Department Of Chemistry

Udai Pratap Autonomous college Varanasi

Class :- B.Sc.

Semester Vth

Topic :- Chemistry of Lanthanides

Sub Title:- Introduction, Electronic configuration and Oxidation states, Lanthanides contraction ,magnetic properties, colour and Electronic spectra, Separation of lanthanides.
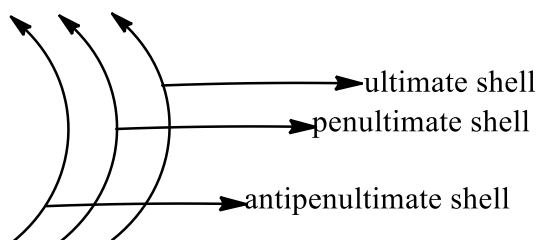
by

Dr. Kashinath Tripathi
Assistant Professor
Udai Pratap College Varanasi

CHEMISTRY OF LANTHANIDES

Introduction:-
Elements in which last electron enters into antepenultimate 4f subshell or energy levels are called f-block elements.

Ultimate shell s-orbitals (ns^2)
Penultimate shell d-orbital (n-1)d $^{0-1}$
Antepenultimate shell f-orbital (n-2)f$^{1-14}$
Generally f block elements are divided into two groups.
1 Lanthenoids (4f block elements)
2 Actinoids (5f block elements)
  Chemistry of 4f block elements and 5f block elements are less diverse.

- In case of 4f block elements this is due to deep buried nature of f-orbitals while in case of actinoids due to their radioactive nature.
- Both lanthenoids and actinoids are also called innertransision elements.
- Lanthenoids are sometimes referred as Rare Earth Elements. However this terminology is not appropriate because they are not particularly rare. Cerium is about as abundant as Copper. Apart from Promethium(Pm) which does not occurs in nature , all the elements are more abundant than Iodine.

Electronic configuration and Oxidation state:-

Table:- Electronic structure and Oxidation states.

Element	Electronic structure of atoms	Electronic structure of M^{3+} ions	Oxidation states
Lanthanum La^{57}	[Xe] 5d^1 6s^2	[Xe]	**+3**
Cerium Ce^{58}	[Xe] 4f^1 5d^1 6s^2	[Xe] 4f^1	**+3**,**+4**
Praseodymium Pr^{59}	[Xe] 4f^3 6s^2	[Xe] 4f^2	**+3**,+4
Neodymium Nd^{60}	[Xe] 4f^4 6s^2	[Xe] 4f^3	+2,**+3**
Promethium Pm^{61}	[Xe] 4f^5 6s^2	[Xe] 4f^4	+2,**+3**
Samarium Sm^{62}	[Xe] 4f^6 6s^2	[Xe] 4f^5	+2,**+3**
Europium Eu^{63}	[Xe] 4f^7 6s^2	[Xe] 4f^6	+2,**+3**
Gadolinium Gd^{64}	[Xe] 4f^7 5d^1 6s^2	[Xe] 4f^7	**+3**
Terbium Tb^{65}	[Xe] 4f^9 6s^2	[Xe] 4f^8	**+3**,+4
Dysprosium Dy^{66}	[Xe] 4f^{10} 6s^2	[Xe] 4f^9	**+3**,+4

Holmium	Ho^{67}	[Xe] 4f^{11} 6s^2	[Xe] 4f^{10}	**+3**
Erbium	Er^{68}	[Xe] 4f^{12} 6s^2	[Xe] 4f^{11}	**+3**
Thulium	Tm^{69}	[Xe] 4f^{13} 6s^2	[Xe] 4f^{12}	+2,**+3**
Ytterbium	Yb^{70}	[Xe] 4f^{14} 6s^2	[Xe] 4f^{13}	+2,**+3**
Lutetium	Lu^{71}	[Xe] 4f^{14} 5d^1 6s^2	[Xe] 4f^{14}	**+3**

Note:- The most important oxidation state is +3. Other well characterized but less important are in bold. The oxidation states that are unstable or in doubts are given in timid.

- In case of Ce, due to more diffuse nature of 4f- orbital its energy is similar to 5d orbital. Due to this reason Due to this reason 4f and 5d orbital have electron on moving from Ce to more energy difference between 4f and 5d orbital hence electron enter into only 4f orbitals.
- For all Lanthanoids most stable oxidation state is +3. Some lanthanoids also show +2 and +4 oxidation state. +2 and +4 oxidation state is more stable when.

1- a noble gas configuration eg Ce^{4+} [f^o]

2- a half filled f- shell eg. Eu^{2+} and Tb^{4+}[f^7]

3- a completely filled f level eg. Yb^{2+} [f^{14}]

- Those elements which are close to this state show (+2) and (+4) oxidation states.
- Thus Sm^{2+} and Tm^{2+} occurs with f^6 and f^{13} arrangement and Pr^{4+} and Nd^{4+} have f^1 and f^2 arrangements.
- The only (+4) and (+2) states which have any aqueous chemistry are Ce^{4+} , Sm^{2+}, Eu^{2+}, and Yb^{2+} .

    Eu^{2+} $\longrightarrow$ 4f^7

    Yb^{2+} $\longrightarrow$ 4f^{14}
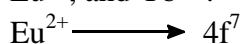
    Both are in stable oxidation state.

    Stability order of ln^{2+} ions are

    $$Eu^{2+} > Yb^{2+} > Sm^{2+} > Tm^{2+} \rightarrow Strong\ reducing\ agent$$
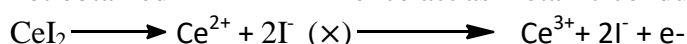
    $\longleftarrow$
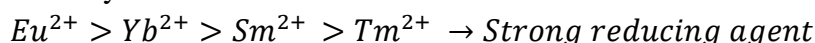
    Increasing order of stability

    - It show dihalide i.e. Lncl$_2$ and LnI$_2$.
    - Conversion of $Eu^{2+} \longrightarrow Eu^{3+}$ involves less gain of energy (i.e. 4033kjmol^{-1}) as compared of that of conversion of $Yb^{2+} \longrightarrow Yb^{3+}$ (i.e. 4197 kjmol^{-1}) .
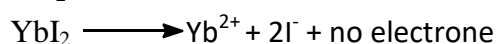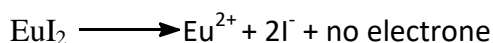   - This is due to small size of Yb which lead to more solution energy.

        LaI$_2$ $\longrightarrow$ La^{2+} + 2I$^-$ (×) $\longrightarrow$ La^{3+}+ 2I$^-$ + e-

not obtained   hence act as metallic conduction

CeI$_2$ $\longrightarrow$ Ce^{2+} + 2I$^-$ (×) $\longrightarrow$ Ce^{3+}+ 2I$^-$ + e-

not obtained   hence act as metallic conduction

But in case of EuI$_2$ and YbI$_2$

EuI$_2$ $\longrightarrow$ Eu^{2+} + 2I$^-$ + no electrone

YbI$_2$ $\longrightarrow$ Yb^{2+} + 2I$^-$ + no electrone

For this reason, EuI$_2$ and YbI$_2$ had known as metallic insulators.

In case of stability of +4 oxidation state is

$$Ce^{4+} > Tb^{4+} > Pr^{4+} > Nd^{4+} > Dy^{4+}$$

$\downarrow$
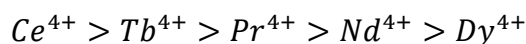
Stable in aqueous medium

Remaining ions are found in solid phase in the form of fluoride.

- Due to stability of +4 stable oxidation state of Ce, it is use as oxidising agents.
- Eu^{2+} and Yb^{2+} show similarity in properties with heavier alkaline earth metal like Ba^{2+} due to similar charge density.
- Like alkaline earth metal Eu and Yb also gives (except Be and Mg) blue colour in liquid NH_3 solution. Colour of solution is due to solvated ions.

  LANTHENOID CONTRACTION

  If we see the ionic radius (Ln^{3+}) of lanthanide series are

Elements		Radius Ln^{3+}
Lanthanum	La^{57}	1.032 or 103pm
Cerium	Ce^{58}	1.020
Praseodymium	Pr^{59}	0.99
Neodymium	Nd^{60}	0.983
Promethium	Pm^{61}	0.97
Samarium	Sm^{62}	0.958
Europium	Eu^{63}	0.947
Gadolinium	Gd^{64}	0.938
Terbium	Tb^{65}	0.931
Dysprosium	Dy^{66}	0.912
Holmium	Ho^{67}	0.901
Erbium	Er^{68}	0.890
Thulium	Tm^{69}	0.880
Ytterbium	Yb^{70}	0.868
Lutetium	Lu^{71}	0.861 or 86pm

  Note:- radii are for six coordination.

  - **Slow or steady decrease in size of lanthanide on moving from Ce to Lu is called Lanthanide contraction.**
  - This is due to poor shielding by f orbital i.e. f orbital are incompletely field and nuclear charge increase continuously thus all the electrons are pulled in closer. The shielding effect of electron decreases in the order

    $$s > p > d > f$$

    The contraction in size from one element to another is fairly small. Decreasing in radius in 14 elements i.e. Ce to Lu is about 0.2A or 20 pm. This is known as Lanthanide contraction.
  - The hardness, melting point and boiling point of the elements all increases from Ce to Lu. This is because attraction between the atoms increases as the size decreases.
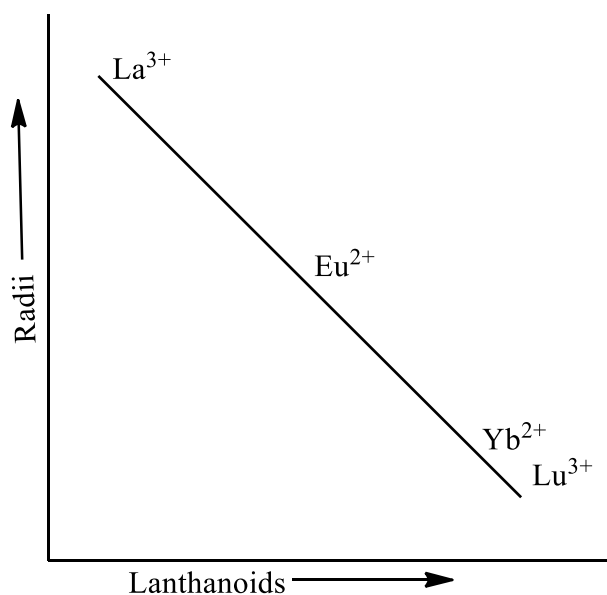
Fig:- Ionic radii of Ln^{3+} ions

Consequence of lanthanides contraction:-

1. Due to size and common +3 oxidation state properties of lanthanides is very similar, due to this their separation is very difficult.
2. The metals are all soft and silvery white. They are electropositive and therefore they are very reactive. The heavier metals are less reactive than lighter ones because they form a layer of oxide on the surface.
3. The standard reduction potentials(E^0) are all high (range from -2.48 to -2.26 volts). It show that lanthanide are much more reactive than Al (E^0=-1.66volts) and are slightly more reactive than Mg(E^0=-2.37volts) thus it react slowly with cold water and more rapidly on hot water.

$$2Ln + 6H_2O \rightarrow 2Ln(OH)_3 + 3H_2$$
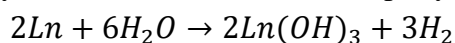
4. On-going from left to right basicity of oxides and hydroxides of lanthanoids decrease. This is due to increase in nuclear force.

La_2O_3

↓

Gd_2O_3 | Decreasing basicity

↓

Lu_2O_3

$La(OH)_3$

↓

$Gd(OH)_3$ | Decreasing basicity

↓
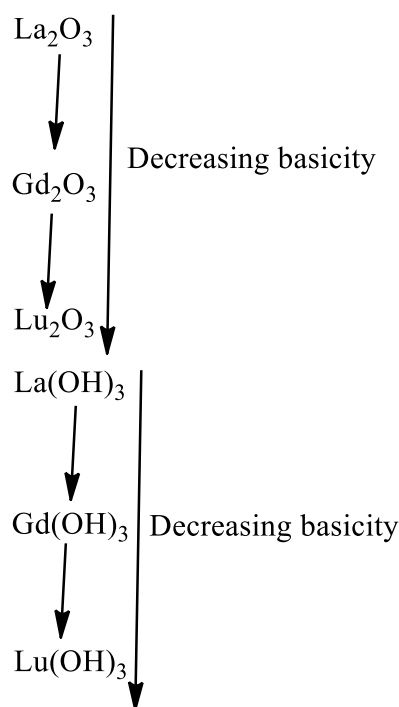
$Lu(OH)_3$

Here Ce form CeO_2 instead of Ce_2O_3 .

- In hydroxide $Ce(OH)_3$ is the most basic and $Lu(OH)_3$ is least basic strength.
- Due to decreases in basicity when $Yb(OH)_3$ and $Lu(OH)_3$ treated in NaOH(conc.) then it form the complexes.

$$Yb(OH)_3 + 3NaOH \longrightarrow 3Na^+ + [Yb(OH)_6]^{3-}$$
$$Lu(OH)_3 + 3NaOH \longrightarrow 3Na^+ + [Lu(OH)_6]^{3-}$$
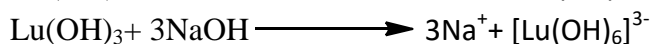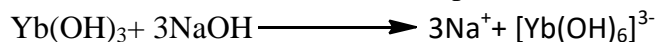
- These metal hydroxides form metal complexes with base because they are least basic so it can react with base.
- The above reaction for strong complex formation tendency of Yb and Lu due to small in size and less basicity of $Yb(OH)_3$ and $Lu(OH)_3$.

Sc^{164}	Ti^{147}	V^{134}	Cr^{128}	Mn	Fe	Co	Ni	Cu	Zn
Y^{184}	Zr^{160}	Nb^{143}	Mo^{130}	Tc	Ru	Rh	Pd	Ag	Cd
La^{187}	Hf^{159}	Ta^{143}	W^{130}	Re	Os	Ir	Pt	Au	Hg

When we see the atomic size of 3d, 4d, 5d series the atomic radii of 4d series elements are greater than 3d series and 5d series element have greater atomic radii than 4d series but in actual practice in IIIB series element atomic size gradually increases but latter when compare 4d and 5d series element atomic radii of Zr =Hf, Nb =Ta, Mo=W .

- This is due to poor shielding by f-orbitals size of 5d series member is similar to that of size of 4d series member.
- Due to same atomic radii, similarity in properties of 4d and 5d series member in comparison to that of 3d/4d and 3d/5d.

Colour and Electronic Spectra :-

Electronic spectra of lanthanides have following characteristic:-
- Lanthanides have large number of peaks due to large number of microstates.
- Electronic spectra of lanthanide are largely independent of nature of ligands. This is due to deep buried nature of 4f orbital.
- Absorption peaks of lanthanides are sharper than of d block system. This is due to little effect of ligand vibration over f- orbital.
- Absorption peaks of lanthanides are very weak. i.e. they have less value of molar extinction coefficient($\in$). This is due to poor possibility of orbital mixing.
- Colour of Ln^{3+} ions having f^n and f^{14-n} are similar.
- Colour of Ln^{3+} ion is mainly due to f $\rightarrow$ f transition. Ln^{2+} and Ln^{4+} ions generally have intense colour which is due to charge transfer.

$Sm^{2+} \longrightarrow$ Blood red colour ($4f^6$)

$Eu^{2+} \longrightarrow$ Pale greenish yellow colour ($4f^7$)

This colour is due to metal to ligands charge transfer (MLCT)

$Ce^{4+} \longrightarrow$ orange red ($4f^0$)

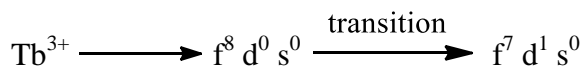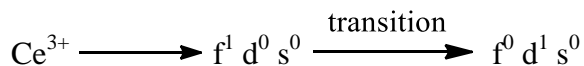This colour is due to ligands to metal charge transfer (LMCT)

Table:- Colour of Ln^{3+} ions (all the lanthanides are as Ln^{3+})

Note :- In lanthanides (Ln^{3+}) ions f^n and f^{14-n} have same colour.

Elements (Ln^{3+})		Colours
Lanthanum La^{3+} (f^0)	Lutetium Lu^{3+} (f^{14})	Colourless
Cerium Ce^{3+} (f^1)	Ytterbium Yb^{3+} (f^{13})	Colourless
Praseodymium Pr^{3+} (f^2)	Thulium Tm^{3+} (f^{12})	Green
Neodymium Nd^{3+} (f^3)	Erbium Er^{3+} (f^{11})	Reddish
Promethium Pm^{3+} (f^4)	Holmium Ho^{3+} (f^{10})	Pink yellow
Samarium Sm^{3+} (f^5)	Dysprosium Dy^{3+} (f^9)	Pale pink
Europium Eu^{3+} (f^6)	Terbium Tb^{3+} (f^8)	Pale pink
Gadolinium Gd^{3+} (f^7)	Gadolinium Gd^{3+} (f^7)	Colourless

- Gd^{3+} ($4f^7$) is colourless due to half field f orbital for this reason it is laporte as well as spin forbidden. The reason is that due to buried 4f orbital there is no interaction with ligands thus laporte relaxation is not possible.
- In case of Ce^{3+} ($4f^1$) there is f $\rightarrow$ f transition but colourless because this transition takes place in the IR Region.

In case of spectra of Ce^{3+}

$$Ce^{3+} \longrightarrow f^1 \, d^0 \, s^0 \xrightarrow{\text{transition}} f^0 \, d^1 \, s^0$$

$$Tb^{3+} \longrightarrow f^8 \, d^0 \, s^0 \xrightarrow{\text{transition}} f^7 \, d^1 \, s^0$$

f $\rightarrow$ d transition is favourable due to following two reasons.

1 f $\rightarrow$ d transition is laporte allowed.
2 f $\rightarrow$ d transition leads to stability of f- orbitals.

f $\rightarrow$ d transition fall in the UV region, due to this transition there is no colour.
- Intense broad peak corresponding to this transition appears in the UV region.
- The broad peaks in f- orbital is due to transition occurs from f $\rightarrow$ d therefore broad peaks observed due to interaction of d-orbitals with ligands.
- Complexes of lanthanides show strong emission spectrum due to this they are used in TV screen, phosphoresce and cathode ray protection. This strong tendency is due to

1- Large number of microstate there is more possibility of intersystem crossing. Hence more tendency of Phosphoresce.
2- Due to more distance between the f- orbital and ligands there is very less probability of relaxation of excited state electron by transferring their energy to ligand vibration but in d- block metals distance between d-orbital and ligands are small thus there is more possibility of relaxation by transferring their energy to ligands vibration hence more tendency of non radiative transition.

Absorption spectra of lanthanides ions are useful both for the qualitative detection and quantitative estimation of lanthanides.
Lanthanides elements are sometimes used as biological tracers for drugs in humans and animals. This is because lanthanides elements can quite easily be followed in the body by spectroscopy because there peaks are narrow and very characteristics.

Magnetic Properties:-

La^{3+}, Ce^{4+} have an f^0 configuration and Lu^{3+} has an f^{14} configuration thus it is **diamagnetic.**

All other f states contain unpaired electrons and are therefore **paramagnetic.**
For transition metals the magnetic moment can be calculated by

$$\mu_{s+l} = \sqrt{4s(s+1) + l(l+1)}$$

For first row transition element due to quenching of orbital contribution (i.e. quenching of l) only s is responsible for magnetic moment thus

$$\mu_s = \sqrt{\sqrt{4s(s+1)}}$$

Or

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.} \qquad \text{where n is unpaired electron.}$$

This simple relatonship work with $La^{3+}(f^0)$ Lu^{3+} $(4f^{14})$ and Gd^{3+} $(4f^7)$

For La^{3+} and Lu^{3+} where n = 0 thus

$$\mu_s = \sqrt{0(0+2)} = 0 \text{ B.M.}$$

For $4f^7$

$$\mu_s = \sqrt{7(7+2)} = \sqrt{63} = 7.93 \text{ B.M.}$$

But other f electrons do not obey this simple relationship. The 4f electron are well shielded from external fields by the overlapping of 5s and 5p electrons . thus magnetic effect of the motion of the electron in its orbital is not quenched out.

Thus magnetic moment is calculated by spin and orbital motion of electron. Thus

$$\mu = g\sqrt{j(j+1)} \text{ B.M.}$$

Where J is total angular momentum quantum number and g is the lande splitting factor.

J= L-S for less than half filled subshell.

J= L+S for more than half filled subshell.

J= S for half filled.

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(j+1)}$$

Or $g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(j+1)}$

For $Ce^{3+} = 4f^1$

| +3 | +2 | +1 | 0 | -1 | -2 | -3 |
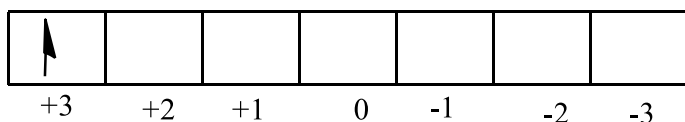
$S = \frac{1}{2}$, L = +3,   J= (L-S) $=\frac{5}{2}$

After putting the value we calculate g values the magnetic moment.

Calculated magnetic moment of Ce^{3+} = 2.54B.M. and observed value is 2.3-2.5 B.M. It shows that observed value is very near to calculated value thus angular orbital moment contribute for magnetic moments of lanthanides.

For Pr^{3+} calculated value is 3.58 B.M. The calculated value is very close to experimental values 3.47 B.M.

The calculated magnetic moments by the above formula for lanthanides have good agreement with observed values. For most lanthanides the value of λ is about 1000 cm^{-1}. However the λ value for Eu^{3+} and Sm^{3+} is about 300 cm^{-1} which is very small. This means that the difference in energy between the ground state and the next state is small.

  ➢ Due to the small energy gap the energy of thermal motion of electron is sufficient to promote some electron and partially populated the higher energy state. Thus there is difference of calculated value and observed value.

Ions	Calculated value (B.M.)	Observed value (B.M.)
Sm^{3+}	0.84	1.5-1.6
Eu^{3+}	0	3.4-3.6

  If we see the magnetic moment of Eu^{3+} at low temperature then magnetic moment is close to zero as expected.
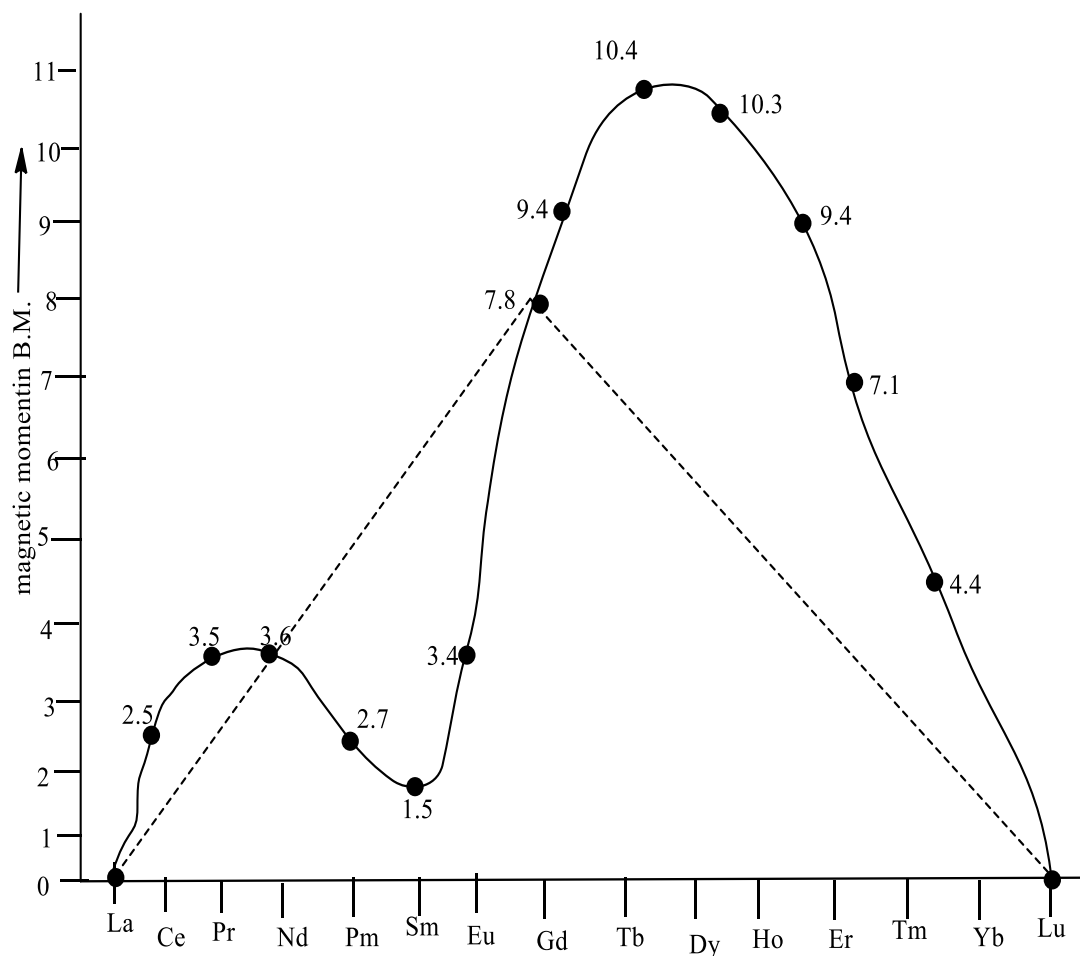
Fig.:- Paramagnetic moments of lanthanide ions(Ln^{3+}) at 300K (27^0 C). Spin only value are shown as broken line and spin plus orbital motion as solid line.

Complex Formation Tendency:-

- Due to deep buried nature of 4f orbitals complex formation tendency of Ln^{3+} ion is poor than that of d-block metal as well as actinides.
- Ln^{3+} ions behave as hard acid. They prefer to bind ligands having hard donor atom as hard ligand.e.g. F^-,O_2^-, OH_2 , $edta^{4-}$ etc.
- Complexes of lanthanides are more stable with polydentate ligands e.g. glycinate ($NH_2CH_2COO^-$), $edta^{4-}$, DMG, acac etc.

11

- Lanthanides do-not prefer to form complexes with π accepter ligands like CO. This is due deep buried nature and symmetry difference of 4f orbital, due to which this orbital is unable to back donate electrons into vacant orbital of ligand.
- Organometallic compounds of lanthanides do not obey 18e- rule. The stability of complexes is largely dependent upon strength of electrostatic interaction. Due to this Ln^{3+} ion prefer to form organometallic compounds with ligands having negatively charged carbon atom.eg. CH_3^- Cp^-. $C_8H_8^{2-}$ etc.
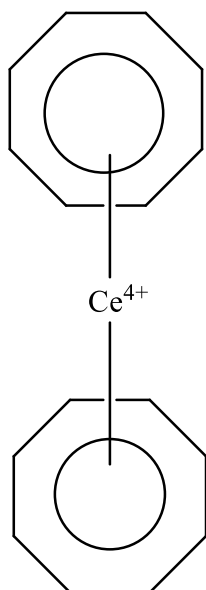
Fig.- Cerenocene
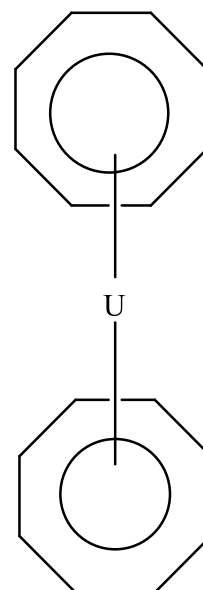
Fig.- Uranocene

- Due to large size of lanthanides coordination number six is uncommon for lanthanides.

  Common coordination number for lanthanides are 8,9,10,12.

| complex	Coordination number	Geometry
$[Ln(H_2O)_9]^{3+}$	9	Tricapped trigonal prism
$[Ce(NO_3)_6]^{2-}$	12	Icosahedron complex or Ball and stick model
$[Ce(NO_3)_4(OPPh_3)_2]$	10	Icosahedron
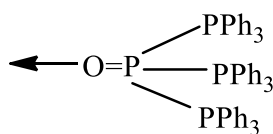
Monodentate

- $\beta-$diketone complexes of lanthanides are volatile in nature due to this they are using as separation of lanthanides by using gas chromatography.
- Complex of Eu^{3+} with their ligands are used as NMR shift reagents.
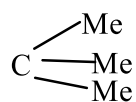

$\beta-$diketone
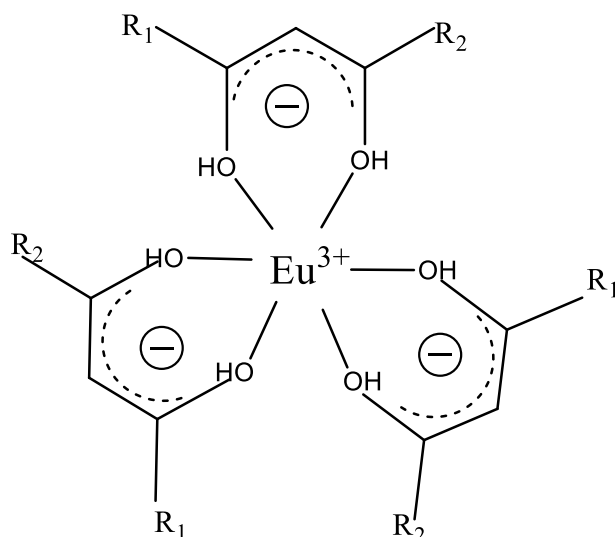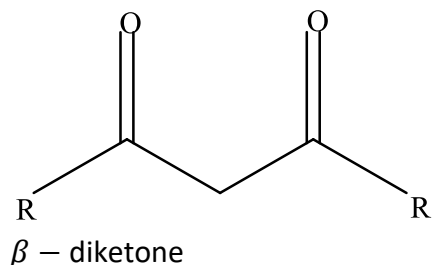
If $R_1=R_2 =$
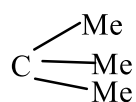
then $[Eu(dpm)_3]$

If $R_1 =$

and $R_2 =C_3F_7$ then $[Eu(fod)_3]$

Separation of Lanthanides:-

Separation of lanthanides is very difficult due to more similarity in there properties i.e. +3 oxidation states have similar size.

Following method have been suggested for separation of lanthanides ions.

(1) Valency Change Method:- Some lanthanides i.e. $Ce^{4+}, Eu^{2+}, Yb^{2+}$ is stable oxidation thus this method is applicable for separation of Ce, Eu, and Yb.

(2) Precipitation method:-
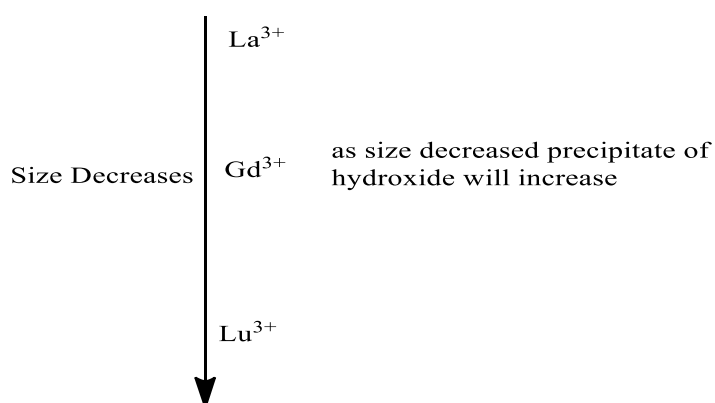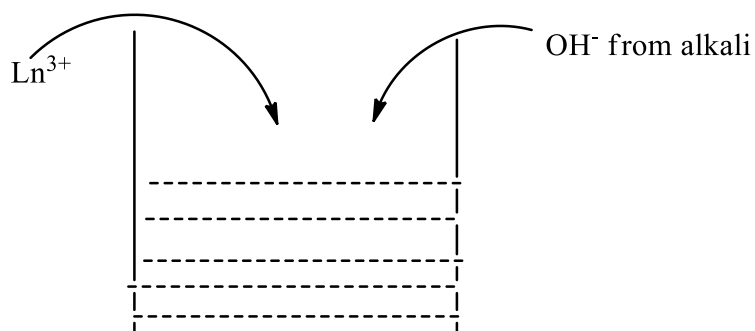
Lanthanides can be precipitated by using small amount of precipitating agent like OH^-. Ln^{3+} ions having smallest size undergo fastest precipitation. This solution can be filtered. The precipitate contain more amount of small Ln^{3+} ion. This ppt. can dissolve in HNO_3. Again in this solution precipitating agent is added which again lead to more precipitate of smallest Ln^{3+} ion by repeating this process Ln^{3+} ion can be separated.

Ion Exchange Chromatography (Cation Exchange):-

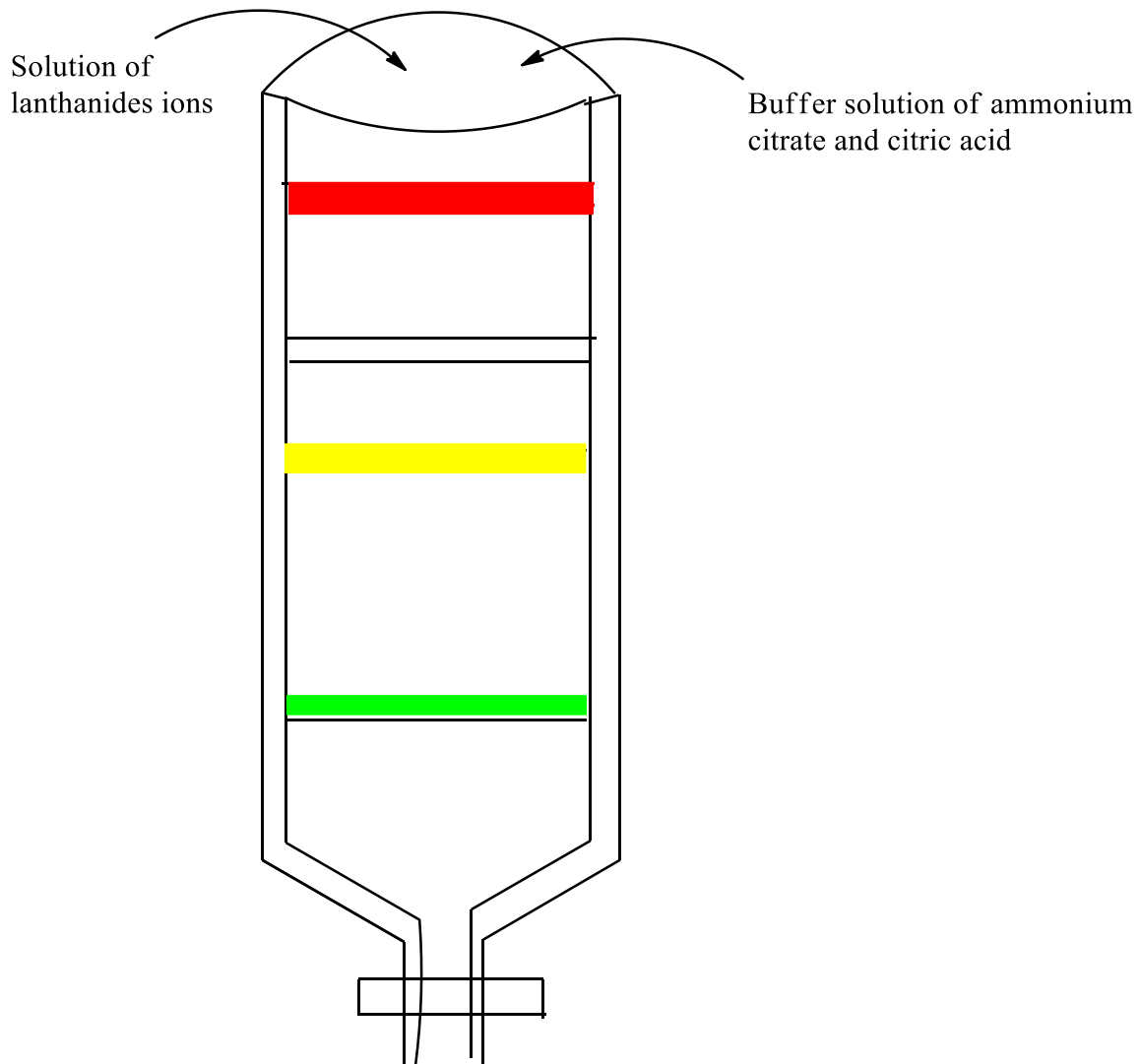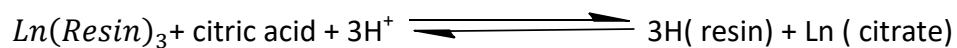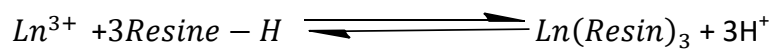This is most efficient method for separation of lanthanides.

Fig. Ion Exchange chromatography

Largest ions have minimum hydration and smallest ions have maximum hydration.

Cation exchange resins are DOWREX-50.

Ln^{3+} +3$Resine - H$ $\rightleftharpoons$ $Ln(Resin)_3$ + 3H⁺

$Ln(Resin)_3$+ citric acid + 3H⁺ $\rightleftharpoons$ 3H(resin) + Ln (citrate)

Dowex-50 is a sulphonated polystyrene and contain the functional group –SO_3H. Ln^{3+} ions are absorbed with resine.

- Complexing agents are buffer solution of citric acid/ammonium citrate or dilute solution of $(NH_4)_3$(H.EDTA) at PH-8.
- Complex formation tendency of smallest ion is very high with buffer complexing solution.

- Due to smallest size of Lu, it has strong tendency of complex formation with citrate ions and hence it will come first from the column. Thus during separation smallest size cation will come first from column while largest size cation will come last from column.