

Lanthanide and Actinide Chemistry

Second Edition

Simon Cotton
University of Birmingham, UK

WILEY

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