

LECTURE NOTES

ON

**CHM 411: COORDINATION CHEMISTRY**

DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF AGRICULTURE, ABEOKUTA(UNAAB)

*LECTURERS IN CHARGE*

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**COURSE DESCRIPTION**

CHM 412: Chemistry of Lanthanides and Actinides

2UNITS

Detail treatment of f-block transition elements: Lanthanides series and actinides series elements.

Compounds of the elements.

## THE CHEMISTRY OF LANTHANIDES

### INTRODUCTION

Lanthanides(also called lanthanoids) are called first inner transition series or third transition and come immediately after lanthanum. They are classified as f block elements along with the actinides. They are commonly called the rare earths. They are characterized by the filling up of the 4f energy levels which are not usually involved in bonding. These highly electropositive elements have a common oxidation state of +3 and generally resemble each other in their chemical and physical properties. They have a generic symbol “Ln”.

### DISCOVERY AND OCCURRENCE (see Table 1)

In 1794, Swedish chemist, Gadolin, discovered an oxide called yttria. Yttria was broken down to– yttria, erbia and terbia. Over the years, more separation was achieved, and more oxide discovered e.g. lutetia. The names were later obtained by changing the ending –a to –um.

Major sources of lanthanides are Monazite sand-composed of phosphates of thorium, cerium, neodymium and lanthanum; the phosphate portion of monazite contains small traces of other lanthanide ions and the only lanthanide that does not occur naturally is promethium, which is made artificially by nuclear reaction. Bastnaesite, found in USA and Madagascar is a mixed fluorocarbonate  $M^{III}CO_3F$  where M is La or the lanthanide metals. It provides 20% total supply of lanthanides. An also very small amount of xenotime mineral is mined.

**Table 1: Abundance of the elements and number of isotopes**

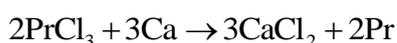
Atomic No.	Element	Abundance(ppm) in earth's crust	Relative abundance	Naturally occurring isotopes
58	Ce	66	26	4
59	Pr	9.1	37	1
60	Nd	40	27	7
61	Pm	0	-	0
62	Sm	7	40	7
63	Eu	2.1	49=	2
64	Gd	6.1	41	7
65	Tb	1.2	56=	1
66	Dy	4.5	42	7
67	Ho	1.3	55	1
68	Er	3.5	43	6
69	Tm	0.5	61	1
70	Yb	3.1	44	7
71	Lu	0.8	59	2

## ***EXTRACTION AND SEPARATION OF THE LANTHANIDES***

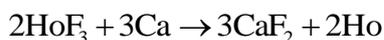
They are extracted from the earlier mentioned ores. Monazite is treated with hot concentrated  $\text{H}_2\text{SO}_4$ . Th, La and the Ln dissolve as sulphates and are separated from insoluble material. Th is precipitated as  $\text{ThO}_2$  by partial neutralization with  $\text{NH}_4\text{OH}$ .  $\text{Na}_2\text{SO}_4$  is used to salt out La and the lighter Ln as sulphates, leaving the heavy lanthanides in solution. The light Ln are oxidized with bleaching powder  $\text{Ca}(\text{OCl})_2$ .  $\text{Ce}^{2+}$  is oxidized to  $\text{Ce}^{4+}$  which is precipitated as  $\text{Ce}(\text{IO}_3)_4$  and removed. The extraction process from bastnaesite is slightly simpler since it does not contain Th.

The different lanthanides elements can be separated by various methods;

Reduction of their Trihalides: La, Ce, Pr, Nd and Gd may be obtained by reduction of their trichlorides with calcium at about  $1000^\circ\text{C}$  in an argon filled vessel e.g.

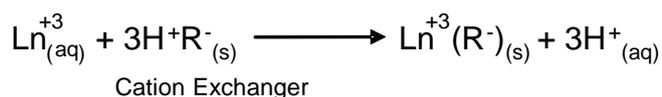


The heavier Ln like Tb, Dy, Ho, Er and Tm can also be obtained by this method but the trifluorides is used, since their trichloride is volatile. Also since the heavier Ln have higher melting points and so require a temperature of  $1400^\circ\text{C}$ . At this temperature  $\text{CaCl}_2$  boils. Li is sometimes used instead of Ca.



Eu, Sm and Yb are obtained by chemical reduction of their trioxides.

Ion exchange: The basis of the lanthanide series separation on an ion exchange column is their ability to form complex ions. All lanthanides form  $+3$  ions,  $\text{M}^{+3}$  whose ionic radii decrease progressively with increasing atomic number from  $\text{Ce}^{+3}$  to  $\text{Lu}^{+3}$ . As a solution containing  $+3$  lanthanides ions is placed at the top of a column of cation exchange resin[e.g. is Dowex-50 made of a sulphonated polystyrene and contains functional groups  $-\text{SO}_3\text{H}$ .] The  $\text{Ln}^{+3}$  ions are absorbed into the resin and an equivalent amount of hydrogen ions are released from the column;



A citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution. Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column. By the correct choice of conditions the lutetium ion,  $\text{Lu}^{+3}_{(\text{aq})}$ , emerges first from the column, followed by the cations ytterbium, thulium, erbium, etc, in order of increasing

ionic radius. By using a long ion-exchange column, the elements may be obtained at 99.9% with one pass.

**Valency change:** The different properties of the various oxidation states makes separation very easy [ie the properties of  $\text{Ln}^{+4}$  and  $\text{Ln}^{+2}$  are very different from that of  $\text{Ln}^{+3}$ ]. Cerium can be separated from Ln mixtures because it is the only one which has a  $\text{Ln}^{+4}$  ions stable in aqueous solution. A solution containing mixture of  $\text{Ln}^{+3}$  ions can be oxidized with NaOCl under alkaline conditions to produce  $\text{Ce}^{+4}$ . Because of the higher charge,  $\text{Ce}^{+4}$  is much smaller and less basic than  $\text{Ce}^{+3}$  or any other  $\text{Ln}^{+3}$ . The  $\text{Ce}^{+4}$  is separated by carefully controlled precipitation of  $\text{CeO}_2$  or  $\text{Ce}(\text{IO}_3)_4$ , leaving the trivalent ions in solution. Also,  $\text{Eu}^{2+}$  can be separated from a mixture of  $\text{Ln}^{+3}$ . If a solution of  $\text{Ln}^{+3}$  ions is reduced electrolytically using a Hg cathode or Zn amalgam, then  $\text{Eu}^{2+}$  is produced. If  $\text{H}_2\text{SO}_4$  is present,  $\text{EuSO}_4$  which is insoluble will be precipitate. This can be filtered off.

Other methods are Solvent Extraction, Precipitation, Thermal reaction, Fractional crystallization, Complex formation.

### ***Lanthanide Contraction***

Each succeeding lanthanides differs from its immediate predecessor in having one or more electron in the 4f (though there are some exceptions) and an extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus. This leads to a gradual increase in the attraction of the nucleus to the electrons in the outermost shell as the nuclear charge increases, and a consequent contraction in the atomic radius.

In lanthanide contraction, the ionic radii of the lanthanides decrease progressively with increase atomic number from lanthanum ( $\text{La}^{+3}=0.115\text{nm}$ ) to Lutetium ( $\text{Lu}^{+3}=0.093\text{nm}$ ) (see Table 2). As the ionic radii contract along the lanthanide series, the ability to form complex ions increases and this is the basis of their separation on an ion exchange column.

### **ELECTRONIC STRUCTURE (see Table 2)**

La has one 5d and two 6s electrons; the next element cerium, however, while still retaining two 6s electrons has two electrons in the 4f orbital and none in the 5d orbital. The atoms of the elements from cerium to lutetium have between 2 and 14 electrons in the 4f orbital.

The filling up of the 4f orbital is regular with one exception; Europium has the outer electronic structure of  $[\text{Xe}]4f^7 5s^2 5p^6 5d^0 6s^2$  and the next element gadolinium has an extra electron in the 5d shell,  $[\text{Xe}]4f^7 5s^2 5p^6 5d^1 6s^2$  [when all seven 4f shells are singly occupied, a

degree of stability is conferred on the atom]. Ytterbium has a full complement of 4f electrons ( $[\text{Xe}]4f^{14}5s^25p^65d^06s^2$ ) and the extra electron in the lutetium atom enters the 5d shell ( $[\text{Xe}]4f^{14}5s^25p^65d^16s^2$ ). Only lanthanum, gadolinium and lutetium have single 5d electrons. The other lanthanides do not have electrons on their 5d orbitals.

## GENERAL PROPERTIES

Because of their close size, they have similar properties.

### *Physical Properties*

1. The metals are silvery white in colour.
2. They generally have high melting and boiling points and are very hard
3. They are good conductors of heat and electricity.
4. Many of the lanthanide ions form coloured ions
5. The lanthanides exhibit a principal oxidation state of +3 in which the  $M^{+3}$  ion contains an outer shell containing 8 electrons and an underlying layer containing up to 14 4f electrons.
6. They exhibit paramagnetism because of the presence of unpaired electrons

### *Chemical Properties*

In chemical reactivity, they resemble calcium.

1. They readily tarnish in air and burn to give oxides (all give trioxides except Ce which forms  $\text{CeO}_2$ ).
2. They also combine with the following non-metals –N, S, halogens, H.
3. The hydrides are non-stoichiometric but have a composition of  $\text{MH}_3$ . These hydrides liberate hydrogen from water.
4. The lanthanides also liberate hydrogen from water as does their hydrides and a vigorous evolution of same gas from dilute non-oxidizing acids.

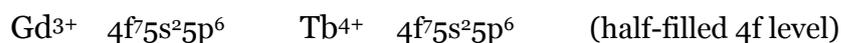
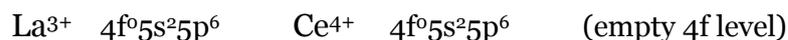


5. Lanthanide compounds are generally predominantly ionic and usually contain lanthanide metal in its +3 oxidation states.

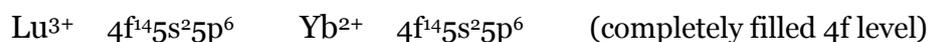
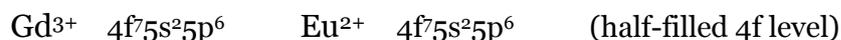
## Oxidation States

Lanthanides exhibit a principal oxidation state of +3 which contain an outer shell containing 8 electrons and an underlying layer containing up to 14 electrons. The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable. Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with  $\text{La}^{+3}$  i.e. an empty 4f level-noble gas configuration). Also,  $\text{Tb}^{4+}$  exists

which has the same electronic structure as  $Gd^{3+}$  i.e. a half-filled 4f level. An empty, a half-filled and a completely filled 4f shell confers some extra stability on a particular oxidation state.

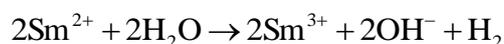
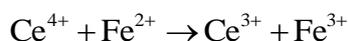


Also,  $Eu^{+2}$  is isoelectronic with  $Gd^{+3}$  i.e. half-filled 4f level and  $Yb^{+2}$  is isoelectronic with  $Lu^{+3}$



In addition, +2 and +4 states exist for elements that are close to these states. For example,  $Sm^{2+}$  and  $Tm^{2+}$  occur with  $f^6$  and  $f^{13}$  arrangements and  $Pr^{4+}$  and  $Nd^{4+}$  have  $f^1$  and  $f^2$  arrangements.

The most stable oxidation state is  $Ln^{3+}$  and  $Ln^{2+}$  and  $Ln^{4+}$  are less stable.  $Ce^{4+}$  is strongly oxidizing and  $Sm^{2+}$  is strongly reducing:



{ $Ce^{4+}$  and  $Sm^{2+}$  are converted to +3 state, showing that it is the most stable oxidation state}

## CHEMICAL PROPERTIES OF THE COMPOUNDS OF VARIOUS OXIDATION STATES

### Oxidation State(+3)

The trivalent state is characteristic of all the lanthanides. The standard potentials ( $E^0$ ) are all high and vary in a regular way over a small range (-2.48 to -2.26 volts) depending on the size. They are more reactive than aluminum (-1.66 volts) and slightly more than magnesium (-2.36 volts).

### Hydroxides:

Based on their reactivity, they react slowly with cold water, but more rapidly on heating to form the hydroxide.

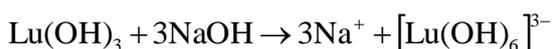
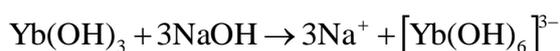


**Table 2: Electronic Structure, Oxidation States and some Physical data of the first inner transition series elements.**

Element	Symbol	Atomic No.	Electronic configuration		Oxidation States	Sum of 1 <sup>st</sup> three Ionisation energies (kJmol <sup>-1</sup> )	Atomic radius (nm)	Ionic Radii M <sup>3+</sup> (nm)	E <sup>o</sup> (V) Ln <sup>3+</sup> /Ln	Density /gcm <sup>-3</sup>	M.p / <sup>o</sup> C
			Atom	M <sup>3+</sup>							
Lanthanum	La	57	2.8.18.18.8(1).2 [Xe]4f <sup>0</sup> 5d <sup>1</sup> 6s <sup>2</sup>	[Xe]	<b>+3</b>	3493	0.187	0.115	-2.52	6.19	920
Cerium	Ce	58	2.8.18.18(2).8.2 [Xe]4f <sup>2</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>1</sup>	<b>+3</b> +4	3512	0.183	0.111	-2.34	6.78	795
Praseodymium	Pr	59	2.8.18.18(3).8.2 [Xe]4f <sup>3</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>2</sup>	<b>+3</b> (+4)	3623	0.182	0.109	-2.35	6.78	935
Neodymium	Nd	60	2.8.18.18(4).8.2 [Xe]4f <sup>4</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>3</sup>	(+2) <b>+3</b>	3705	0.181	0.108	-2.32	7.00	1020
Promethium	Pm	61	2.8.18.18(5).8.2 [Xe]4f <sup>5</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>4</sup>	(+2) <b>+3</b>	-	-	0.106	-2.29	-	1030
Samarium	Sm	62	2.8.18.18(6).8.2 [Xe]4f <sup>6</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>5</sup>	(+2) <b>+3</b>	3898	0.179	0.104	-2.30	7.54	1070
Europium	Eu	63	2.8.18.18(7).8.2 [Xe]4f <sup>7</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>6</sup>	+2 <b>+3</b>	4033	0.204	0.112	-1.99	5.24	826
Gadolinium	Gd	64	2.8.18.18(7).8(1).2 [Xe]4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	[Xe]4f <sup>7</sup>	<b>+3</b>	3744	0.180	0.102	-2.29	7.95	1310
Terbium	Tb	65	2.8.18.18(9).8.2 [Xe]4f <sup>9</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>8</sup>	<b>+3</b> (+4)	3792	0.178	0.100	-2.30	8.27	1360
Dysprosium	Dy	66	2.8.18.18(10).8.2 [Xe]4f <sup>10</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>9</sup>	<b>+3</b> (+4)	3898	0.177	0.099	-2.29	8.56	1410
Holmium	Ho	67	2.8.18.18(11).8.2 [Xe]4f <sup>11</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>10</sup>	<b>+3</b>	3937	0.176	0.097	-2.33	8.80	1460
Erbium	Er	68	2.8.18.18(12).8.2 [Xe]4f <sup>12</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>11</sup>	<b>+3</b>	3908	0.175	0.096	-2.31	9.16	1500
Thulium	Tm	69	2.8.18.18(13).8.2 [Xe]4f <sup>13</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>12</sup>	(+2) <b>+3</b>	4038	0.174	0.095	-2.31	9.33	1540
Ytterbium	Yb	70	2.8.18.18(14).8.2 [Xe]4f <sup>14</sup> 5d <sup>0</sup> 6s <sup>2</sup>	[Xe]4f <sup>13</sup>	+2 <b>+3</b>	4197	0.194	0.094	-2.22	6.98	824
Lutetium	Lu	71	2.8.18.18(14).8(1).2 [Xe]4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	[Xe]4f <sup>14</sup>	<b>+3</b>	3898	0.174	0.093	-2.30	9.84	1650

Most usual oxidation state is in **bold**. Oxidation state that is unstable or in doubt are in parentheses 54Xe

The hydroxides which are definite compounds are precipitated as gelatinous precipitates by the addition of  $\text{NH}_4\text{OH}$  to aqueous solutions. They can be obtained in the crystalline form by aging  $\text{Ln}_2\text{O}_3$  in strong alkali at high temperature and pressure. They are ionic and basic. They are less basic than  $\text{Ca}(\text{OH})_2$  but more basic than  $\text{Al}(\text{OH})_3$  which is amphoteric. The hydroxides are basic enough as to absorb  $\text{CO}_2$  and form carbonates. The basicities of the hydroxides decreases with increasing atomic number as will be expected for decreasing ionic radii.  $\text{Ce}(\text{OH})_3$  is the most basic while  $\text{Lu}(\text{OH})_3$  is the least basic. The decrease in basic properties can be seen by dissolving the hydroxides of the later members in hot concentrated sodium hydroxide which produces complexes.

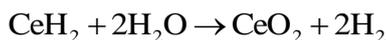


### **Oxides:**

The metals readily tarnish in air and on heating in oxygen, they all give the oxides,  $\text{Ln}_2\text{O}_3$  which resembles Ca to Ba group Cerium alone forms  $\text{CeO}_2$ . They oxides are also ionic and basic and readily reacts with water to give the hydroxides. Yb and Lu form a protective oxide film which prevents the whole metal forming oxide unless heated to  $1000^\circ\text{C}$ .

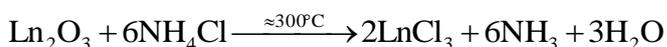
### **Hydrides:**

The hydrides are formed when the metal reacts with  $\text{H}_2$ . This requires heating up to  $300\text{-}400^\circ\text{C}$  to initiate the reaction. The products-dihydrides,  $(\text{LnH}_2)$  are solids: black, metallic and conduct electricity. This is because the Ln ion exists in the +3 and has  $2\text{H}^-$  ion and an electron which occupies a conduction band. Exceptions are Eu and Yb which form the divalent compounds;  $\text{EuH}_2$  and  $\text{YbH}_2$ . These are salt-like and contain  $\text{M}^{2+}$  and two  $\text{H}^-$ . Yb forms non-stoichiometric hydrides approximately  $\text{YbH}_{2.5}$ . The hydrides generally, liberate hydrogen from water, are stable to heat up to  $900^\circ\text{C}$  and react with  $\text{O}_2$  to form the oxide. The dihydrides take up H when heated under pressure and all but Eu form saltlike hydrides  $\text{LnH}_3$ (which has  $\text{Ln}^{3+}$  and three  $\text{H}^-$ .) since there are no delocalized electron, they do not show metallic conduction.



### **Halides:**

The anhydrous halides  $\text{LnX}_3$  can be prepared by heating the metal and the halogen. It can also be prepared by heating the oxide with an excess of ammonium halide.



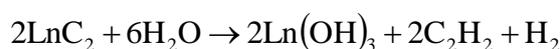
The fluorides are of particular importance among the halides, because of their insolubility. Addition of HF acid or  $\text{Na}^+\text{F}^-$  precipitates the fluorides from the  $\text{Ln}^{3+}$  solutions and this is a characteristic test for lanthanides. The fluorides, particularly of the heavier lanthanides (with smaller Ln ions) are slightly soluble in excess HF owing to formation of

soluble complex,  $[LnF(H_2O)_n]^{2+}$ . They may be redissolved in 3M nitric acid saturated with boric acid, which removes  $F^-$  as  $BF_4^-$ . The chlorides are deliquescent, soluble in water from which they crystallize as hydrates (with Ce to Nd having  $7H_2O$  and Nd to Lu having  $6H_2O$ ). If the hydrated halides are heated, they form oxohalides instead of dehydrating to anhydrous halides. However cerium gives  $CeO_2$ . The bromides and iodides are similar to chlorides.



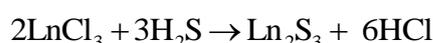
### **Carbides:**

The lanthanides also form carbides of stoichiometry  $LnC_2$  and  $Ln_4(C_2)_3$ . They are formed by the arc melting of the metals with carbon in an inert atmosphere. They can also be formed by reducing the oxides  $Ln_2O_3$ , with carbon in an electric furnace. The lanthanide carbides,  $LnC_2$  are more reactive than  $CaC_2$ . They react with water to give ethyne, hydrogen, ethane and ethene. They are best described as acetylides of  $Ln^{3+}$ ,  $C_2^{2-}$  and the extra electron in the conduction band which makes it show metallic conductivity.



### **Reaction with other elements:**

Numerous other compounds are obtained by direct reaction of the lanthanides at elevated temperature with some elements-S, group (V) elements ( $X=N, P, As, Sb$  or  $Bi$ ). The sulphides are formed by reaction of the chloride with hydrogen sulphide at  $1100^\circ C$ . The lanthanides also react with boron at elevated temperature to give borides,  $LnB_4$  and  $LnB_6$ .



With the group V elements they form  $LnX$  etc that have NaCl structure.  $LnN$  is hydrolysed by water in a similar way like  $AlN$ .



### **Oxo salts:**

Oxo salts of lanthanides also exist which includes nitrates, sulphates, phosphates, carbonates, oxalates etc. Examples are the hydrated salts of common acids which contain the ions  $[Ln(H_2O)_n]^{3+}$ , which are readily obtained by dissolving the oxide in acid and crystallizing. Others are double salts which are very common such as  $2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ ,  $Ln(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$  and  $Ln_2(SO_4)_3 \cdot 3Na_2SO_4 \cdot 12H_2O$ .

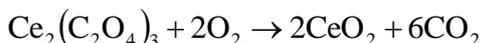
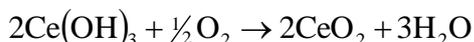
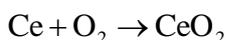
### **Oxidation State(+4)**

This oxidation state is most important to cerium and a little to praseodymium and terbium.  $Ce(4+)$  is the only  $Ln(4+)$  that exists in solution.

### **Cerium (IV):**

The high charge of the ion leads it being heavily hydrated and except in strongly acidic solutions, the hydrated  $\text{Ce}^{4+}$  will be hydrolysed giving polymeric species and  $\text{H}^+$ . Cerium (IV) in solution (also called ceric) is obtained by treatment of Ce(III) solutions with very powerful oxidizing agents e.g. ammonium periodisulphate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  or bismuthate in nitric acid. The Ce(IV) solutions are strong oxidizing agents, so are used in redox titrations instead of  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ . The aqueous Ce(IV) oxidizes concentrated HCl to  $\text{Cl}_2$ . They are also used in organic reactions like the oxidation of alcohols, aldehydes and ketones at the  $\alpha$ -carbon atom. Solid ceric compounds include  $\text{CeO}_2$ ,  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$  and  $\text{CeF}_4$ .

$\text{CeO}_2$  is white when pure and is obtained by heating the metal or  $\text{Ce}(\text{OH})_3$  or  $\text{Ce}_2^{\text{III}}$  (oxalates) $_3$  in air or oxygen. It is rather inert, not being attacked by either strong acids or alkalis. However, it can be dissolved by acids in the presence of reducing agents ( $\text{H}_2\text{O}_2$ ,  $\text{Sn}^{2+}$ ) giving  $\text{Ce}^{3+}$  in solution.



The hydrous oxide,  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ , is a yellow gelatinous precipitate. It can be obtained on treating Ce(IV) solution with bases. It redissolves fairly easily in acid.  $\text{CeF}_4$  is white compound and has a three dimensional crystal structure with the metal in at the centre of a square antiprism. It is easily hydrolysed by water. It is obtained by treating  $\text{CeCl}_3$  or  $\text{CeF}_3$  with fluorine at room temperature.

Many stable complex ions are formed for example,  $[\text{Ce}(\text{NO}_3)_6]^{2-}$  ion or (ammonium cerium (IV) nitrate  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]^{2-}$ ) where bidentate  $\text{NO}_3^-$  ions afford 12-coordination.

### **Other Lanthanides (IV)**

The elements of Pr, Nd, Tb and Dy also form compounds of (+IV) states which are generally unstable in water, occur only as solids and form only oxides, fluorides and a few fluoro complexes. Examples are  $\text{PrO}_2$ ,  $\text{PrF}_4$ ,  $\text{Na}_2[\text{PrF}_6]$ ,  $\text{TbO}_2$ ,  $\text{TbF}_4$ ,  $\text{DyF}_4$ , and  $\text{Cs}_3[\text{DyF}_7]$ .

### **Oxidation State(+2)**

Only lanthanide elements Sm, Eu and Yb have aqueous chemistry at oxidation state (+II).  $[\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}]$ . The most stable is  $\text{Eu}^{2+}$  which is stable in water but the solution is strongly reducing. The  $\text{Eu}^{2+}(\text{aq})$  ion is readily obtained by reducing  $\text{Eu}^{3+}(\text{aq})$  with Zn, Zn/Hg, Mg or electrolysis. Eu(II) bears strong similarities to Calcium in many ways; the insolubility of their sulphates and carbonates in water, the insolubility of the dichloride in strong HCl and the solubility of the metals in liquid  $\text{NH}_3$ . They however differ in that the

dihalides  $\text{EuX}_2$  have a magnetic moment of 7.9BM showing 7 unpaired electrons, whereas Ca compounds are diamagnetic.

$\text{Sm}^{2+}$ ,  $\text{Yb}^{2+}$  can be obtained by the electrolytic reduction of their trivalent ions in aqueous solution. They are readily oxidized by air and form sulphates, hydroxide, carbonates, halides and phosphates.

They form solid dihalide compounds,  $\text{LnCl}_2$  and  $\text{LnI}_2$ . The dihalides compounds have 8-coordinated  $\text{Ln}^{2+}$  ions while 7-coordination is found in  $\text{EuI}_2$ . The  $\text{LnX}_2$  compounds react with donor solvents to give solvates e.g.  $\text{LnX}_2(\text{THF})_x$ .

### **Metallic properties:**

The hardness, melting and boiling points of the elements all increase from Ce to Lu due to attraction between the atoms increase as the size decreases. This makes them good conductors of electricity and heat.

### **Coordination Complexes:**

$\text{Ln}^{3+}$  forms complexes of high coordination numbers. The coordination numbers for  $[\text{Ln}(\text{OH}_2)_n]^{3+}$  in aqueous solution are up to 9 for the early lanthanoids and 8 for the later smaller members. The  $\text{Ln}^{3+}$  ions readily form complexes with F<sup>-</sup> and O-donor ligands eg with  $\text{H}_2\text{O}$ , EDTA,  $\beta$ -diketonate, citric acid, oxalic acid ligands. Partially fluorinated  $\beta$ -diketonate ligand  $\text{CF}_3\text{COCHCOCF}_3$ (Fod) produces complexes with  $\text{Ln}^{3+}$  that are volatile and soluble in organic solvents {because of their volatility, they are used as precursors for the synthesis of lanthanoid-containing superconductors by vapour deposition}

Charged ligands have highest affinity for the smallest  $\text{Ln}^{3+}$  ion.

Examples of Metal complexes:

Coordination number	Complex	Shape
4	[Lu(2,6-dimethylphenyl) <sub>4</sub> ] <sup>-</sup>	Tetrahedral
6	[Ce <sup>IV</sup> Cl <sub>6</sub> ] <sup>2-</sup>	Octahedral
6	[Er(NCS) <sub>6</sub> ]	Octahedral
7	[Y(acetylacetonate) <sub>3</sub> H <sub>2</sub> O]	Mono-capped trigonal prism
8	[La(acetylacetonate) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Square antiprism
8	[Ce <sup>IV</sup> (acetylacetonate) <sub>4</sub> ]	Square antiprism
8	[Eu(acetylacetonate) <sub>3</sub> (phenanthroline)]	Square antiprism
8	[Ho(tropolonate) <sub>4</sub> ] <sup>-</sup>	Docecahedral
9	[Nd(H <sub>2</sub> O) <sub>9</sub> ] <sup>3+</sup>	Tri-capped trigonal prism
9	[Sm(NH <sub>3</sub> ) <sub>9</sub> ] <sup>3+</sup>	Tri-capped trigonal prism
10	[Ce <sup>IV</sup> (CO <sub>3</sub> -O, O') <sub>5</sub> ] <sup>6-</sup>	
10	[Ce <sup>IV</sup> (NO <sub>3</sub> ) <sub>4</sub> (Ph <sub>3</sub> PO) <sub>2</sub> ]	(each nitrate ion is bidentate)
11	[La(OH <sub>2</sub> ) <sub>5</sub> (NO <sub>3</sub> -O, O') <sub>3</sub> ] <sup>2-</sup>	
12	[Ce <sup>IV</sup> (NO <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup>	Icosahedral (each nitrate ion is bidentate)
12	[La(NO <sub>3</sub> -O, O') <sub>6</sub> ] <sup>3-</sup> , [La(OH <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> -O, O') <sub>5</sub> ] <sup>2-</sup>	

### Organometallic compounds

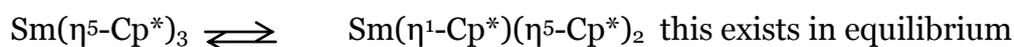
The organometallic compounds of the lanthanoids are dominated by good donor ligands, with complexes of acceptor ligands being rare. This is attributed to

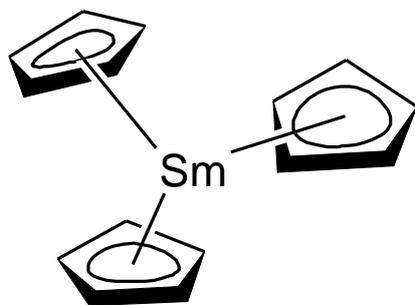
- ◆ The lack of orbitals because the 5d orbitals are empty and the 4f orbitals are buried so this restricts the number of bonding modes that are available to the lanthanoid ions.
- ◆ The strong electropositive nature of the lanthanoids means they need good donor (eg alkoxide, amide and halide ligands which are both  $\sigma$  and  $\pi$  donors), not good acceptor ligands (eg CO and phosphine ligands which are both  $\sigma$  donors and  $\pi$  acceptors)

The bonding in the organometallic lanthanoid complex that do form is predominantly ionic and governed by electrostatic factors and steric requirements. All organometallic complexes are strong Lewis acids and are very sensitive to air and moisture.

Examples of organometallic lanthanoid compounds:

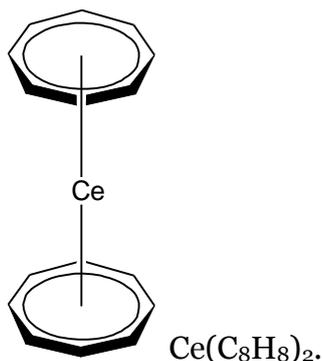
Ln(Cp)<sub>3</sub> compounds (Cp-cyclopentadienyl compounds)





$$\text{Sm}(\eta^5\text{-Cp}^*)_3$$

These complexes contain  $\text{Ln}^{3+}$  ion with a limited number of  $\text{Ln}^{2+}$  compounds.  $\sigma$ -Bonded alkyl groups are common with compounds containing cyclopentadienyl ligands tending to dominate. Cp groups are electrostatically bound to a central cation. Other examples are  $\eta^8$ -Cyclooctatetraene ligands eg  $\text{Ce}(\text{C}_8\text{H}_8)_2$ .



$$\text{Ce}(\text{C}_8\text{H}_8)_2$$

### Optical properties and Spectra of Lanthanoid complexes

Lanthanide ions are weakly coloured. The spectra of their complexes show much narrower and more distinct absorption bands which is associated with weak  $f-f$  transition. The  $4f$  orbitals are deeply embedded inside the atom and well shielded by  $5s$  and  $5p$  electrons. The  $f$  electrons are practically unaffected by complex formation; hence colour remains almost constant for a particular ion regardless of the ligands (see Table 3). The bands due to  $f-f$  transition are sharp compared to the broad bands for  $d-d$  transition. Absorption bands due to  $4f-5d$  transitions are broad and are affected by ligand environment

All lanthanoid ions (except  $\text{La}^{3+}$  ( $f^0$ ) and  $\text{Lu}^{3+}$  ( $f^{14}$ )) show luminescence  $\text{Eu}^{3+}$  ( $f^6$ ) and  $\text{Tb}^{3+}$  ( $f^8$ ) showing particularly strong emissions. This has been attributed to the large number of excited states that exist which decays to the ground state with either emission of energy (fluorescence) or non-radiative pathways. The origin of this is  $f-f$  transition. The luminescence of lanthanoid complexes is the reason they are used as phosphors on TV screens and fluorescent lighting.

### The Colours Of Some Aqueous Lanthanides

Ions	No of 4f e`s	Colour	Ions	No of 4f e`s	Colour	Ions	No of 4f e`s	Colour	Isoelectronic Ln <sup>3+</sup>
La <sup>3+</sup>	4f <sup>0</sup>	Colourless	Lu <sup>3+</sup>	4f <sup>14</sup>	Colourless	Ce <sup>4+</sup>	4f <sup>0</sup>	Orange-red	La <sup>3+</sup> Colourless
Ce <sup>3+</sup>	4f <sup>1</sup>	Colourless	Yb <sup>3+</sup>	4f <sup>13</sup>	Colourless	Sm <sup>2+</sup>	4f <sup>6</sup>	Yellow	Eu <sup>3+</sup> Pale pink
Pr <sup>3+</sup>	4f <sup>2</sup>	Green	Tm <sup>3+</sup>	4f <sup>12</sup>	Green	Eu <sup>2+</sup>	4f <sup>7</sup>	Pale greenish yellow	Gd <sup>3+</sup> Colourless
Nd <sup>3+</sup>	4f <sup>3</sup>	Lilac	Er <sup>3+</sup>	4f <sup>11</sup>	Lilac	Yb <sup>2+</sup>	4f <sup>14</sup>	Colourless	Lu <sup>3+</sup> Colourless
Pm <sup>3+</sup>	4f <sup>4</sup>	pink	Ho <sup>3+</sup>	4f <sup>10</sup>	Pink				
Sm <sup>3+</sup>	4f <sup>5</sup>	Yellow	Dy <sup>3+</sup>	4f <sup>9</sup>	Yellow				
Eu <sup>3+</sup>	4f <sup>6</sup>	Pale pink	Tb <sup>3+</sup>	4f <sup>8</sup>	Pale pink				
Gd <sup>3+</sup>	4f <sup>7</sup>	Colourless							

\*Elements with (n) f electrons often have similar colour to those with (14-n)f electrons.

### Magnetic properties

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f subshell the magnetic effects of the different electrons do not cancel out each other as they do in a completed subshell, and this factor gives rise to the interesting magnetic behaviour of these elements. At higher temperatures, all the lanthanides except lutetium are paramagnetic (weakly magnetic), and this paramagnetism frequently shows a strong anisotropy. As the temperature is lowered, many of the metals exhibit a point below which they become antiferromagnetism (i.e., magnetic moments of the ions are aligned but some are opposed to others), and, as the temperatures are lowered still further, many of them go through a series of spin rearrangements, which may or may not be in conformity with the regular crystal lattice. Finally, at still lower temperatures, a number of these elements become ferromagnetic (i.e., strongly magnetic, like iron). Some of the metals have saturation moments (magnetism observed when all the magnetic moments of the ions are aligned) greater than iron, cobalt, or nickel. They also show a strong anisotropy in their magnetic behaviour depending on the crystal direction. Study of the magnetism of rare-earth elements has had great influence on present-day theories of magnetism.

### APPLICATIONS OF LANTHANIDES

1. Use as catalysts: Lanthanide catalysts have been repeatedly recommended for use in numerous organic reactions, including the hydrogenation of ketones to form secondary alcohols, the hydrogenation of olefins to form alkanes, the dehydrogenation of alcohols and butanes, and the formation of polyesters.
2. Use in the glasses industry: Cerium oxide has been found to be a more rapid polishing agent for glass than rouge, and are used in the polishing of lenses for cameras, binoculars,

and eyeglasses, as well as in polishing mirrors and television faceplates. Neodymium is added to some glasses to counteract the yellowish tint caused by iron impurities. Very pure neodymium oxide, when added in sufficient quantities (1–5 percent), gives a beautiful purple glass. Praseodymium and neodymium are added to glass to make welders' and glassblowers' goggles, that absorb the bright-yellow light from the sodium flame. The same combination is sometimes added to the glass used in television faceplates to decrease the glare from outside light sources. A beautiful yellow ceramic stain results from the addition of about 3 percent praseodymium oxide to zirconium oxide. Cerium oxide increases the opacity of white porcelain enamels.

3. Use in the metallurgical industry: Small amounts of misch metal and cerium have long been added to other metals or alloys to remove their nonmetallic impurities. Misch metal added to cast iron makes a more malleable nodular iron. Added to some steels, it makes them less brittle. The addition of misch metal to certain alloys has been reported to increase the tensile strength and improve the hot workability and the high-temperature oxidation resistance. The flints of cigarette lighters are an alloy of misch metal and iron. The addition of misch metal or pure rare-earth elements to magnesium increases its high-temperature strength and its creep resistance—that is, resistance to slow deformation under prolonged use. This alloy also makes better castings if small amounts of zirconium or other metals are added, and such alloys are used in jet-engine and precision castings.
4. Use in the television industry: It has been found that if a small amount of europium oxide ( $\text{Eu}_2\text{O}_3$ ) is added to yttrium oxide ( $\text{Y}_2\text{O}_3$ ), it gives a brilliant-red phosphor. Colour television screens utilize red, green, and blue phosphors. In the past, a zinc–cadmium sulfide was used as the red phosphor, but it was not completely satisfactory because its fluorescent band was too wide, and it could not be made to fluoresce as intensely as the other phosphors. The  $\text{Y}_2\text{O}_3$ – $\text{Eu}_2\text{O}_3$  phosphor corrected these disadvantages and made possible much brighter and more natural coloured pictures. Many of the early rare-earth screens used europium–yttrium orthovanadate phosphor, but the industry is shifting heavily toward the oxide phosphor. Some television companies have substituted gadolinium oxide for the yttrium oxide. The rare-earth phosphors are also finding use in mercury-arc lights, which are used for sporting events and special street lighting. Instead of the unhealthy-looking blue light of the mercury arc, the phosphors give an intense white radiation similar to daylight. Considerable amounts of mixed rare-earth fluorides are used to make cored carbon rods, which are used as arcs in searchlights and in some of the lights used by the motion-picture industry.

5. Other applications: Another significant industrial application of rare earths is in the manufacture of strong permanent magnets. Alloys of cobalt with rare earths, such as cobalt–samarium, produce permanent magnets that are far superior to most of the varieties now on the market. Another relatively recent development is the use of a barium phosphate–europium phosphor in a sensitive X-ray film that forms satisfactory images with only half the exposure.

Europium, gadolinium, and dysprosium have large capture cross sections for thermal neutrons—that is, they absorb large numbers of neutrons per unit of area exposed. These elements, therefore, are incorporated into control rods used to regulate the operation of nuclear reactors or to shut them down should they get out of control.

Complexes of europium, praseodymium, or ytterbium with derivatives of camphor are useful reagents for analysis of optically-active organic compounds, which often are obtained as mixtures containing unknown proportions of two components that differ only in that their molecular structures are mirror images of each other. Determination of these proportions can be very difficult, but the rare-earth complexes provide asymmetric environments in which each component absorbs electromagnetic radiation of a particular frequency in the presence of a strong magnetic field. Proportions then can be determined by measuring the intensities of the separate absorptions.

### Introduction to Actinide series

The group also known as Heavier elements or inner series transition elements following actinium element contains metal. Actinides series elements of which uranium( U, elt 92) and plutonium( Pu, elt 94) are best known are built up by completion of the 5f orbitals.

#### Arrangement of the Actinides Series Elements in Periodic Table

They are found at the final row of the periodic table followed by filling of the 6p orbital.

S/N	Atomic no	Element	Symbol	Oxidation states
1	89	Actinium	Ac	III
2	90	Thorium	Th	(III), IV
3	91	Protactinium	Pa	(III), IV, V
4	92	Uranium	U	III,IV,V VI
5	93	Neptunium	Np	III,IV,V,VI,VII
6	94	Plutonium	Pu	III,IV,V,VI,VII
7	95	Americium	Am	II,III,(IV),VI
8	96	Curium	Cm	III,(IV)
9	97	Berkelium	Bk	III,IV
10	98	Californium	Cf	(II),III,IV
11	99	Einsteinium	Es	(II),III
12	100	Fermium	Fm	(II),III
13	101	Mandeleevium	Md	(II),III
14	102	Nobelium	No	II,III
15	103	Lawrencium	Lr	III
16	104	Rutherfordium	Rf	

#### Occurrence and Preparation of The Elements

With the exception of Th and U( natural) the actinoids are man made, synthesized by artificial radioactivity i.e by bombardment with slow moving neutron.

#### General Properties

- 1) The elements are all metals with fairly high melting points though the values are considerably lower than for the transition elements.
- 2) The sizes of the ions decreases regularly along the series because of the poor screening of the nuclear charge by the f- orbital results in an actinide contraction similar to the lanthanide contraction.
- 3) The actinides are much more dense.
- 4) They are reactive metals like La and the lanthanons.

**Compounds of Actinides Series**

Th shows +2, +3, +4 oxidation state. +4 is the most stable and the  $\text{Th}^{4+}$  ion is known both in the solid and in solution with basic character.  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  is the best known salt, and it is very soluble in water.