

# Contents

Preface . . . . .	ix
Foreword . . . . .	xi
<b>1 Introduction . . . . .</b>	<b>1</b>
References . . . . .	5
<b>2 Chirality and Enantiomers . . . . .</b>	<b>7</b>
2.1 Chirality . . . . .	7
2.1.1 Brief Historical Review . . . . .	7
2.1.2 Definition of Chirality . . . . .	13
2.1.3 Definition of a Prochiral Object . . . . .	17
2.1.4 Definition of Elements of Chirality . . . . .	19
2.1.5 Principal Elements of Chirality Encountered in Organometallic and Coordination Chemistry . . . . .	20
2.2 Enantiomers and Racemic Compounds . . . . .	24
2.2.1 Enantiomers . . . . .	24
2.2.2 Racemic Compounds . . . . .	24
2.2.3 Diastereomers . . . . .	27
2.2.4 Enantiomeric and Diastereomeric Excesses . . . . .	29
2.2.5 Racemization and Configurational Stability . . . . .	30
2.3 Absolute Configurations and System Descriptors . . . . .	32
2.3.1 Definition of the Absolute and Relative Configuration of a Molecule . . . . .	32
2.3.2 Absolute Configuration and Universal Descriptors . . . . .	33
2.4 Physical Properties of Enantiomers and Racemics . . . . .	43
2.4.1 Optical Properties . . . . .	43
2.4.2 Determination of Absolute Configuration . . . . .	48
2.4.3 Determination of the Enantiomeric Excess ( <i>ee</i> ) . . . . .	50
2.5 Principles of Resolution and Preparation of Enantiomers . . . . .	55
2.5.1 Spontaneous Resolution . . . . .	55
2.5.2 Use of a Chiral Auxiliary . . . . .	56
2.5.3 Chromatography . . . . .	57
2.5.4 Enantioselective Synthesis . . . . .	58
2.6 Summary . . . . .	61
References . . . . .	61
<b>3 Some Examples of Chiral Organometallic Complexes and Asymmetric Catalysis . . . . .</b>	<b>65</b>
3.1 Chirality at Metal Half-sandwich Compounds . . . . .	65
3.1.1 Chiral Three-legged Piano Stool: the CpMnL <sup>1</sup> L <sup>2</sup> L <sup>3</sup> Model . . . . .	65
3.1.2 Chiral Three-legged Piano Stool: the CpReL <sup>1</sup> L <sup>2</sup> L <sup>3</sup> Model . . . . .	68
3.1.3 Other Related Complexes with Chiral-at-Metal Centre . . . . .	71

3.2	Chiral-at-metal Complexes in Organic Synthesis . . . . .	75
3.2.1	The Chiral Acyl–Iron Complex . . . . .	75
3.2.2	The Chiral Cyclic Acyl–Cobalt Complex . . . . .	79
3.2.3	The Lewis Acid–Rhenium Complex . . . . .	79
3.3	Asymmetric Catalysis by Chiral Complexes . . . . .	80
3.3.1	Asymmetric Hydrogenation . . . . .	80
3.3.2	Asymmetric Epoxidation and Dihydroxylation . . . . .	88
3.3.3	Gold Complexes in Asymmetric Catalysis . . . . .	89
3.3.4	Asymmetric Nucleophilic Catalysis . . . . .	91
3.4	Summary . . . . .	94
	References . . . . .	94
<b>4</b>	<b>Chiral Recognition in Organometallic and Coordination Compounds . . . . .</b>	<b>99</b>
4.1	Octahedral Metal Complexes with Helical Chirality . . . . .	101
4.1.1	Heterochiral Recognition . . . . .	101
4.1.2	Homochiral Recognition . . . . .	102
4.1.3	Chiral Recognition Using Modified Cyclodextrins . . . . .	103
4.2	Chiral Recognition Using the Chiral Anion Strategy . . . . .	105
4.2.1	Tris(tetrachlorobenzenediolato) Phosphate Anion (TRISPHAT) . . . . .	105
4.2.2	1,1'-binaphthyl-2,2'-diyl Phosphate Anion (BNP) . . . . .	111
4.2.3	Bis(binaphthol) Borate Anion (BNB) . . . . .	113
4.3	Brief Introduction to DNA Discrimination by Octahedral Polypyridyl Metal Complexes . . . . .	114
4.3.1	Introduction . . . . .	114
4.3.2	Background on DNA Binding with Chiral Octahedral Metal Complexes – the $[\text{Ru}(\text{phen})_3]^{2+}$ Example . . . . .	115
4.3.3	Molecular Light Switches for DNA . . . . .	116
4.4	Summary . . . . .	117
	References . . . . .	117
<b>5</b>	<b>Chirality in Supramolecular Coordination Compounds . . . . .</b>	<b>121</b>
5.1	Self-assembly of Chiral Polynuclear Complexes from Achiral Building Units . . . . .	121
5.1.1	Helicates . . . . .	121
5.1.2	Molecular Catenanes and Knots . . . . .	129
5.1.3	Chiral Tetrahedra . . . . .	133
5.1.4	Chiral Anti(prism) . . . . .	143
5.1.5	Chiral Octahedra and Cuboctahedra . . . . .	146
5.1.6	Chiral Metallo-macrocycles with Organometallic Half-sandwich Complexes . . . . .	147
5.2	Chirality Transfer in Polynuclear Complexes: Enantioselective Synthesis . . . . .	153
5.2.1	Chirality Transfer via Resolved Bridging Ligands . . . . .	154
5.2.2	Chirality Transfer via a Resolved Chiral Auxiliary Coordinated to a Metal or the Use of Resolved Metallo-bricks . . . . .	162
5.3	Summary . . . . .	172
	References . . . . .	172
<b>6</b>	<b>Chiral Enantiopure Molecular Materials . . . . .</b>	<b>179</b>
6.1	General Considerations . . . . .	179

6.1.1	Types of Organization . . . . .	179
6.1.2	Properties . . . . .	180
6.1.3	Chiral and Enantiopure Materials . . . . .	180
6.2	Conductors . . . . .	181
6.2.1	General Considerations . . . . .	181
6.2.2	Why Enantiopure Molecular Conductors? . . . . .	182
6.2.3	Strategies to Obtain Enantiopure Conductors . . . . .	183
6.3	Metallomesogens . . . . .	189
6.3.1	General Considerations . . . . .	189
6.3.2	Metallomesogens with the Chiral Element Attached Directly to the Metal . . . . .	189
6.3.3	Metallomesogens with the Chiral Element(s) in the Ligands . . . . .	190
6.3.4	Metallomesogens Where the Metal and Ligands Generate Helical Chirality . . . . .	193
6.3.5	Metallomesogens Based on Chiral Phthalocyanines . . . . .	199
6.4	Porous Metalorganic Coordination Networks (MOCN) . . . . .	204
6.4.1	General Considerations . . . . .	204
6.4.2	Main Strategies to Obtain Enantiopure MOCNs . . . . .	205
6.4.3	1D MOCNs . . . . .	206
6.4.4	2D and 3D MOCNs . . . . .	209
6.5	Molecular Magnets . . . . .	215
6.5.1	Why Enantiopure Molecular Magnets? . . . . .	215
6.5.2	Strategies and Synthesis . . . . .	216
6.5.3	Enantioselective Synthesis or Resolution of Chiral Ligands . . . . .	216
6.5.4	Chiral Inductive Effect of Resolved Building Blocks in the Formation of Supramolecular Structures . . . . .	218
6.5.5	Chiral Inductive Effect of Resolved Templates . . . . .	222
6.6	Chiral Surfaces . . . . .	224
6.6.1	General Considerations . . . . .	224
6.6.2	Spontaneous Resolution of Chiral Molecules at a Metal Surface in 2D Space . . . . .	225
6.6.3	Induction of Chirality by Enantiopure Chiral Molecules in 3D, Resulting in Enantiopure Structures at Metal Surfaces . . . . .	228
6.6.4	Formation of Chiral Metal Surfaces by Electrodeposition in the Presence of a Chiral Ionic Medium . . . . .	229
6.6.5	Formation of Chiral Nanoparticles . . . . .	229
6.7	Summary . . . . .	232
	References . . . . .	233
	<b>Index . . . . .</b>	<b>239</b>