

Contents

<i>Preface</i>	vii
<i>About the Editors</i>	ix
<i>Acknowledgements</i>	xi
<i>List of Abbreviations</i>	xxi
1. The Chemistry of Rare-Earth Metals	1
<i>Thomas Behrsing, Glen B. Deacon, and Peter Junk</i>	
1.1 Introduction: The Rare-Earth Elements	1
1.2 General Properties	3
1.3 Discovery, Location and Abundance of Rare Earths	7
1.4 Uses of the Rare Earths	12
1.5 General Chemistry Properties of Rare-Earth Elements and Compounds	17
References	30
2. The Chemistry of the Actinides	37
<i>Robert J. Baker</i>	
2.1 Discovery and Synthesis of the Actinide Elements	37
2.2 Occurrence and Extraction	50
2.3 Periodicity, Electronic Configuration and Oxidation States	53
2.4 Structure and Bonding	64
References	72

3.	Solid-State Chemistry: Synthesis and Structural Diversity in Lanthanide and Actinide Complexes	79
	<i>Matthew L. Marsh, Frankie D. White, Wesley M. Potter, and Thomas E. Albrecht-Schoenartz</i>	
3.1	Introduction	79
3.2	Intermetallics, Oxides and Hydroxides	81
3.3	Halides	87
3.4	Oxyanions	95
3.5	Summary	112
	References	112
4.	Coordination Chemistry of Lanthanides	119
	<i>Yaofeng Chen</i>	
4.1	Introduction	119
4.2	Coordination Numbers	120
4.3	Complexes	121
	References	140
5.	Coordination Chemistry of Actinides	149
	<i>Grégory Nocton and Marinella Mazzanti</i>	
5.1	Introduction	149
5.2	Aqua Ions	151
5.3	Common Precursors	152
5.4	Uranyl(VI) Complexes	157
5.5	Actinyl(V) and Cation–Cation Interactions	162
5.6	Non-Actinyl Complexes of Actinides in High Oxidation State (VI and V)	169
5.7	Complexes of An ^{II} , An ^{III} and An ^{IV}	172
5.8	Actinide Complexes Containing Multiply Bonded Atoms	188
5.9	Conclusions	199
	References	201
6.	Organometallic Chemistry of Lanthanides	209
	<i>Wenliang Huang and Paula L. Diaconescu</i>	
6.1	Introduction	209

6.2	Organometallic Chemistry of Lanthanide Ions in Unconventional Oxidation States	212
6.3	Lanthanide Complexes Containing Ln-C σ -Bonds	222
6.4	Lanthanide π -Complexes Containing Carbocyclic and Acyclic π -Ligands	241
6.5	Lanthanide Carbene Complexes	266
6.6	Summary and Outlook for the Organometallic Chemistry of Lanthanides	293
	References	295
7.	Organoactinide Chemistry	311
	<i>David J. H. Emslie, Nicholas R. Andreychuk, and Carlos A. Cruz</i>	
7.1	Introduction	311
7.2	Anhydrous Halide, Triflate, Amido and Aryloxy Starting Materials	313
7.3	Homoleptic Hydride, Borohydride, Aluminohydride, and Aminodiboronate Complexes and Their Lewis Base Adducts	316
7.4	Homoleptic Acyclic Hydrocarbyl Compounds and Their Lewis Base Adducts	320
7.5	Ligand Attachment Protocols for the Synthesis of Heteroleptic Compounds	324
7.6	Cyclopentadienyl Actinide Complexes	332
7.7	Organoactinide Complexes Bearing Non-Cyclopentadienyl π -Ligands	355
7.8	Neutral and Anionic Non-Cyclopentadienyl Hydrocarbyl Complexes	391
7.9	Neutral and Anionic Hydride Complexes	398
7.10	Cationic Alkyl and Related Complexes	404
7.11	Carbene Complexes	409
7.12	Cyanide, Carbonyl and Isonitrile Compounds	413
7.13	Agostic Interactions and Metal-Alkane Coordination	414
	References	416
8.	Small Molecule Activation by Lanthanide Complexes	441
	<i>Conrad A. P. Goodwin and David P. Mills</i>	

8.1	Introduction and Scope of the Review	441
8.2	CO Reactivity	443
8.3	CO ₂ /CS ₂ /COS Reactivity	447
8.4	CH ₄ Reactivity	452
8.5	N ₂ Reactivity	454
8.6	NO _x Reactivity	459
8.7	RN ₃ Reactivity	461
8.8	Ce(IV) Reactivity	463
8.9	Summary	464
	References	465
9.	Small Molecule Activation by Actinide Complexes	471
	<i>Christopher Hoerger and Karsten Meyer</i>	
9.1	Introduction and Scope of the Review	471
9.2	Carbon Monoxide	472
9.3	Carbon Dioxide	477
9.4	Nitric and Nitrous Oxide	480
9.5	Dinitrogen	483
9.6	Water	485
9.7	Azides	486
	References	488
10.	Modern Applications of the Actinides in Catalysis	495
	<i>Rami J. Batrice, Isabell S. R. Karmel, Guy Yardeni, and Moris S. Eisen</i>	
10.1	General	495
10.2	Introduction	496
10.3	Catalytic Reactions of Alkynes	497
10.4	Catalytic Synthesis of Esters from Aldehydes	514
10.5	Catalytic Addition of Protic Nucleophiles to Heterocumulenes	519
10.6	Dehydrocoupling of Silanes and Amines	522
10.7	Uranium-Catalyzed Reduction of Azides and Hydrazines	524
10.8	Other Catalytic Reactions	525
10.9	Actinide-Catalyzed Polymerization Reactions	529

10.10	Uranium-Catalyzed Electrocatalytic Production of Dihydrogen from Water and Coupling of Carbon Monoxide	538
10.11	Reductive Homologation and Functionalization of Carbon Monoxide	539
10.12	Conclusions	540
	Acknowledgments	540
	References	541
11.	Computational Aspects of f-Element Chemistry	549
	<i>Andrew Kerridge</i>	
11.1	Introduction	549
11.2	Simulation Methodologies	550
11.3	Summary and Outlook	569
	References	570
12.	Spectroscopy of the Actinides	575
	<i>Yvonne Rechkemmer and Joris van Slageren</i>	
12.1	General	575
12.2	EXAFS	578
12.3	XANES	579
12.4	XMD	580
12.5	High Resolution X-ray Absorption, High-Energy-Resolution Fluorescence-Detection X-ray Absorption Spectroscopy and Resonant Inelastic X-ray Scattering Spectroscopy	580
12.6	XPS	582
	References	583
13.	Electronic Spectroscopy on Non-Metallic Actinide Systems	587
	<i>Yvonne Rechkemmer and Joris van Slageren</i>	
13.1	Methods	587
13.2	Types of Transitions and Comparison to Lanthanide Systems	588
13.3	Actinyl Compounds and Related Systems	591
	References	599

14.	Vibrational Spectroscopy of Non-Metallic Actinide Compounds	603
	<i>Yvonne Rechkemmer and Joris van Slageren</i>	
14.1	General	603
	References	607
15.	Electron Paramagnetic Resonance of Non-Metallic Actinide Systems	609
	<i>Yvonne Rechkemmer and Joris van Slageren</i>	
15.1	General	609
	References	615
16.	Nuclear Magnetic Resonance of Actinides	617
	<i>Peter Kaden</i>	
16.1	Introduction	617
16.2	NMR Spectroscopy of Actinide Containing Compounds	618
16.3	New Studies of Actinide Complexes	623
16.4	Conclusion and Outlook	628
	References	629
17.	Applications of Rare Earths	633
	<i>Jean-Claude G. Bünzli</i>	
17.1	Rare Earths: The Vitamins of High Technology	633
17.2	Catalysts	642
17.3	Pigments and Additives for Glass, Ceramic and Leather Industries	645
17.4	Magnets	646
17.5	Metallurgy, Alloys and Compounds	650
17.6	Ceramics	652
17.7	Photonics (Phosphors)	653
17.8	Applications in Biosciences	664
17.9	Agriculture and Feed for Livestock	676
17.10	Energy-Related and Futuristic Applications	677
17.11	Summary of Applications per Rare-Earth Element	682

Further Reading	684
References	684
18. Applications of Actinides	687
<i>Jean-Claude G. Bünzli, Louise S. Natrajan, and Mark J. Sarsfield</i>	
18.1 Basic Properties	687
18.2 Applications of Actinides: Summary	688
18.3 Metallurgy and Metals	689
18.4 Photonic Applications	692
18.5 Tracers for Dating	695
18.6 Semi-Conductor Properties	695
18.7 Actinides in Catalysis	696
18.8 Radioactive Sources	697
18.9 Nuclear Power Generation	699
18.10 Nuclear Weapons	703
References	703

Cy	Cyclohexyl
Dipp	2,6-diisopropyl phenyl
DME	1,2-dimethoxyethane
DMP	2,6-diis(Me) phenyl
DMAP	4-dimethylaminopyridine
EXAFS	Extended X-ray absorption fine structure
^t Bu	Isobutyl
ⁱ Pr	Isopropyl
TI	trans 1,2-dichloroethane
LMCT	Ligand to metal charge transfer
Me	Methyl
Me ₃	2,4,6-trimethyl phenyl
Me ^t	2,4,6-triisobutyl phenyl
MO	Molecular orbital
Ph	Phenyl
Phen	1,10-phenanthroline
^t Bu	Tertbutyl
THF	Tetrahydrofuran
Tri ⁱ p	2,4,6-triisopropyl phenyl
XANES	X-ray absorption near edge structure
Xyl	2,6-dimethyl phenyl