

## Contents

Preface *XIII*

List of Contributors *XV*

1	<b>Electronic Structure and Magnetic Properties of Lanthanide Molecular Complexes</b>	1
	<i>Lorenzo Sorace and Dante Gatteschi</i>	
1.1	Introduction	1
1.2	Free Ion Electronic Structure	3
1.2.1	Free Ion Magnetism	6
1.3	Electronic Structure of Lanthanide Ions in a Ligand Field	7
1.3.1	Stevens' Formalism	9
1.3.2	Wybourne's Formalism	9
1.3.3	Standardization	13
1.3.4	Calculation of Crystal Field Parameters	13
1.4	Magnetic Properties of Isolated Lanthanide Ions	16
1.4.1	Effect of a Magnetic Field	16
1.4.2	EPR Spectroscopy of Lanthanide Complexes	17
1.5	Exchange Coupling in Systems Containing Orbitally Degenerate Lanthanides	21
	Acknowledgements	23
	References	23
2	<b>Mononuclear Lanthanide Complexes: Use of the Crystal Field Theory to Design Single-Ion Magnets and Spin Qubits</b>	27
	<i>Juan M. Clemente-Juan, Eugenio Coronado, and Alejandro Gaita-Ariño</i>	
2.1	Introduction	27
2.2	Modelling the Magnetic Properties of Lanthanide Single-Ion Magnets: The Use of the Crystal Field Model	29
2.2.1	Theoretical Background	29

2.2.2	How to Determine the Crystal-Field Parameters: 1. The Ishikawa Approach	30
2.2.3	How to Determine the Crystal-Field Parameters: 2. The Point Charge Electrostatic Model	34
2.2.4	How to Determine the Crystal-Field Parameters: 3. The Effective Point Charge Model	36
2.3	Magneto-Structural Correlations for Some Typical Symmetries	40
2.4	Impact of Lanthanide Complexes in Quantum Computing	44
2.4.1	Quantum Computing Paradigms and Design Criteria	45
2.4.2	Combining Physical Qubit Implementations with Lanthanide Complexes	48
2.4.3	Molecular Spin Qubits	50
2.5	Conclusions	53
	Acknowledgements	54
	References	55
<b>3</b>	<b>Polynuclear Lanthanide Single Molecule Magnets</b>	<b>61</b>
	<i>Jinkui Tang and Peng Zhang</i>	
3.1	Introduction	61
3.2	Synthetic Strategies	62
3.2.1	Dy <sub>3</sub> Triangles and Their Derivatives	64
3.2.1.1	Seminal Dy <sub>3</sub> Triangle	64
3.2.1.2	Other Triangular Dy <sub>3</sub> Systems	65
3.2.1.3	The Coupling of Dy <sub>3</sub> Triangles	68
3.2.2	Linear Polynuclear Lanthanide Complexes Showing Robust SMM Behaviour	71
3.2.2.1	Linear Dy <sub>3</sub> SMMs	72
3.2.2.2	Linear Dy <sub>4</sub> SMMs	73
3.2.3	Planar Dy <sub>4</sub> SMMs	75
3.2.4	Dy <sub>n</sub> SMMs Having Multiple μ <sub>n</sub> -O ( $n > 4$ ) Bridges	78
3.2.4.1	The Dy <sub>4</sub> Grids Fixed by μ <sub>4</sub> -O Atom	78
3.2.4.2	The Dy <sub>4</sub> Tetrahedron Fixed by μ <sub>4</sub> -O Atom	80
3.2.4.3	The Dy <sub>5</sub> Pyramid Fixed by μ <sub>5</sub> -O Atom	80
3.2.5	Hydrazone-Based Lanthanide SMMs	82
3.2.5.1	The Assembly of Dy <sub>6</sub> Triangular Prism with Dy <sub>2</sub> Units	83
3.2.5.2	A Dy <sub>3</sub> Molecular Cluster Pair (Dy <sub>6</sub> )	84
3.2.6	The Organometallic Synthesis — A New Approach	85
3.3	Conclusion	86
	References	86
<b>4</b>	<b>Lanthanides in Extended Molecular Networks</b>	<b>89</b>
	<i>Roberta Sessoli and Kevin Bernot</i>	
4.1	Introduction	89

4.2	Extended Networks Based on Gd <sup>3+</sup>	91
4.2.1	Metal-Organic Frameworks	91
4.2.1.1	Magneto-Caloric Effect	91
4.2.1.2	Slow Magnetic Relaxation and Phonon Bottleneck Effects	94
4.2.2	Magnetic Chains	96
4.2.2.1	Magnetic Interactions Involving Gd <sup>3+</sup> Ions	96
4.2.2.2	Gadolinium-Radical Chains	96
4.3	Extended Networks Based on Anisotropic Ions	101
4.3.1	SCM in a Nutshell	101
4.3.2	An Overview of Monodimensional Lanthanide Chains Based on Anisotropic Ions	104
4.3.2.1	Chains Based on 4f Ions	104
4.3.2.2	Chains Based on 3d–4f Ions	106
4.3.2.3	Chains Based on Radicals and 4f Ions	111
4.3.3	The Key Point of Noncollinearity of Magnetic Anisotropy	112
4.4	Conclusions	119
	References	119
<b>5</b>	<b>Experimental Aspects of Lanthanide Single-Molecule Magnet Physics</b>	<b>125</b>
	<i>Kasper S. Pedersen, Daniel N. Woodruff, Jesper Bendix, and Rodolphe Clérac</i>	
5.1	Introduction	125
5.2	Manifestation of Single-Molecule Magnet Behaviour	127
5.2.1	Magnetization and ac Susceptibility Measurements	127
5.2.2	NMR Spectroscopy	132
5.2.3	Muon Spin Rotation	133
5.3	Quantifying the Magnetic Anisotropy	135
5.4	Splitting of the Ground Multiplet	139
5.4.1	Magnetic Resonance Spectroscopies	139
5.4.2	Luminescence Spectroscopy	140
5.4.3	Inelastic Neutron Scattering	141
5.5	Observation of the Signatures of Exchange Coupling	146
5.5.1	Chemical Substitution	146
5.5.2	X-Ray Magnetic Circular Dichroism	147
5.6	Concluding Remarks and Perspectives	149
	References	150
<b>6</b>	<b>Computational Modelling of the Magnetic Properties of Lanthanide Compounds</b>	<b>153</b>
	<i>Liviu Ungur and Liviu F. Chibotaru</i>	
6.1	Introduction	153
6.2	<i>Ab Initio</i> Description of Lanthanides and its Relation to Other Methods	153

6.2.1	<i>Ab Initio</i> Approach for the Electronic Structure of Lanthanides	155
6.2.1.1	Accounting for <i>Static</i> Electron Correlation within CASSCF	155
6.2.1.2	Accounting for Dynamical Electron Correlation: An Important Step Towards Accurate Predictions	155
6.2.1.3	Accounting for Relativistic Effects within the Douglas–Kroll–Hess Theory	156
6.2.1.4	Spin–Orbit Multiplets of Free Lanthanide Ions: Relativistic CASSCF/RASSI Method in Work	157
6.2.2	<i>Ab Initio</i> Versus Two-Component DFT	159
6.2.3	<i>Ab Initio</i> Versus Phenomenological Crystal Field Theory for Lanthanides	159
6.3	<i>Ab Initio</i> Calculation of Anisotropic Magnetic Properties of Mononuclear Complexes	160
6.3.1	Implementation of <i>Ab Initio</i> Methodology: SINGLE_ANISO Program	161
6.3.2	Temperature-Dependent Magnetic Susceptibility and Field-Dependent Magnetization	163
6.3.3	Magnetic Anisotropy in Low-Lying Doublets	164
6.3.4	<i>Ab Initio</i> Crystal Field	166
6.4	<i>Ab Initio</i> Calculation of Anisotropic Magnetic Properties of Polynuclear Complexes	169
6.4.1	Two-Step Approach for the Calculation of Electronic Structure of Polynuclear Lanthanide Complexes	170
6.4.2	Key Rules for Cluster Fragmentation	170
6.4.3	Implementation of <i>Ab Initio</i> Methodology: POLY_ANISO Program	171
6.4.4	Noncollinear Magnetic Structure of $\text{Ln}_n$ Complexes	172
6.4.5	Mixed Lanthanide–Transition Metal Compounds	176
6.4.6	Lanthanide-Containing Magnetic Chains	178
6.5	Conclusions	180
	References	181
7	<b>Lanthanide Complexes as Realizations of Qubits and Qugates for Quantum Computing</b>	185
	<i>Guillem Aromí, Fernando Luis, and Olivier Roubeau</i>	
7.1	Introduction to Quantum Computation	185
7.1.1	General Introduction	185
7.1.2	Definition of Qubits, Qugates, Timescales and Essential Requirements	186
7.1.3	Current Proposals for the QC Hardware	189
7.1.3.1	Trapped Ions	189
7.1.3.2	Nuclear Spins	190
7.1.3.3	Superconducting Qubits	191

7.1.3.4	Spin Qubits	191
7.1.3.5	Photons	191
7.1.3.6	Hybrid Proposals and Quantum Circuits	192
7.2	Quantum Computing with Electron Spin Qubits	192
7.2.1	Electronic Spins in Semiconductors: QDs and Dopants	192
7.2.1.1	Quantum Dots	193
7.2.1.2	Dopants and Defects	193
7.2.2	Electronic Spins in Molecules: Organic Radicals and Transition Metal Complexes	194
7.2.2.1	Organic Radicals	194
7.2.2.2	Transition Metal Complexes	195
7.3	Single Lanthanide Ions as Spin Qubits	197
7.3.1	Quantum Coherence of Lanthanide Ions Doped into Crystalline Solids	198
7.3.2	Control of the Magnetic Anisotropy of Lanthanide Ions: Chemical Design of Spin Qubits	199
7.3.2.1	Mononuclear Single Molecule Magnets	199
7.3.2.2	Gadolinium(III) POMs as Spin Qubits	200
7.3.2.3	Mononuclear SMMs of Ln(III) Ions with Nonzero Orbital Moment	202
7.4	Lanthanide Molecules as Prototypes of Two-Qubit Quantum Gates	204
7.4.1	A Family of Asymmetric [Ln <sub>2</sub> ] Complexes with Weak Magnetic Coupling	204
7.4.2	Heterometallic [LnLn'] Complexes: A Fabric of Chemical Asymmetry and Individual Qubits	208
7.4.3	Evaluating Qubit Properties	209
7.4.4	Weak Coupling	211
7.4.5	Asymmetry and Energy Diagrams	212
7.4.6	Decoherence of the Molecular Quantum Processor Prototypes	215
7.5	Conclusions and Outlook	215
	References	216
<b>8</b>	<b>Bis(phthalocyaninato) Lanthanide(III) Complexes – from Molecular Magnetism to Spintronic Devices</b>	<b>223</b>
	<i>Yanhua Lan, Svetlana Klyatskaya, and Mario Ruben</i>	
8.1	Introduction	223
8.1.1	Molecular Magnetism	223
8.1.2	Multinuclear Versus Mononuclear: d- Versus f-Metal Ions	224
8.1.3	Molecular Versus Organic Spintronics	227
8.2	Synthesis and Structure of LnPc <sub>2</sub> Complexes	229
8.2.1	Synthesis of Bis(phthalocyaninato) Lanthanide(III) Complexes	229

8.2.2	Synthesis of Heteroleptic Lanthanide(III) Complexes Containing Porphyrin-Based Ligands	235
8.2.3	Oxidation States of Bis(phthalocyaninato) Lanthanide(III) Complexes	239
8.2.4	Rotation Angles and Skew Angles in $\text{LnPc}_2$ in Relation to the Lanthanide Contraction	243
8.3	Bulk Magnetism of $\text{LnPc}_2$ Complexes	246
8.3.1	Magnetism of Bis(phthalocyaninato) Lanthanide(III) Complexes	246
8.3.2	Three Spin Systems in $[\text{TbPc}_2]^0$ Single-Ion Molecular Magnets (SIMMs)	246
8.3.2.1	The Organic Radical ( $S$ )	246
8.3.2.2	The Electronic Spin ( $J$ )	248
8.3.2.3	The Nuclear Spin ( $I$ )	249
8.3.3	Further SIMs of $\text{LnPc}_2$ with $\text{Ln} = \text{Tb}, \text{Dy}$ and $\text{Ho}$	249
8.3.4	Internal Kondo in $\text{LnPc}_2$ Complexes with $\text{Ln} = \text{Ce}, \text{Yb}$	255
8.3.5	Stable Organic Radicals $S = 1/2$ in $\text{LnPc}_2$ with $\text{Ln} = \text{Y}, \text{Lu}$	257
8.3.6	A Special Case: Half-Filling of the f-Orbitals in $\text{GdPc}_2$ and its Consequences	258
8.4	Surface Magnetism of $\text{LnPc}_2$ Complexes	259
8.4.1	Deposition of $[\text{TbPc}_2]^0$ SIMMs on Nonmagnetic Substrates	261
8.4.1.1	Highly Oriented Pyrolytic Graphite	261
8.4.1.2	$\text{Au}(111)$	262
8.4.1.3	$\text{Cu}(111)$	263
8.4.1.4	$\text{Cu}(100)$	265
8.4.2	Deposition of $[\text{TbPc}_2]^0$ SIMs on Magnetic Substrates	267
8.4.2.1	Nickel Thin Films	267
8.4.2.2	Cobalt Thin Films	269
8.4.2.3	LSMO	269
8.4.2.4	Manganese and Cobalt Oxide Layers	269
8.4.2.5	Spin Polarized Scanning Tunnelling Microscopy (SP-STM) on $\text{Co}/\text{Ir}(111)$	270
8.5	Molecular Spintronic Devices on the Base of $[\text{TbPc}_2]^0$ SIMs	272
8.5.1	Graphene Transistor	274
8.5.2	Supramolecular Spin Valve	276
8.5.3	Molecular Spin Resonator	278
8.5.4	Molecular Spin Transistor	280
8.6	Conclusion and Outlook	281
	Abbreviations	283
	References	284

<b>9</b>	<b>Lanthanides and the Magnetocaloric Effect</b>	293
	<i>Joseph W. Sharples and David Collison</i>	
9.1	Applications of Magnets	293
9.2	Cold Reasoning	294
9.3	Current Technologies	294
9.4	How Paramagnets Act as Refrigerants	295
9.5	More Parameters	297
9.6	Aims	298
9.7	Important Concepts for a Large Magnetocaloric Effect	298
9.7.1	Spin	298
9.7.1.1	Examples	299
9.7.2	Nature of Exchange Coupling	301
9.7.2.1	Paramagnetism	301
9.7.2.2	Ferromagnetism	303
9.7.2.3	Antiferromagnetism	304
9.7.3	Active Metal Percentage	305
9.7.4	Density	307
9.7.5	Anisotropy or Spin: What Kind?	308
9.7.6	Dimensionality	310
9.8	High-Performance MCE Materials	311
9.9	Outlook	312
	References	313
<b>10</b>	<b>Actinide Single-Molecule Magnets</b>	315
	<i>Stephen T. Liddle and Joris van Slageren</i>	
10.1	Introduction	315
10.2	Literature Survey of Published Actinide Single-Molecule Magnets	322
10.2.1	Single-Molecule Magnets of f <sup>3</sup> Actinides (U <sup>3+</sup> , Np <sup>4+</sup> )	322
10.2.2	Single-Molecule Magnets of f <sup>1</sup> Actinides (U <sup>5+</sup> )	330
10.2.3	Miscellaneous: {Np <sup>V</sup> O <sub>2</sub> Cl <sub>2</sub> }•{Np <sup>V</sup> O <sub>2</sub> Cl(THF) <sub>3</sub> } <sub>2</sub> (15)	332
10.3	Magnetic Coupling in Actinides	332
10.3.1	5f–5f Couplings	333
10.3.2	5f–4f Couplings	335
10.3.3	5f–3d Couplings	335
10.3.4	5f–2p Couplings	336
10.4	Conclusions	336
	References	336
	<b>Index</b>	341

