]$

Neutral complexes :

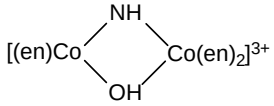
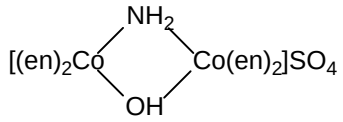
- Triammine trichlorocobalt (III) $[Co(Cl_3)(NH_3)_3]$
- Diammine dibromodichloroplatinum (IV) $[PtCl_2\ Br_2(NH_3)_2]$
- Triaquotrichloro chromium (III) trihydrate $[CrCl_3(H_2O)_3].3H_2O$

Nomenclature of co-ordination compounds :

- Name the cation, then anion.
- Nonionic compounds are given one-word name.

- Name of ligands
  a) Ligands are named first and central atom last.
  b) Ligands are named in alphabetical order.
  c) Neutral ligands are named the same as the molecule (except aqua and ammine)
  d) Anionic ligands are named by adding–0 to the suffix of the name (chloride becomes chloro)
  e) The ligand name is proceeded by a prefix viz di, tri, tetra, penta, hexa etc to indicate the number of ligands present.
- In a neutral or cationic complex, the name of the central atom is followed by it's oxidation number in Roman numerals in parentheses.
- In anionic complex, the suffixate is added to the name of central metal, followed by it oxidation number in Roman numerals in parentheses.
- In case of bridging ligand the word μ (mu) is written before the name ligand.

Name of some complex compounds :

$[Cr(H_2O)_5Cl]SO_4$	Penta aqua chloro chromium (III) sulphate
$[Cr(H_2O)_4Cl_2]Cl$	Tetra aquadichloro chromium (III) chloride
$K_2[PtCl_4]$	Potassium tetra chloroplatinate (II)
$[Co(en)_2Cl_2]Cl$	Dichlorobis (ethylenediammine) cobalt (III) chloride
$[Pt(NH_3)_4Cl_2][Pt+Cl_4]$	Tetraamminedi -chloroplatinum (IV), Tetrachlorophlatinate(II)
	Bis(ethylene diamine) cobalt(III) –μ-imido-μ - hydroxo bis(ethylene diamine), Cobalt (III) ion.
$[Fe(H_2O)_4(C_2O_4)_2]_2SO_4$	Tetraqua oxalato iron (III) sulphate
$[Ag(NH_3)_2]Cl$	Diammine silver (I) chloride
$[Cu(NH_3)_4]SO_4$	Tetrammine copper (II) sulphate
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate (II) ion
$[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$	Hexamine chromium (III) trioxalato cobaltate (III)
	Bis (ethylene diammine) Cobalt(III) μ-amido-μ-hydroxo bis (ethylene diammine) cobalt (III) sulphate

- **Isomerism :** Two or more compounds having the same molecular formula but different properties are called isomers and the phenomenon is called isomerism.
- **Structural isomerism :** the isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers.

1) Ionisation isomerism: The compounds which have same molecular formula but give different ions in solution are called ionisation isomers.

- In this type of isomerism the interchange of groups within or outside the co-ordination entity.
- The counter ion itself is a ligand in such type of isomers.
  Ex: 1. $[Co(NH_3)_4ClBr]Cl$ and $[Co(NH_3)_4Cl_2]Br$

$[Co(NH_3)_4ClBr]Cl \rightarrow$ Tetramminebromochloro cobalt (III) chloride $[Co(NH_3)_4Cl_2]Br \rightarrow$ Cobalt tetrammine dichloro (III) bromide

2. $[CoBr(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]Br$

$[CoBr(NH_3)_5]SO_4 \rightarrow$ Pentamminebromo Cobalt (III) sulphate

$[CoSO_4(NH_3)_5]Br \rightarrow$ Pentamminesulphato Cobalt(III)bromide

2) Hydrate isomerism :

The compounds which have the similar molecular formula but differ in the number of water molecules present as ligands or as molecules of hydration are called hydrate isomers.

- This isomerism is similar to that of ionisation isomerism.

Ex : $[CrCl_3(H_2O)_3]$, $[CrCl(H_2O)_5]Cl_2.H_2O$ and $[CrCl_2(H_2O)_4]Cl.2H_2O$

3) Co-ordination isomerism :

- The type of isomerism occurs in compounds containing both cationic and anionic entities and the isomers differ in the distribution of ligands in the co-ordination entity of cationic and anionic parts.

Ex: i) $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$

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

4) Linkage isomerism :

The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.

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

Pentaamminenitrito cobalt (III) chloride	Pentaamminenitro cobalt (III) chloride

- In complex 'A' oxygen atom of NO_2^- is the electron pair donar and in B nitrogen atom of NO_2^- is the electronpair donar NO_2^- is ambidentate ligand.
- **Ambidentate liands :** The unidentate ligands which can bind to the central atom through two donor atoms are called as ambidentate ligands.

Ex : – CN (cyano), –NC (iso cyano)

– SCN (thiocyanato), –NCS (isothiocyanato).

Stereoisomers :

- The isomers which have the same position of atoms or groups but they differ in the spatial arrangements around the central atom.
- Stereoisomerism is of tow types (a) Geometrical isomerism and (b) Optical isomerism.

Geometrical isomerism :

- This kind of isomerism gives rise to two kinds of isomers, namely cis and trans isomer.

Cis isomer:

- When two ligands of same type occupy adjacent positions in co-ordination sphere of the central atom then it is called as cis isomer.

Trans isomer :

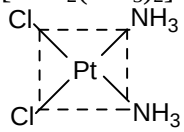
- When two ligands of same type occupy opposite positions to each other in co-ordination sphere of the central atom then it is called as trans isomer.
- Geometrical isomerism is important in complexes of co-ordination number 4 or 6.

Geometrical isomerism in complexes of co-ordination number 4:

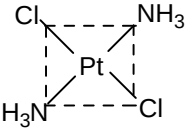
- Complexes having co-ordination number 4 adopt tetrahedral or square planar geometry.
- Geometrical isomerism is not possible in tetrahedral complexes.
- Square planar complexes of the type MA_2X_2, MA_2XY, $MABX_2$, MABXY can exist as geometrical isomers.

(Here A and B are neutral ligands such as H_2O, NH_3, CO, NO, C_2H_5N whereas X and Y are anionic ligands such as Cl^-, NO_2^-, CN^-, SCN^{-1} etc.)

1) $[PtCl_2(NH_3)_2]$

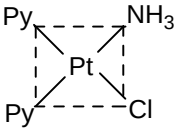


Cis-(Pale yellow)

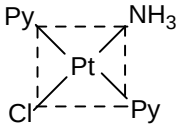


Trans (Dark yellow)

2) $[PtCl(C_5H_5N)_2(NH_3)]$

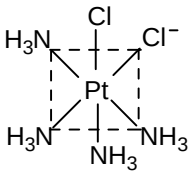


Cis

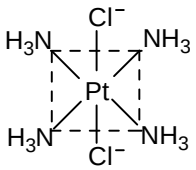


Trans

- Geometrical isomerism is also shown by octahedron complexes in which the co-ordination number of the central metal atom is 6.
- MA_2X_4, MA_4X_2, MA_4XY etc. types of complexes exhibit geometrical isomerism. Ex: $[CoCl_2(NH_3)_4]^+$

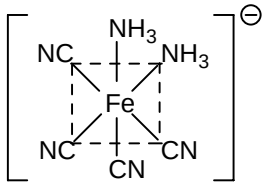


Cis-(Violet)

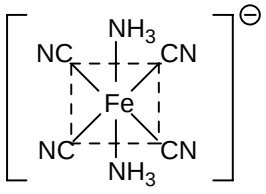


Trans(Green)

2) $[Fe(CN)_4\ (NH_3)_2]^-$



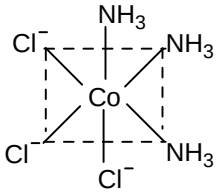
Cis



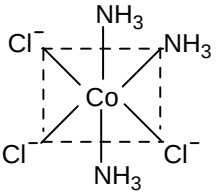
Trans

- Octahedral complexes of the type $[MA_3B_3]$ like $[Co(NO_2)_3(NH_3)_3]$ also exist in two geometrical isomers.
- When the three ligands (with same donor atoms) are on the same triangular face of the octahedron, the isomer is called facial or fac isomer.
- When the three ligands are on the same equatorial plane of the octahedron i.e. around the meridian of the octahedron, the isomer is called meridional or merisomer.

Ex : $[CoCl_3(NH_3)_3]$



Fac isomer



Meridional isomer

- In facial isomer, the three ligands are at the corners of a triangular face while in meridional isomer, the three ligands are at the three corners of a square plane.

Optical isomerism :

- The isomerism which arises due to the rotation of the plane of a polarised light in a polarimeter is called as optical isomerism.
- The isomer which rotates plane polarised light towards right side is called dextro rotatory substance denoted by d – or (+).
- The isomer which rotates plane polarised light towards left side is called laevorotatory substance denoted by *l* – or (–).
- Optical isomers are called as enantiomorphs or enantiomers.

Enantiomers :

- A pair of substances with same molecular formula but differ in the rotation of plane polarised light are called as enantiomers.
- Enantiomers are non –super imposable.

Racemic mixture :

- A 1 : 1 equilibrium mixture of d – and *l* – forms which gives a net zero rotation of plane polarised light is called as racemic mixture.

Chiralty :

- The property of possessing atleast one atom that is attached to four non-identical groups.
- Generally optical isomers are octahedral co-ordination compounds.
  Ex: $[Co(en)_2Cl_2]^+$, $[Cr(C_2O_4)_3]^{3-}$, $[CrCl_2(NH_3)_2en]^+$, $[Pt\ Cl_2(en)_2]^{2+}$ etc show optical isomerism.

Effective Atomic Number (EAN) :

- The sum of the number of electrons, donated by all ligands and those present on the central metal ion or atom in complex is called as effective atomic number (EAN).
- Generally EAN of central metal ion will be equal to the number of electrons in the nearest noble gas.
- If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possess greater stability.

  EAN = [(atomic number of central metal) – (the oxidation state of the metal) + (the number of electrons gained by the metal from the ligands through co-ordination)] = [Z metal – (ox.state of the metal) + 2(coordination number of the metal)].

Ex: 1) $[Fe(CN)_6]^{4-}$ EAN = [26 – (2) + 2(6)] = 36
2) $[Co(NH_3)_6]^{3+}$ EAN = [27 – 3 + 2(6)] = 36
3) $[Ni(CO)_4]$ EAN = [28 – 0 + 2(4)] = 36
4) $[Fe(CN)_6]^{3-}$ EAN = [26 – 3 + 2(6)] = 35
5) $[Ni\ (CN)_4]^{2-}$ EAN = [28 – 2+ 2(4)] = 36
6) $[Cu(NH_3)_4]^{2+}$ EAN = [29 – 2 + 4(2)] = 35
7) $[Ag(NH_3)_2]^+$ EAN = [47 – 1 + 2(2)] = 42

<u>LANTHANIDES:</u>

- The f'- block consists of the two series of inner transition elements
  a) Lanthanides(The fourteen elements following Lanthanum)
  b) Actinides (The fourteen elements following Actinium)
- Lanthanides are also called "rare earth elements"

- Lanthanum closely resembles the Lanthanides, Actinium closely resembles Actinides, hence these are usually included in any discussion of Lanthanides and Actinides
- The Lanthanides resemble one another more closely because they exhibit a common stable oxidation state like transition elements.

ELECTRONIC CONFIGURATION:

- The general electronic configuration of f-block elements is $(n - 2)\ f^{1-14}\ (n - 1)\ d^{0,1}\ ns^2$

Elements	Symbol	At. No	Configuration
Lanthanum	La	57	$[Xe]5d^16s^2$
Cerium	Ce	58	$[Xe]4f^1\ 5d^16s^2$
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$
Neodymium	Nd	60	$[Xe]4f^4 6s^2$
Promethium	Pm	61	$[Xe]4f^5 6s^2$
Samarium	Sm	62	$[Xe]4f^6 6s^2$
Europium	Eu	63	$[Xe]4f^7 6s^2$
Gadolinium	Gd	64	$[Xe]4f^7\ 5d^16s^2$
Terbium	Tb	65	$[Xe]4f^9 6s^2$
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$
Erbium	Er	68	$[Xe]4f^{12} 6s^2$
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$
Lutetium	Lu	71	$[Xe]4f^{14}\ 5d^16s^2$

- The Lanthanides occur as orthophosphates in monazite sand.
- The Monazite sand contains 30% Thorium phosphate, 60% La, Ce, Pr, Nb phosphates and 10% Y and other heavy lanthanide phosphates.

PHYSICAL PROPERTIES:

DENSITY :

- Lanthanides have densities ranging between 6.77 to 9.74g cm^{-3}
- Densities in general increases with increase in atomic number.

MELTING POINT & BOILING POINTS

- Lanthanides have fairly high melting points however no definite trend is observed.

ELECTROPOSITIVE CHARACTER :

- Lanthanide metals are highly electropositive due to their low Ionisation energy.

IONISATION ENERGY :

- Lanthanides have fairly low Ionisation energies. The IE_1 & IE_2 values are quite comparable to those of alkaline earth metals particularly calcium. (IE_1 600 KJ/mole, IE_2 1200 KJ/mole) La, Gd, Lu have low IE_3 values due to empty, half filled and completely filled f orbitals respectively

MAGNETIC BEHAVIOUR :

- Lanthanide ions (M^{3+}) generally show paramagnetism due to the unpaired electrons in f-orbitals.
- Lanthanide ions like La^{+3}, Ce^{+4} (configuration) Yb^{+2} & Lu^{+3} (f^{14} configuration) are diamagnetic
- The paramagnetism is maximum in Neodymium.

- Magnetic susceptibility of Actinides is relatively higher than those of Lanthanides of same electronic configuration.

COLOUR:

- Many of the Lanthanide ions are coloured in solid state as well as in solutions.
- The colour is attributed to f-f transitions since they have partly filled f-orbitals. (Absorption bands are narrow probably because of the excitation within f-level)
- Ions with f^0, f^{14} configuration are colourless.
  Ex :- $La^{+3}(4f^0) Lu^{+3}(4f^{14})$ are colourless
  Nd^{3+}, Er^{3+} – Pink : Sm^{3+}, Dy^{3+} – Yellow
- The Lanthanide ion with $4f^n$ configuration and $4f^{(14-n)}$ configuration have same colour.
  Ex (1):- $Nd^{3+}\left(4f^3\right)$ and $Er^{3+}\left(4f^{11}\right)$ have same colour (pink)
  Ex (2):- $Sm^{3+}\left(4f^5\right)$ and $Dy^{3+}\left(4f^9\right)$ have same colour (yellow)

RADIOACTIVITY

- All Lanthanides except promethium and samarium are non-radioactive

OXIDATION STATES

- The common oxidation state exhibited by Lanthanides is + 3.
- Lanthanides can also exhibit occasionally +2 and +4 ions in solution or in their solid compounds.
- Irregularities arises mainly from the extra stability of empty, half filled or fully filled f-subshell.
- +3 oxidation state in Lanthanum, Gadolinium and Lutetium are especially stable because +3 ions of these elements have an empty (f^0), a halffilled [f^7] and completely filled (f^{14})] configurations.
- Cerium, Terbium also exhibit oxidation state of +4 because Ce^{+4} has configuration ($4f^0$), Tb^{+4} has the configuration ($4f^7$)
- Pr, Nd, Dy also exhibit +4 state in their oxides only.
- Europium, Ytterbium can show +2 oxidation state due to $4f^7, 4f^{14}$ configuration respectively.

CHEMICAL REACTIVITY OF LANTHANIDES:

- The lanthanides have very close similarity. The separation of lanthanides from one another is very difficult.
- Lanthanides can be separated by ion exchange method
- Monazite is the starting material for the preparation lanthanides.
- The lanthanides are separated from monazite and are converted into chlorides (or) oxides.
- The lanthanides are obtained by the electrolysis of their molten chlorides.
- The lanthanides are obtained by the reduction of their anhydrous halides with electro positive metals like Na, Mg.
- The lanthanides slowly react with cold water and quickly react with hot water.
  $2M + 6H_2O \rightarrow 2M\left(OH\right)_3 + 3H_2$
- As the size of M^{+3} ion decreases the covalent character in M-OH bond and their basic strength in their hydroxides decreases gradually from $La(OH)_3$ to $Lu(OH)_3$. This is due to Lanthanide contraction
- Lanthanides form oxides of the type M_2O_3 (or) MO_2 . These oxdies are ionic in nature.
- Lanthanide ions cannot easily form co-ordinate compounds because of their large size.
- Lanthanide ions can form complexes with chelating ligands.

LANTHANIDE CONTRACTION:

- The decrease in atomic radii (derived from the structures of metals) is not quite regular but it is regular in their M^{+3} ions.
- As atomic number increases in Lanthanides series, for every proton added to the nucleus, the extra electron goes to fill 4f - orbitals. The 4f- electrons constitute inner shells and are rather ineffective in screening the nuclear charge. Gradual increase in the effective nuclear charge is responsible for decrease in size of Lanthanides. This phenomenon is called Lanthanide contraction

CONSEQUENCES.

- The similarities between 4d & 5d series elements are more closer than 3d & 4d elements.
- The atomic sizes of Zr & Hf, Nb & Ta, Mo & W are almost same.
- The separation of lanthanides is very difficult due to closer atomic radii.
- Inert pair effect.