

1

Introduction to the Lanthanides

By the end of this chapter you should be able to:

- understand that lanthanides differ in their properties from the s- and d-block metals;
- recall characteristic properties of these elements;
- appreciate reasons for their positioning in the Periodic Table;
- understand how the size of the lanthanide ions affects certain properties and how this can be used in the extraction and separation of the elements;
- understand how to obtain pure samples of individual Ln^{3+} ions.

1.1 Introduction

Lanthanide chemistry started in Scandinavia. In 1794, Johann Gadolin succeeded in obtaining an 'earth' (oxide) from a black mineral subsequently known as gadolinite; he called the earth yttria. Soon afterwards, M.H. Klaproth, J.J. Berzelius and W. Hisinger obtained ceria, another earth, from cerite. However, it was not until 1839–1843 that the Swede C.G. Mosander first separated these earths into their component oxides; thus, ceria was resolved into the oxides of cerium and lanthanum and a mixed oxide 'didymia' (a mixture of the oxides of the metals from Pr through Gd). The original yttria was similarly separated into substances called erbia, terbia, and yttria (though some 40 years later, the first two names were to be reversed!). This kind of confusion was made worse by the fact that the newly discovered means of spectroscopic analysis permitted misidentifications, so that around 70 'new' elements were erroneously claimed in the course of the century.

Nor was Mendeleev's revolutionary Periodic Table a help. When he first published his Periodic Table in 1869, he was able to include only lanthanum, cerium, didymium (now known to have been a mixture of Pr and Nd), another mixture in the form of erbia, and yttrium; unreliable information about atomic mass made correct positioning of these elements in the table difficult. Some had not yet been isolated as elements. There was no way of predicting how many of these elements there would be until Henry Moseley (1887–1915) analysed the X-ray spectra of elements and gave meaning to the concept of atomic number. He showed that there were 15 elements from lanthanum to lutetium (which had only been identified in 1907). The discovery of radioactive promethium had to wait until after World War II.

It was the pronounced similarity of the lanthanides to each other, especially each to its neighbours (a consequence of their general adoption of the +3 oxidation state in aqueous solution), that caused their classification and eventual separation to be an extremely difficult undertaking.

Subsequently, it was not until the work of Bohr and of Moseley that it was known precisely how many of these elements there were. Most current versions of the Periodic Table place lanthanum under scandium and yttrium.

1.2 Characteristics of the Lanthanides

The lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals, akin to the Group II metals:

- 1) A very wide range of coordination numbers (generally 6–12, but numbers of 2, 3, or 4 are known).
- 2) Coordination geometries are determined by ligand steric factors rather than crystal field effects.
- 3) They form labile ‘ionic’ complexes that undergo facile exchange of ligand.
- 4) The 4f orbitals in the Ln^{3+} ion do not participate directly in bonding, being well shielded by the $5s^2$ and $5p^6$ orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.
- 5) Small crystal-field splittings and very sharp electronic spectra in comparison with the d-block metals.
- 6) They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).
- 7) They readily form hydrated complexes (on account of the high hydration energy of the small Ln^{3+} ion), and this can cause uncertainty in assigning coordination numbers.
- 8) Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.
- 9) The chemistry is largely that of one (3+) oxidation state (certainly in aqueous solution).
- 10) They do not form $\text{Ln}=\text{O}$ or $\text{Ln}\equiv\text{N}$ multiple bonds of the type known for many transition metals and certain actinides.
- 11) Unlike the transition metals, they do not form stable carbonyls and have (virtually) no chemistry in the 0 oxidation state.

1.3 Occurrence and Abundance of the Lanthanides

Table 1.1 presents the abundance of the lanthanides in Earth’s crust and in the solar system as a whole. (Although not in the same units, the values in each list are internally consistent.)

Table 1.1 Abundance of the lanthanides.

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Crust (ppm)	35	66	9.1	40	0.0	7	2.1	6.1	1.2	4.5	1.3	3.5	0.5	3.1	0.8	31
Solar system (with respect to 10^7 atoms Si)	4.5	1.2	1.7	8.5	0.0	2.5	1.0	3.3	0.6	3.9	0.9	2.5	0.4	2.4	0.4	40.0

Two patterns emerge from these data:

- 1) The lighter lanthanides are more abundant than the heavier ones.
- 2) The elements with even atomic number are more abundant than those with odd atomic number.

Overall, cerium, the most abundant lanthanide on Earth, has a similar crustal concentration to the lighter Ni and Cu, whilst even Tm and Lu, the rarest lanthanides, are more abundant than Bi, Ag, or the platinum metals.

The abundances are a consequence of how the elements were synthesized by atomic fusion in the cores of stars, with heavy elements only made in supernovae. Synthesis of heavier nuclei requires higher temperature and pressures and so gets progressively harder as the atomic number increases. The odd/even alternation (often referred to as the Oddo–Harkins rule) is again general. It reflects the facts that elements with odd mass numbers have larger nuclear capture cross sections and are more likely to take up another neutron, so elements with odd atomic number (and hence odd mass number) are less common than those with even mass number. Even-atomic-number nuclei are more stable when formed.

1.4 Lanthanide Ores

Traditionally, there are three principal sources of the lanthanides (Table 1.2): Bastnäs site LnFCO_3 ; Monazite $(\text{Ln, Th})\text{PO}_4$ (richer in earlier lanthanides); and Xenotime $(\text{Y, Ln})\text{PO}_4$ (richer in later lanthanides). Since the 1980s, when China became the leading source of these elements, mines have opened in several parts of China – Bayan Obo in Inner Mongolia; Sichuan in the southwest; Weishan in Shandong province in the east; and finally southern China, notably Jianxi province in the southeast. The ores in the Jianxi province are unique to China – ion-absorption ores, weathered granites with lanthanides adsorbed onto the surface of aluminium silicates, which fall into two types.

There is concern that the ion-absorption ores in particular may be depleted by 2025. Among these ion-absorption ones, the Longnan deposits are an example that is low in cerium and early lanthanides but rich in the ‘heavier metals’ (including yttrium, because the Y^{3+} ion is similar in size to the later lanthanide ions); these tend to be more sought-after on account of their rarity. The Xunwu deposits, also ion-absorption ores, are rich in the lighter metals, notably neodymium, in demand because of its widespread use in $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic alloys.

Table 1.2 Typical abundance of the lanthanides in ores^a.

(%)	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	
Monazite	20	43	4.5	16	0	3	0.1	1.5	0.05	0.6	0.05	0.2	0.02	0.1	0.02	2.5	
Bastnasite	33.2	49.1	4.3	12	0	0.8	0.12	0.17	160	310	50	35	8	6	1	0.1	
Xenotime	0.5	5.0	0.7	2.2	0	1.9	0.2	4.0	1.0	8.6	2.0	5.4	0.9	6.2	0.4	60.0	
Laterite Longnan	1.8	0	0.7	3.0	0	2.8	0.1	6.0	1.3	6.7	1.6	4.9	0.7	2.5	0.4	65	
Laterite Xunwu	43.4	2.4	9.0	31.7	0	3.9	0.5	3.0	Trace	Trace	Trace	Trace	Trace	Trace	0.3	0.1	8.0

^a Bold values are in ppm.

The Bayan Obo mine has the largest deposit of lanthanide ores in the world, contributing about half of the Chinese production, mainly drawn from monazite and fluorocarbonates like bastnäsite. The Bayan Obo deposit is actually very complex, containing large amounts of iron and many other metals, notably niobium. The rare earth oxide content of these Chinese deposits amounts to *ca.* 6.0% (Bayan Obo); 3.7% (Sichuan); 3.13% (Weishan); and 0.05% to 0.5% (Jianxi). Overall, at present, China is believed to contribute >95% of the annual production of lanthanides. Figure 1.1 indicates production trends in the latter part of the twentieth century.

China is moving from being predominantly a miner of lanthanides to a country making more use of its metallurgical and technological expertise, thus retaining more of the lanthanides to produce value-added products. Other factors include a crack-down on illegal mining, which some estimates suggest may amount to about 15–20% of Chinese production, as well as restricting inefficient and polluting operations (e.g. radioactive thorium is a side product of mining monazite). From 2010, this led to supply restrictions, so that other countries are looking further afield for lanthanide deposits. In one case, ‘deep-sea mud’ sediments on the seabed of the Pacific Ocean have been suggested as a rare-earth resource, though technological problems and ecological damage (plus the fact that the lanthanides are present at less than 0.1% level) is likely to push this into the very distant future. Recovery from coal and coal byproducts like coal ash is also being examined; burning coal concentrates lanthanides in the ash by a factor of 6 to 10 times. The average rare earth concentration in coal ash is 445 ppm, but some have much higher levels.

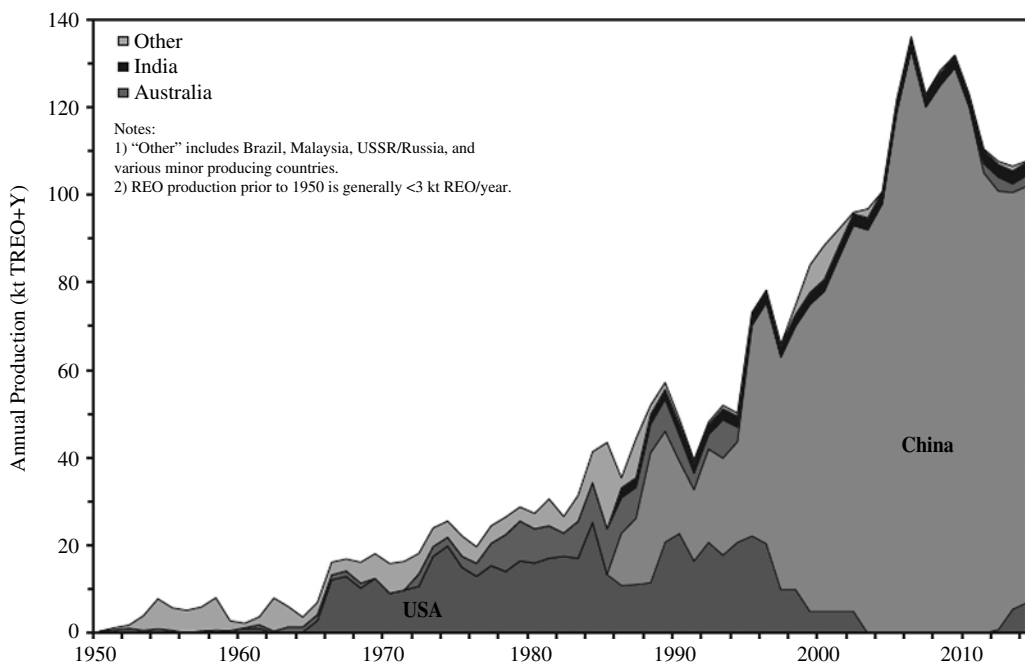


Figure 1.1 Production of total rare earth oxides plus yttrium oxide, 1950–2015, split by country. Reproduced with permission from: Z. Weng, S. M. Jowitt, G. M. Mudd, and N. Haque, *Economic Geology*, 2015, 110, 1925–1952.

1.5 Extracting and Separating the Lanthanides

These two processes are not necessarily coterminous. Whilst electronic, optical, and magnetic applications require individual pure lanthanides, the greatest quantity of lanthanides is used in mixtures (e.g. in mischmetal or oxide catalysts).

1.5.1 Extraction

After initial concentration by crushing, grinding, and froth flotation, bastnasite is treated with 10% HCl to remove calcite, by which time the mixture contains around 70% lanthanide oxides. This is roasted to oxidize the cerium content to Ce^{IV} ; on further extraction with HCl, the Ce remains as CeO_2 , whilst the lanthanides in the (+3) state dissolve as a solution of the chlorides.

Monazite is usually treated with NaOH at 150 °C to remove phosphate as Na_3PO_4 , leaving a mixture of the hydrated oxides, which are dissolved in boiling HCl at pH 3.5, separating the lanthanides from insoluble ThO_2 . Sulfuric acid can also be used to dissolve the lanthanides.

An alternative method of mining lanthanides that has attracted attention is *agomining*, which involves using 'hyperaccumulating' plants to extract valuable metals from the soil. Analysis of soil samples at a former uranium mine in Australia has shown levels of light rare earths ca. 1000 $\mu\text{g/g}$, well worth extracting. A study of the fern *Dicranopteris linearis* has shown that it can accumulate rare earths from the tailings of former rare earth element (REE) mines in southern China at commercially harvestable levels. Extraction using either sulphuric acid or EDTA can be followed by precipitation as the insoluble oxalates, followed by calcination to the oxide.

1.5.2 Separating the Lanthanides

These can be divided into four types: chemical separations, fractional crystallization, ion-exchange methods, and solvent extraction. Of these, only solvent extraction is used on a commercial scale (apart from initial separation of cerium). Chemical separations rely on using stabilities of unusual oxidation states; thus, Eu^{2+} is the only ion in that oxidation state formed on reduction by zinc amalgam and can then be precipitated as EuSO_4 (note the similarity with heavier Group 2 metals). Repeated (and tedious) fractional crystallization, which made use of slight solubility differences between the salts of neighbouring lanthanides, such as the bromates $\text{Ln}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$, ethyl sulfates and double nitrates, were once the only possible way of obtaining pure lanthanides, as with the 15 000 recrystallizations carried out by the American C. James to get pure thulium bromate (1911) (Figure 1.2 indicates the principle of this method).

Ion-exchange chromatography is not of real commercial importance for large-scale production, but

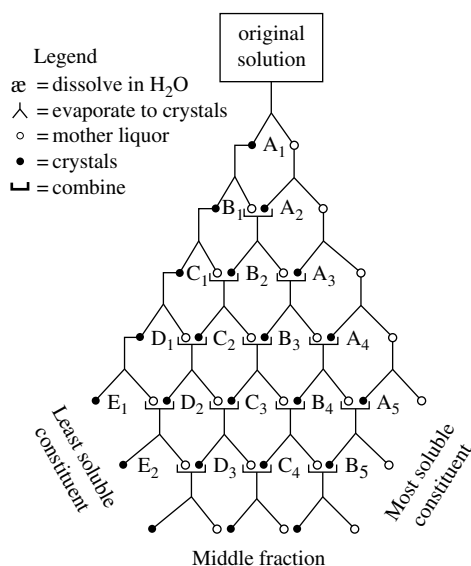


Figure 1.2 Representation of the system of fractional crystallization used to separate salts of the rare-earth elements (reproduced with permission from D.M. Yost, H. Russell, and C.S. Garner, *The Rare Earth Elements and Their Compounds*, John Wiley, 1947.)

historically it was the method by which fast high-purity separation of the lanthanides first became feasible. This was a spinoff from the Manhattan project. As radioactive lanthanide isotopes are important products of the fission of ^{235}U and therefore need to be separated from uranium, ion-exchange chromatography, using synthetic resins containing sulfonic acid groups, was found to effect this separation. The ion-exchange technique was then applied to the large-scale separation of the individual lanthanides (1945).

It was found that if Ln^{3+} ions were adsorbed at the top of a cation-exchange resin, then treated with a complexing agent such as buffered citric acid, then the cations tended to be eluted in reverse atomic number order (Figure 1.3a); the anionic ligand binds most strongly to the heaviest (and smallest) cation, which has the highest charge density. A disadvantage of this approach when scaled up to high concentration is that the peaks tend to overlap (Figure 1.3b).

It was subsequently found that amine polycarboxylates such as EDTA^{4-} gave stronger complexes and much better separation. In practice, some Cu^{2+} ions ('retainer') are added to prevent precipitation of either the free acid H_4EDTA or the lanthanide complex $\text{HLn}(\text{EDTA}) \cdot x\text{H}_2\text{O}$ on the resin. The major disadvantage of this method is that it is a slow process for large-scale separations.

Solvent extraction has come to be used for the initial stage of the separation process, to give material with up to 99.9% purity. In 1949, it was found that Ce^{4+} could readily be separated from Ln^{3+} ions by extraction from a solution in nitric acid into tributyl phosphate $[(\text{BuO})_3\text{PO}]$. Subsequently, the process was extended to separating the lanthanides using a nonpolar organic solvent such as kerosene and an extractant such as $(\text{BuO})_3\text{PO}$ or bis (2-ethylhexyl)phosphinic acid $[[\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)_2\text{P} = \text{O}(\text{OH})]$ to extract the lanthanides from aqueous nitrate solutions. The heavier lanthanides form complexes that are more soluble in the aqueous layer. After the two immiscible solvents have been agitated together and separated, the organic layer is treated with acid and the lanthanide is extracted. The solvent is recycled and the aqueous layer put through further stages.

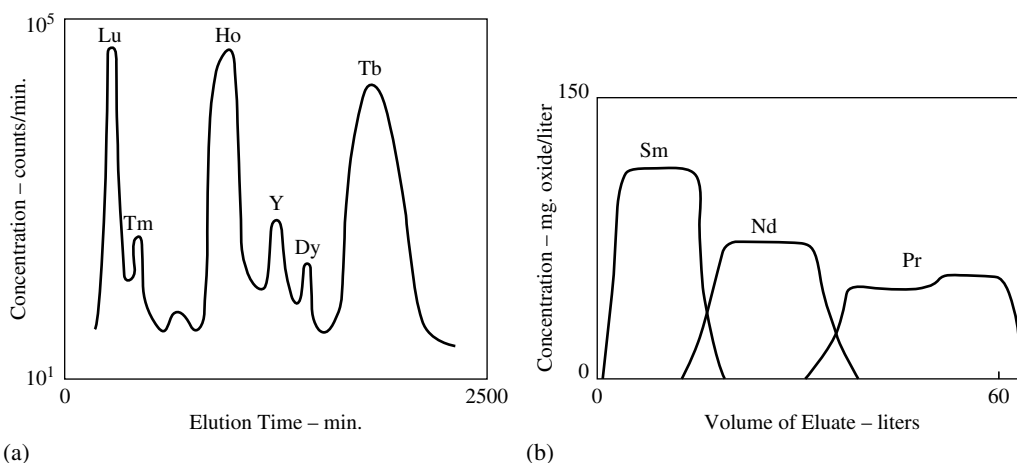


Figure 1.3 (a) Cation-exchange chromatography of lanthanides, (b) overlap of peaks at high concentration. (a) Tracer-scale elution with 5% citrate at pH 3.20 (Adapted from B.H. Ketell et al., 1947). (b) Macro-scale elution with 0.1% citrate at pH 5.30. Reproduced with permission of F.H. Spedding et al., 1950 / American Chemical Society.

For a lanthanide Ln_A distributed between two phases, a distribution coefficient D_A is defined:

$$D_A = [\text{Ln}_A \text{ in organic phase}] / [\text{Ln}_A \text{ in aqueous phase}]$$

For two lanthanides Ln_A and Ln_B in a mixture being separated, a separation factor β_B^A can be defined, where

$$\beta_B^A = D_A / D_B$$

β is very close to unity for two adjacent lanthanides in the Periodic Table (obviously, the larger β is, the better the separation).

In practice, this process is run using an automated continuous counter-current circuit in which the organic solvent flows in the opposite direction to the aqueous layer containing the lanthanides. An equilibrium is set up between the lanthanide ions in the aqueous phase and the organic layer, where there tends to be a relative enhancement of the concentration of the heavier lanthanides in the organic layer. Because the separation between adjacent lanthanides in each exchange is relatively slight, over a thousand exchanges are used (see Figure 1.4). This method affords lanthanides of purity up to the 99.9% purity level and is thus well suited to large-scale separation, the products

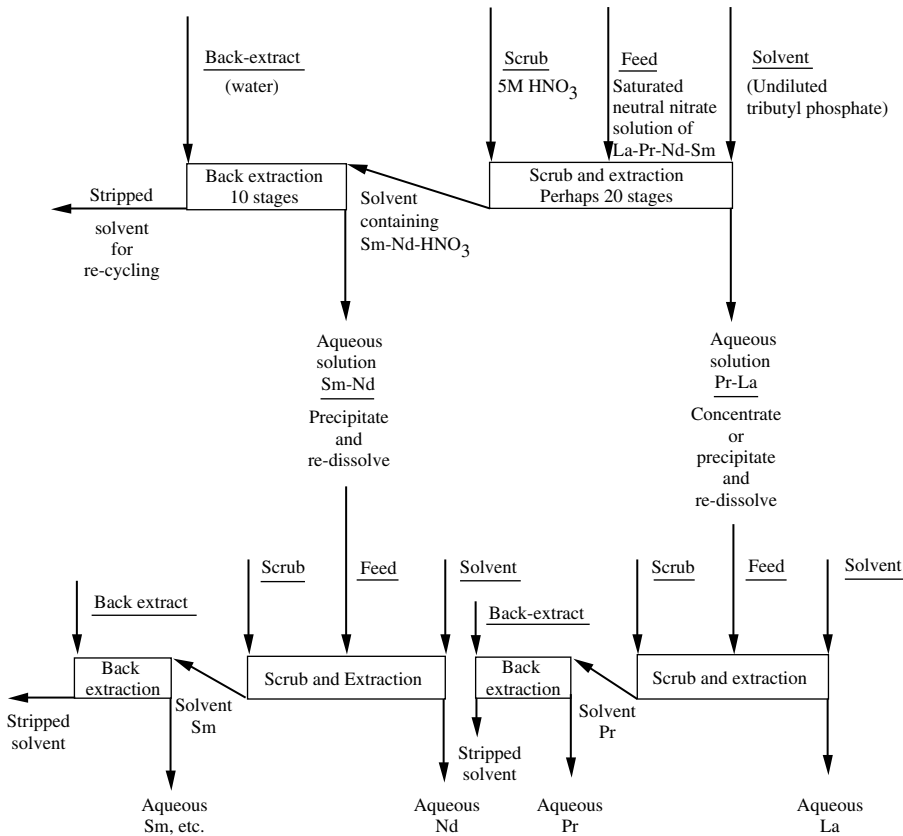


Figure 1.4 Schematic diagram of lanthanide separation by solvent extraction. Reproduced with permission of R.J. Callow, 1966 / Elsevier.

being suited to ordinary chemical use. However, for electronic or spectroscopic use (phosphor grade), 99.999% purity is necessary. Currently ion-exchange is used for final purification to these levels. The desired lanthanides are precipitated as the oxalate or hydroxide and converted into the oxides (the standard starting material for many syntheses) by thermal decomposition.

Various separation methods have been described; a recent one involves the use of supercritical carbon dioxide at 40 °C and 100 atm to convert the lanthanides into their carbonates whilst the quadrivalent metals (e.g. Th and Ce) remain as their oxides.

1.6 The Position of the Lanthanides in the Periodic Table

As already mentioned, neither Mendeleev nor his successors could place the lanthanides in the Periodic Table. Not only was there no recognizable atomic theory until many years afterwards, but, more relevant to how groupings of elements were made in those days, there was no comparable block of elements for making comparisons. The lanthanides were *sui generis*. The problem was solved by the combined (but separate) efforts of Moseley and Bohr, the former showing that La – Lu was composed of 15 elements with atomic numbers from 57 to 71, whilst the latter concluded that the fourth quantum shell could accommodate 32 electrons, and that the lanthanides were associated with placing electrons into the 4f orbitals.

The Periodic Table places elements in atomic number order, with the lanthanides falling between barium (56) and hafnium (72). For reasons of space, most present-day Periodic Tables are presented with Groups IIA and IVB (2 and 4) separated only by the Group IIIB (3) elements. Normally La (and Ac) are grouped with Sc and Y, but arguments have been advanced for an alternative format, in which Lu (and Lr) are grouped with Sc and Y (see, e.g., W.B. Jensen, *J. Chem. Educ.*, 1982, **59**, 634) on the grounds that trends in properties (e.g. atomic radius, I.E., melting point) in the block Sc – Y – Lu parallel those in the Group Ti – Zr – Hf rather closely, and that there are resemblances in the structures of certain binary compounds. Certainly on size grounds, Lu resembles Y and Sc (it is intermediate in size between them) rather more than does La, owing to the effects of the *lanthanide contraction*. The resemblances between Sc and Lu are, however, by no means complete (see Chapter 7, section 7.3.4).

1.7 The Lanthanide Contraction

The basic concept is that there is a decrease in radius of the lanthanide ion Ln^{3+} on crossing the series from La to Lu. This is caused by the poor screening of the 4f electrons. This causes neighbouring lanthanides to have similar, but not identical, properties, and is discussed in more detail in Section 2.4.

1.8 Recycling Lanthanides

Lanthanides find increasing use in high-tech application – wind turbines, hybrid/electric cars and fluorescent lamps – as well as consumer devices such as laptops and smart phones, to name a few. The particular magnetic properties and electronic structure of each lanthanide lead to niche uses for particular metals, as in optical fibres (Er); automobile exhaust catalysts (Ce); magnets (Nd, Dy,

and Pr); battery anodes (La, Ce), and phosphors (Eu, Tb, Y, Ce, La), for example. In 2013, it was estimated that 375 000 tonnes of lanthanides would be used in 2020 (though COVID-19 may well have affected this outcome), yet recycling is minimal – less than 1% in 2011. The fact that numbers of different lanthanides are found together in an ore means that ramping up production of a currently ‘in-demand’ metal like neodymium leads to a concomitant surplus of metals such as lanthanum and cerium; this could be obviated by effective recycling programmes. It would also reduce dependence on imports for value-added manufacturing. Currently a good deal of research is being directed to this; discussion of just a few of the approaches being probed follows.

The quantity of neodymium used in high-tech applications varies enormously: a hybrid car uses around 500 grams of neodymium, but a wind turbine requires around 500 kilograms, and a consumer device like a smartphone around 1 g. Of course, different applications have different ‘lifetimes’. For a wind turbine the lifetime is reckoned to be 20–25 years; for a car 5–10 years; a PC perhaps 3–5 years, whilst a mobile phone’s lifetime is maybe 2 years. More computer hard drives could be recycled if security issues could be addressed – currently, around 35% of used computer hard drives are shredded each year.

In a process developed at the University of Birmingham (U.K.), treating these neodymium-containing materials with hydrogen gas leads to the formation of a powdered hydride (section 3.7); the hydrogen can be removed from this by heating *in vacuo*, and the neodymium reconverted into new magnets. The Ames Laboratory, a U.S. Department of Energy laboratory based in Iowa, has long specialised in lanthanide chemistry. It is investigating a route in which neodymium is dissolved by molten magnesium, from which it can be separated by vacuum distillation. Other routes for obtaining neodymium have included wet processes such as membrane-assisted solvent extraction (MSX) and complexation with a tripodal nitroxide ligand $[(2\text{-}^t\text{BuNO})\text{C}_6\text{H}_4\text{CH}_2\text{N}]_3^{3-}$ (TriNO_x^{3-}). The latter process gives good separations between neodymium and dysprosium, another lanthanide that is frequently added to neodymium-containing magnets to improve their performance. Another approach has used ionic liquids like betainium bis(trifluoromethylsulfonyl)imide, $[\text{Hbet}][\text{Tf}_2\text{N}]$. This process has the advantage over traditional processes, which use acid to dissolve rare earth alloys, as the ionic liquid can be recycled.

This ionic liquid has also been utilised to recover used Y_2O_3 : Eu^{3+} phosphor material from lamps. The lanthanides can be precipitated out with oxalate (section 4.3.2), and heated to decompose them to the oxide. An alternative way of recovering high-value europium from ‘end-of-life’ lamp phosphors is to photoreduce Eu(III) selectively to Eu(II) , which can then be precipitated as insoluble EuSO_4 . The waste powder from phosphors contains around 20% of rare earths, including both critical (Y, Eu, Tb) and less critical (La, Ce, Gd) elements. *Critical* is a term used to refer to elements highly in demand but in short supply.

At current prices of rare earth ores, recycling is perhaps twice as expensive as new material, but that could change if prices once again rise.

1.9 Isotopes

Table 1.4 lists the stable isotopes of scandium, yttrium, and the lanthanides. A few have only one stable isotope; others have several.

For the synthetic chemist, the fact that certain lanthanides have a number of isotopes means that the mass spectrum of a lanthanide complex of these metals (e.g. Nd, Sm, Eu, Gd, Dy, Er, Yb) will

Table 1.3 Comparison of 4f, 3d, and Group I metals.

	4f	3d	Group I
Electron configurations of ions	Variable	Variable	Noble gas
Stable oxidation states	Usually +3	Variable	1
Coordination numbers in complexes	Commonly 8–10	Usually 6	Often 4–6
Coordination polyhedra in complexes	Minimise repulsion	Directional	Minimise repulsion
Trends in coordination numbers	Often constant in block	Often constant in block	Increase down group
Donor atoms in complexes	'Hard' preferred	'Hard' and 'soft'	'Hard' preferred
Hydration energy	High	Usually moderate	Low
Ligand exchange reactions	Usually fast	Fast and slow	Fast
Magnetic properties of ions	Independent of environment	Depends on environment and ligand field	None
Electronic spectra of ions	Sharp lines	Broad lines	None
Crystal field effects in complexes	Weak	Strong	None
Organometallic compounds	Usually ionic, some with covalent character	Covalently bonded	Ionically bonded
Organometallics in low oxidation states	Few	Common	None
Multiply bonded atoms in complexes	None	Common	None

Table 1.4 Lanthanide isotopes; their abundance and nuclear spins (Data from Pure Appl. Chem., 2003, 75 (6), pp. 683–800).

	Abundance (%)	I		Abundance (%)	I
⁴⁵ Sc	100	7/2	¹⁵⁹ Tb	100	3/2
⁸⁹ Y	100	1/2	¹⁵⁶ Dy	0.056	0
¹³⁸ La	0.090	5	¹⁵⁸ Dy	0.095	0
¹³⁹ La	99.910	7/2	¹⁶⁰ Dy	2.33	0
¹³⁶ Ce	0.185	0	¹⁶¹ Dy	18.89	5/2
¹³⁸ Ce	0.251	0	¹⁶² Dy	25.48	0
¹⁴⁰ Ce	88.450	0	¹⁶³ Dy	24.90	5/2
¹⁴² Ce	11.114	0	¹⁶⁴ Dy	28.26	0
			¹⁶⁵ Ho	100	7/2

Table 1.4 (Continued)

	Abundance (%)	l		Abundance (%)	l
¹⁴¹ Pr	100	5/2	¹⁶² Er	0.14	0
			¹⁶⁴ Er	1.60	0
¹⁴² Nd	27.2	0	¹⁶⁶ Er	33.50	0
¹⁴³ Nd	12.2	7/2	¹⁶⁷ Er	22.87	7/2
¹⁴⁴ Nd	23.8	0	¹⁶⁸ Er	26.98	0
¹⁴⁵ Nd	8.3	7/2	¹⁷⁰ Er	14.91	0
¹⁴⁶ Nd	17.2	0			
¹⁴⁸ Nd	5.7	0	¹⁶⁹ Tm	100	1/2
¹⁵⁰ Nd	5.6	0			
			¹⁶⁸ Yb	0.13	0
¹⁴⁴ Sm	3.07	0	¹⁷⁰ Yb	3.04	0
¹⁴⁷ Sm	14.99	7/2	¹⁷¹ Yb	14.28	1/2
¹⁴⁸ Sm	11.24	0	¹⁷² Yb	21.83	0
¹⁴⁹ Sm	13.82	7/2	¹⁷³ Yb	16.13	5/2
¹⁵⁰ Sm	7.38	0	¹⁷⁴ Yb	31.83	0
¹⁵² Sm	26.75	0	¹⁷⁶ Yb	12.76	0
¹⁵⁴ Sm	22.75	0			
			¹⁷⁵ Lu	97.41	7/2
¹⁵¹ Eu	47.81	5/2	¹⁷⁶ Lu	2.59	7
¹⁵³ Eu	52.19	5/2			
¹⁵² Gd	0.20	0			
¹⁵⁴ Gd	2.18	0			
¹⁵⁵ Gd	14.80	3/2			
¹⁵⁶ Gd	20.47	0			
¹⁵⁷ Gd	15.65	3/2			
¹⁵⁸ Gd	24.84	0			
¹⁶⁰ Gd	21.86	0			

show a number of peaks in a small mass range displaying the isotopic distribution, demonstrating that they arise from a metal-containing ion.

Figure 1.5 shows a small region of the mass spectra of the Gd and Tb complexes of the same Schiff base ligand. The single prominent peak with $m/z = 485$ in the spectrum of the terbium-containing species is due to the ion containing the only terbium isotope, ¹⁵⁹Tb. The strongest peak in this region of the spectrum of the gadolinium-containing analogue, with $m/z = 484$, is due to the ion containing the most abundant Gd isotope, ¹⁵⁸Gd; the other prominent peaks with masses 481–483 and 486, are due to ions with the same formula, which contain the relatively abundant isotopes ^{155–157}Gd and ¹⁶⁰Gd.

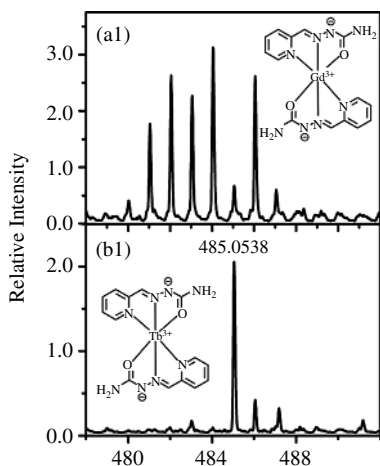


Figure 1.5 Extracts from the mass spectra of Schiff base complexes of gadolinium and terbium. Reproduced by permission of Elsevier from R. N. Soek et al., *J. Mol. Struct.*, 2019, 1184, 254–261.

The rare earth composition of groundwaters varies from place to place. Rare earths present in groundwater can get incorporated into bones as they are fossilised, so that the rare earth ‘signature’ of a fossil can be matched with the location from which it was removed, making it possible to track the source of pilfered fossils. Geologists are starting to use isotope variations of an element as tools. When human remains were found in the same stratigraphic levels in Florida as animals like mammoths, and carbon dating did not provide the answers, rare earth analysis showed that the remains of the humans and late Pleistocene mammals were laid down at the same time, around 12 000 years ago.

Question 1.1 Using the information you have been given in Section 1.2, draw up a table comparing (in three columns) the characteristic features of the s-block metals (use group 1 as typical) and the d-block transition metals.

Answer 1.1 See Table 1.3 for one such comparison.