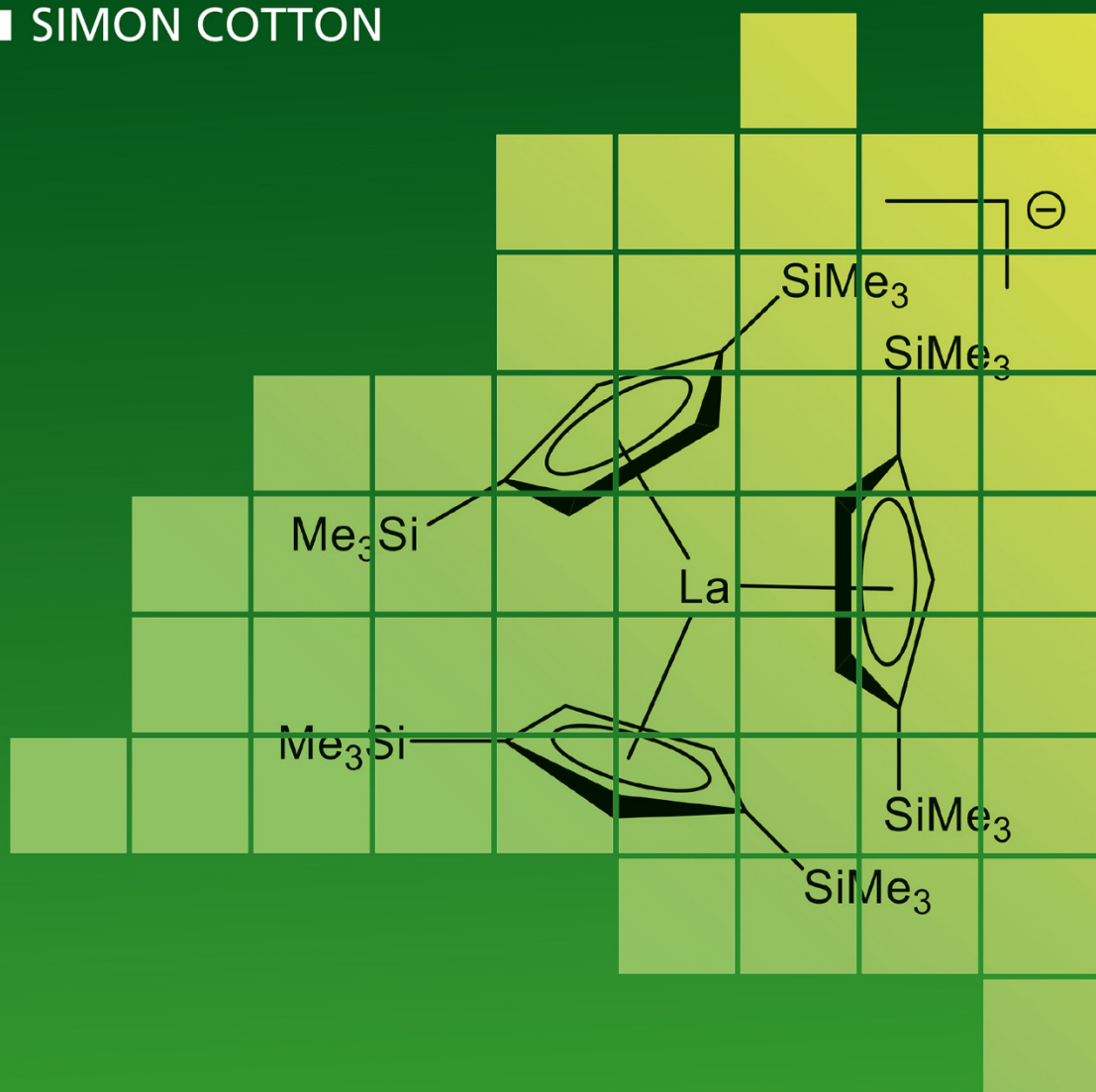


■ SIMON COTTON



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Lanthanide and Actinide Chemistry

Second Edition

Simon Cotton
University of Birmingham, UK

WILEY

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*In memory of Ray and Derek Cotton, my parents.
Remember that it was of your parents you were born;
how can you repay what they have given to you?
(Ecclesiasticus 7.28 RSV)
also in memory of María de los Ángeles Santiago Hernández,
a lovely lady and devout Catholic, who died far too young.
and to Lisa.*

Second edition.

In memory of Frank Alan Hart (1929–2022)

Contents

About the Author	<i>xiii</i>
Preface to the Second Edition	<i>xiv</i>
Preface to the First Edition	<i>xv</i>
About the Companion Website	<i>xvi</i>
1 Introduction to the Lanthanides	1
1.1 Introduction	1
1.2 Characteristics of the Lanthanides	2
1.3 Occurrence and Abundance of the Lanthanides	2
1.4 Lanthanide Ores	3
1.5 Extracting and Separating the Lanthanides	5
1.5.1 Extraction	5
1.5.2 Separating the Lanthanides	5
1.6 The Position of the Lanthanides in the Periodic Table	8
1.7 The Lanthanide Contraction	8
1.8 Recycling Lanthanides	8
1.9 Isotopes	9
2 The Lanthanides – Principles and Energetics	13
2.1 Electron Configurations of the Lanthanides and f Orbitals	13
2.2 What Do f Orbitals Look Like?	14
2.3 How f Orbitals Affect Properties of the Lanthanides	15
2.4 The Lanthanide Contraction	16
2.5 Electron Configurations of the Lanthanide Elements and of Common Ions	16
2.6 Patterns in Ionization Energies	17
2.7 Atomic and Ionic Radii	18
2.8 Patterns in Hydration Energies (Enthalpies) for the Lanthanide Ions	19
2.9 Enthalpy Changes for the Formation of Simple Lanthanide Compounds	20
2.9.1 Stability of Tetrahalides	20
2.9.2 Stability of Dihalides	22
2.9.3 Stability of Aqua Ions	23
2.10 Patterns in Redox Potentials	24
3 The Lanthanide Elements and Simple Binary Compounds	28
3.1 Introduction	28
3.2 The Elements	28
3.2.1 Properties	28
3.2.2 Synthesis	29

3.2.3	Alloys and Uses of the Metals	30
3.3	Binary Compounds	30
3.3.1	Trihalides	30
3.3.2	Tetrahalides	32
3.3.3	Dihalides	32
3.3.4	Oxides	34
3.4	Borides	36
3.5	Carbides	36
3.6	Nitrides	37
3.7	Hydrides	37
3.8	Sulfides	37
4	Coordination Chemistry of the Lanthanides	40
4.1	Introduction	40
4.2	Stability of Complexes	40
4.3	Complexes	42
4.3.1	The Aqua Ions	42
4.3.2	Hydrated Salts	43
4.3.3	Other O-Donors	44
4.3.4	Complexes of β -Diketonates	46
4.3.5	Lewis Base Adducts of β -Diketonate Complexes	47
4.3.6	Nitrate and Carbonate Complexes	47
4.3.7	Crown Ether Complexes	48
4.3.8	Complexes of EDTA and Related Ligands	49
4.3.9	Complexes of N-Donors	50
4.3.10	Complexes of Porphyrins and Related Systems	51
4.3.11	Halide Complexes	52
4.3.12	Complexes of S-Donors	52
4.4	Alkoxides, Alkylamides, and Related Substances	53
4.4.1	Alkylamides	53
4.4.2	Alkoxides	54
4.4.3	Thiolates	56
4.4.4	Borohydrides	57
4.5	Coordination Numbers in Lanthanide Complexes	57
4.5.1	General Principles	57
4.5.2	Examples of the Coordination Numbers	58
4.5.3	The Lanthanide Contraction and Coordination Numbers	60
4.5.4	Formulae and Coordination Numbers	63
4.6	The Coordination Chemistry of the +2 and +4 States	63
4.6.1	The (+2) State	63
4.6.2	The (+4) State	66
4.7	Lanthanides in Living Systems	69
5	Electronic and Magnetic Properties of the Lanthanides	76
5.1	Magnetic and Spectroscopic Properties of the Ln^{3+} Ions	76
5.2	Magnetic Properties of the Ln^{3+} Ions	77
5.2.1	Adiabatic Demagnetization	79
5.2.2	Single Molecule Magnets (SMMs) and Single Ion Magnets (SIMs)	80
5.3	Energy-Level Diagrams for the Lanthanide Ions, and Their Electronic Spectra	84
5.3.1	Electronic Spectra	84

5.3.2	Hypersensitive Transitions	86
5.4	Luminescence Spectra	87
5.4.1	Quenching	92
5.4.2	Antenna Effects	92
5.4.3	Lanthanides in Upconversion	93
5.4.4	Applications of Luminescence to Sensory Probes	95
5.4.4.1	Terbium Luminescence to Detect Anthrax	97
5.4.4.2	Fingerprint Detection	97
5.4.5	Fluorescence and TV	98
5.4.6	Lighting Applications	99
5.4.7	Lasers	99
5.4.8	Euro Banknotes	100
5.5	NMR Applications	100
5.5.1	β -Diketonates as NMR Shift Reagents	100
5.5.2	Magnetic Resonance Imaging (MRI)	102
5.5.3	What Makes a Good MRI Agent?	102
5.5.4	Health Issues with MRI Agents	104
5.5.5	Texaphyrins	104
5.6	Electron Paramagnetic Resonance Spectroscopy	105
5.7	Lanthanides as Probes in Biological Systems	105
6	Organometallic Chemistry of the Lanthanides	110
6.1	Introduction	110
6.2	The +3 Oxidation State	110
6.2.1	Alkyls	111
6.2.2	Aryls	112
6.3	Cyclopentadienyls	113
6.3.1	Compounds of the Unsubstituted Cyclopentadienyl Ligand ($C_5H_5 = Cp$; $C_5Me_5 = Cp^*$)	113
6.3.2	Compounds $[LnCp^*_3]$ ($Cp^* =$ Pentamethylcyclopentadienyl)	116
6.3.3	Bis(cyclopentadienyl) Alkyls and Aryls $LnCp_2R$	117
6.3.4	Bis(pentamethylcyclopentadienyl) Alkyls	118
6.3.5	Hydride Complexes	121
6.4	Cyclooctatetraene Dianion Complexes	121
6.5	The +2 State	122
6.5.1	Alkyls and Aryls	122
6.5.2	Cyclopentadienyls	123
6.5.3	Other Compounds	126
6.6	The +4 State	126
6.7	Metal–Arene Complexes	128
6.8	Carbonyls	129
6.9	Compounds with Lanthanide–Metal Bonds	129
7	The Misfits: Scandium, Yttrium, and Promethium	134
7.1	Introduction	134
7.2	Scandium	134
7.2.1	Binary Compounds of Scandium	135
7.3	Coordination Compounds of Scandium	136
7.3.1	The Aqua Ion and Hydrated Salts	136
7.3.2	Other Complexes	137

- 7.3.3 Alkoxides and Alkylamides 139
- 7.3.4 Patterns in Coordination Number 140
- 7.3.5 Scandium and Yttrium in the (+2) State 144
- 7.4 Organometallic Compounds of Scandium 145
- 7.5 Yttrium 148
- 7.6 Promethium 149

- 8 Introduction to the Actinides 154**
- 8.1 Introduction and Occurrence of the Actinides 154
- 8.2 Synthesis 155
- 8.3 Extraction of Th, Pa, and U 157
- 8.3.1 Extraction of Thorium 157
- 8.3.2 Extraction of Protactinium 157
- 8.3.3 Extraction and Purification of Uranium 157
- 8.3.4 Uranium Extraction from Seawater 157
- 8.4 Uranium Isotope Separation 159
- 8.4.1 Gaseous Diffusion 159
- 8.4.2 Gas Centrifuge 160
- 8.4.3 Electromagnetic Separation 160
- 8.4.4 Laser Separation 160
- 8.5 Characteristics of the Actinides 160
- 8.6 Reduction Potentials of the Actinides 162
- 8.7 Relativistic Effects 163

- 9 Binary Compounds of the Actinides 165**
- 9.1 Introduction 165
- 9.2 Halides 165
- 9.2.1 Syntheses of the Halides 167
- 9.2.2 Structure Types 168
- 9.3 Thorium Halides 170
- 9.4 Uranium Halides 170
- 9.4.1 Uranium(VI) Compounds 170
- 9.4.2 Uranium(V) Compounds 172
- 9.4.3 Uranium(IV) Compounds 172
- 9.4.4 Uranium(III) Compounds 173
- 9.4.5 Uranium Hexafluoride and Isotope Separation 173
- 9.5 Actinide Halides (Ac–Am) Excluding U and Th 175
- 9.5.1 Actinium 175
- 9.5.2 Protactinium 175
- 9.5.3 Neptunium 176
- 9.5.4 Plutonium 177
- 9.5.5 Americium 177
- 9.6 Halides of the Heavier Transactinides 178
- 9.6.1 Curium(III) Chloride 178
- 9.6.2 Californium(III) Chloride, Californium(III) Iodide, and Californium(II) Iodide 178
- 9.6.3 Einsteinium(II) Chloride 179
- 9.7 Oxides 179
- 9.7.1 Thorium Oxide 179
- 9.7.2 Uranium Oxides 180
- 9.7.3 Plutonium Oxides 180

9.8	Sulfides	180
9.9	Uranium Hydride UH_3	181
9.10	Oxyhalides	181
10	Coordination Chemistry of the Actinides	184
10.1	Introduction	184
10.2	General Patterns in the Coordination Chemistry of the Actinides	185
10.3	Coordination Numbers in Actinide Complexes	185
10.4	Types of Complex Formed	187
10.5	Uranium and Thorium Chemistry	187
10.5.1	Uranyl Complexes	187
10.5.2	Coordination Numbers and Geometries in Uranyl Complexes	190
10.5.3	Some Other Complexes	192
10.5.4	Uranyl Nitrate and Its Complexes; Their Role in Processing Nuclear Waste	193
10.5.5	Nuclear Waste Processing	193
10.5.6	Uranium Oxo Complexes	194
10.5.7	Uranium Nitrido Complexes	195
10.5.8	Uranium(V) Complexes	196
10.5.9	Uranium(III) Complexes	197
10.5.10	Uranium(II) Complexes	198
10.6	Complexes of the Actinide(IV) Nitrates and Halides	199
10.6.1	Thorium Nitrate Complexes	199
10.6.2	Uranium(IV) Nitrate Complexes	200
10.6.3	Complexes of the Actinide(IV) Halides	200
10.7	Thiocyanates	202
10.8	Amides, Alkoxides, and Thiolates	203
10.8.1	Amide Chemistry	203
10.8.2	Alkoxides and Aryloxides	207
10.8.3	Borohydrides	209
10.8.4	Uranium Chelate Compounds	209
10.9	Chemistry of Actinium	210
10.10	Chemistry of Protactinium	211
10.11	Chemistry of Neptunium	212
10.11.1	Complexes of Neptunium	213
10.12	Chemistry of Plutonium	214
10.12.1	Aqueous Chemistry	214
10.12.2	Stability of the Oxidation States of Plutonium	215
10.12.3	Coordination Chemistry of Plutonium	216
10.12.4	Plutonium in the Environment	218
10.13	Chemistry of Americium and Subsequent Actinides	220
10.13.1	Potentials	220
10.14	Chemistry of the Later Actinides	222
11	Electronic and Magnetic Properties of the Actinides	228
11.1	Introduction	228
11.2	Absorption Spectra	229
11.2.1	Uranium(VI) – UO_2^{2+} – f^0	229
11.2.2	Uranium(V) – f^1	230
11.2.3	Uranium(IV) – f^2	230

11.2.4	Spectra of the Later Actinides	233
11.3	Magnetic Properties	234
11.3.1	Uranium Single Molecule Magnets	236
12	Organometallic Chemistry of the Actinides	238
12.1	Introduction	238
12.2	Simple σ -Bonded Organometallics	238
12.3	Cyclopentadienyls	242
12.3.1	Oxidation State (VI)	242
12.3.2	Oxidation State (V)	242
12.3.3	Oxidation State (IV)	242
12.3.4	Oxidation State (III)	245
12.4	Compounds of the Pentamethylcyclopentadienyl Ligand ($C_5Me_5 = Cp^*$)	246
12.4.1	Oxidation State (IV)	246
12.4.2	Cationic Species and Catalysts	247
12.4.3	Hydrides	248
12.4.4	Oxidation State (III)	249
12.4.5	Oxidation State (II)	249
12.4.6	Some Recent Chemistry of Neptunium and Plutonium	251
12.5	Tris(pentamethylcyclopentadienyl) Systems	252
12.6	Other Metallacycles	252
12.7	Cyclooctatetraene Dianion Compounds	253
12.8	Arene Complexes	254
12.8.1	Simple Arene Derivatives	254
12.8.2	Arene-Supported Triazacyclononane Derivatives	254
12.9	Carbonyls	256
12.10	Compounds with Actinide-metal Bonds	257
13	Synthesis of the Transactinides and Their Chemistry	260
13.1	Introduction	260
13.2	Finding New Elements	261
13.3	Synthesis of the Transactinides	261
13.4	Naming the Transactinides	265
13.5	Predicting Electronic Arrangements	266
13.6	Identifying the Elements	266
13.7	Predicting Chemistry of the Transactinides	272
13.8	What Is Known about the Chemistry of the Transactinides	273
13.8.1	Element 104	273
13.8.2	Element 105	273
13.8.3	Element 106	274
13.8.4	Element 107	274
13.8.5	Element 108	274
13.8.6	Elements 112 and 114	276
13.9	And the Future?	276
	References	278
	Index	310

About the Author

Dr Simon Cotton obtained his PhD at Imperial College London (1970). After postdoctoral research and teaching appointments at Queen Mary College, London, and the University of East Anglia, he taught chemistry in several different schools, last at Uppingham School from 1996 to 2009. From 2011 to 2016 he taught inorganic and organic chemistry at the University of Birmingham (UK), from which he retired as an honorary Senior Lecturer.

From 1984 until 1997, he was Editor of Lanthanide and Actinide Compounds for the *Dictionary of Organometallic Compounds* and the *Dictionary of Inorganic Compounds*. He authored the account of Lanthanide Coordination Chemistry for the 2nd edition of *Comprehensive Coordination Chemistry* (Pergamon) as well as the accounts of Lanthanide Inorganic and Coordination Chemistry for both the 1st and 2nd editions of the *Encyclopedia of Inorganic Chemistry* (Wiley).

His other books are:

- S. A. Cotton and F. A. Hart, “*The Heavy Transition Elements*”, Macmillan, 1975.
- D. J. Cardin, S. A. Cotton, M. Green and J. A. Labinger, “*Organometallic Compounds of the Lanthanides, Actinides and Early Transition Metals*”, Chapman and Hall, 1985.
- S. A. Cotton, “*Lanthanides and Actinides*”, Macmillan, 1991.
- S. A. Cotton, “*Chemistry of Precious Metals*”, Blackie, 1997.
- S. A. Cotton, “*Every Molecule Tells A Story*”, CRC Press, 2012.
- P. W. May and S. A. Cotton, “*Molecules That Amaze Us*”, CRC Press, 2015.
- S. A. Cotton, “*Building the Late-Mediaeval Suffolk Parish Church*”, SIAH, 2019.

Preface to the Second Edition

In the period since the first edition was written, much has happened in the field of the f-block elements, with new areas developing and massive advances in more established fields. I have tried to reflect that in these pages. Demands on space have meant that I have omitted the section on lanthanides in organic chemistry that appeared in the first edition. On the other hand, the bibliography has been greatly expanded, which I hope will be of use to readers. I am most grateful to all who have helped me produce this edition, particularly the patient Sarah Higginbotham.

This edition is dedicated to the memory of Alan Hart (1929–2022). It is over 30 years since he retired as Reader in Inorganic Chemistry at Queen Mary College, London, and many readers will wonder who he was. Alan was a pioneer in rare earth chemistry, one of his achievements being to demonstrate that these elements regularly had coordination numbers considerably greater than six in their compounds. He led the early studies into lanthanide shift reagents; simultaneously two of his researchers made the first three- and four- coordinate compounds of the lanthanides. The present writer had the opportunity to share with him in the writing of the text *The Heavy Transition Elements* (1975); it was a privilege to work for this modest and self-effacing man, who was the antithesis of ‘celebrity’.

Simon Cotton
University of Birmingham, UK

Preface to the First Edition

This book is aimed at providing a sound introduction to the chemistry of the lanthanides, actinides, and transactinides to undergraduate students. I hope that it will also be of value to teachers of these courses. Whilst not being anything resembling a comprehensive monograph, it does attempt to give a factual basis to the area, and the reader can use a fairly comprehensive bibliography to range further.

Since I wrote a previous book in this area (1991), the reader may wonder why on earth I have bothered again. The world of f-block chemistry has moved on. It is one of active and important research, with names like Bünzli, Evans, Ephritikhine, Lappert, Marks and Parker familiar worldwide (I am conscious that I will have unintentionally omitted names). Not only have several more elements been synthesized (and claims made for others), but lanthanides and their compounds are routinely employed in many areas of synthetic organic chemistry; gadolinium compounds find routine application in MRI scans; and there are other spectroscopic applications, notably in luminescence. Whilst some areas are hardly changed, at this level at least (e.g. actinide magnetism and spectroscopy), a lot more compounds have been described, accounting for the length of the chapters on coordination and organometallic chemistry. I have tried to spell out the energetics of lanthanide chemistry in more detail, and I have also provided some end-of-chapter questions, of variable difficulty, which may prove useful for tutorials. I have supplied most, but not all, of the answers to these in the second edition. (my answers, which are not always definitive).

It is a pleasure to thank all those who have contributed to the book: Professor Derek Woollins, for much encouragement at different stages of the project; Professor James Anderson, for many valuable comments; Martyn Berry, who supplied valuable comment on early versions of several chapters; to Professors Michel Ephritikhine, Allan White and Jack Harrowfield, and Dr J.A.G. Williams, and many others, for exchanging e-mails, correspondence and ideas. I'm very grateful to Dr Mary P. Neu for much information on plutonium. The staff of the Libraries of the Chemistry Department of Cambridge University and of the Royal Society of Chemistry, as well as the British Library, have been quite indispensable in helping with access to the primary literature. I would also wish to thank a number of friends – once again Dr Alan Hart, who got me interested in lanthanides in the first place; Professor James Anderson (again), Dr Andrew Platt, Dr John Fawcett, and Professor Paul Raithby, for continued research collaboration and obtaining spectra and structures from unpromising crystals, so that I have kept a toe-hold in the area. Over the last eight years, a number of Uppingham sixth form students have contributed to my efforts in lanthanide coordination chemistry – John Bower, Oliver Noy, Rachel How, Vilius Franckevicius, Leon Catallo, Franz Niecknig, Victoria Fisher, Alex Tait, and Joanna Harris. Finally, thanks are most certainly due to Dom Paul-Emmanuel Clénet and the Benedictine community of the Abbey of Bec, for continued hospitality during several Augusts when I have been compiling the book.

Simon Cotton

About the Companion Website

This book is accompanied by a companion website:

www.wiley.com/go/lanthanideandactinidechemistry2e



This website includes:

- Extended Bibliography

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): Bastnäsite 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 bastnäsité. 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.

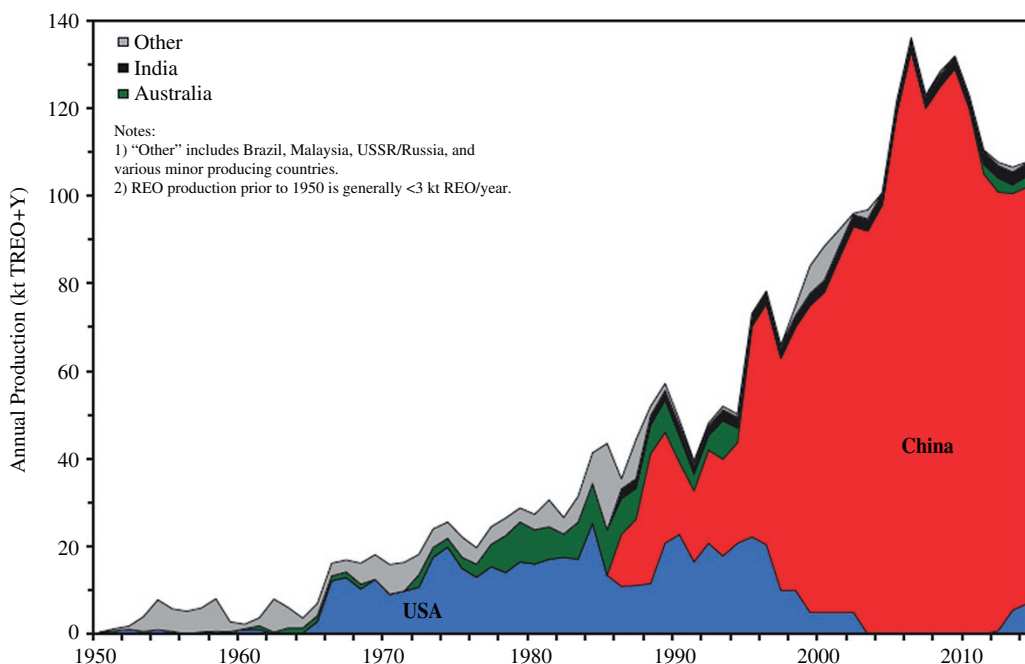


Figure 1.1 Production of total rare earth oxides plus yttrium oxide, 1950–2015, split by country. Reproduced with permission from: Z. Weng, S. M. Jowitt, G. M. Mudd, and N. Haque, *Economic Geology*, 2015, 110, 1925–1952.

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

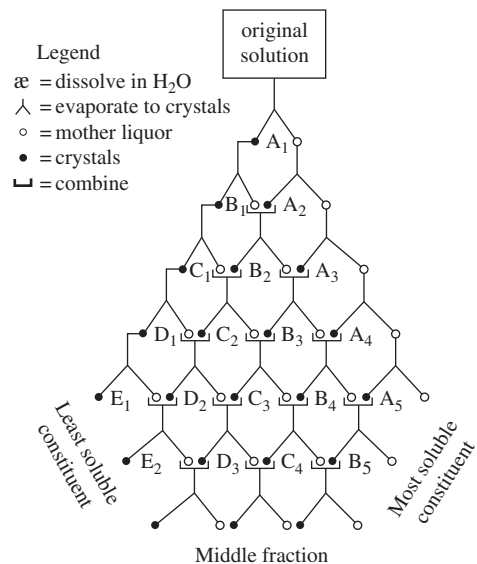


Figure 1.2 Representation of the system of fractional crystallization used to separate salts of the rare-earth elements (reproduced with permission from D.M. Yost, H. Russell, and C.S. Garner, *The Rare Earth Elements and Their Compounds*, John Wiley, 1947.)

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.

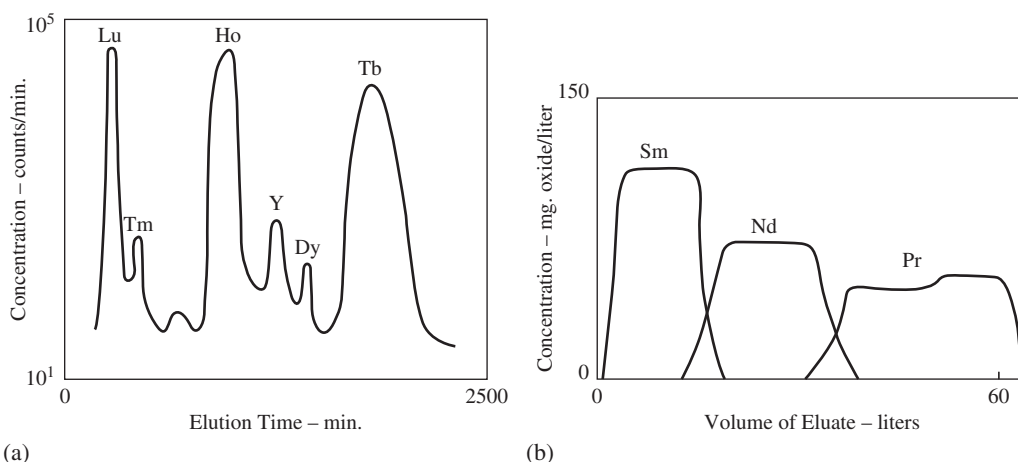


Figure 1.3 (a) Cation-exchange chromatography of lanthanides, (b) overlap of peaks at high concentration. (a) Tracer-scale elution with 5% citrate at pH 3.20 (Adapted from B.H. Ketell et al., 1947). (b) Macro-scale elution with 0.1% citrate at pH 5.30. Reproduced with permission of F.H. Spedding et al.,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

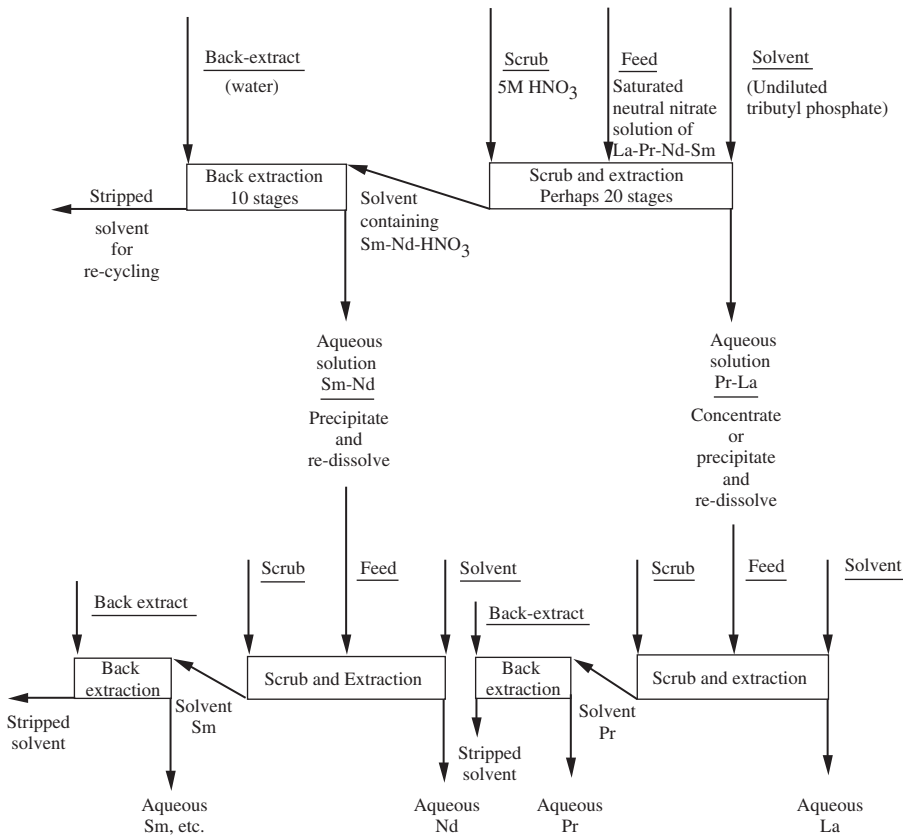


Figure 1.4 Schematic diagram of lanthanide separation by solvent extraction. Reproduced with permission of R.J. Callow, 1966 / Elsevier.

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 $[(2\text{-}^t\text{BuNO})\text{C}_6\text{H}_4\text{CH}_2)_3\text{N}]^{3-}$ (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 (%)	I		Abundance (%)	I
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.

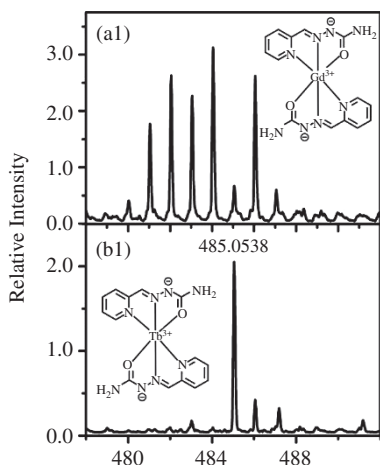


Figure 1.5 Extracts from the mass spectra of Schiff base complexes of gadolinium and terbium. Reproduced by permission of Elsevier from R. N. Soek et al., *J. Mol. Struct.*, 2019, 1184, 254–261.

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.