

*Contents**Preface*

<b>1 What is different about macrocyclic ligand complexes?</b>	1
1.1 Background	1
1.2 Steric and electronic considerations	4
1.3 Some representative macrocyclic systems	12
<b>2 Synthetic procedures</b>	21
2.1 Two major synthetic categories	21
2.2 Direct macrocycle syntheses	22
2.3 Metal-ion template syntheses	26
2.4 Further considerations	48
2.5 Concluding remarks	49
<b>3 Macrocyclic systems – some further categories</b>	51
3.1 Preliminary remarks	51
3.2 Macrocycles with pendant functional groups	51
3.3 Interlocked macrocyclic ligands – the catenands	60
3.4 Binucleating macrocycles	62
3.5 Bicyclic-ligand complexes incorporating a void adjacent to the metal ion	76
3.6 The cage macrocycles	78
<b>4 The metal-ion chemistry of polyether and related macrocyclic systems</b>	90
4.1 The crown polyethers	90
4.2 The cryptands	127
4.3 Generation of alkalides and electrides	134
4.4 Concluding remarks	135

vi *Contents*

<b>5 Host-guest chemistry: macrocyclic hosts and non-metallic guests</b>	136
5.1 Introductory remarks	136
5.2 Host-guest complexation involving crowns and related polyether ligands	138
5.3 Host-guest complexation involving the cyclophanes	160
5.4 The cyclodextrins as hosts	164
<b>6 Thermodynamic considerations</b>	174
6.1 Techniques for obtaining thermodynamic data	174
6.2 Macrocyclic effect	176
6.3 Cyclic ligands and metal-ion selectivity	185
<b>7 Kinetic and mechanistic considerations</b>	192
7.1 Introduction	192
7.2 Formation kinetics	193
7.3 Dissociation kinetics	200
7.4 The kinetic macrocyclic effect – final comments	200
<b>8 Redox properties</b>	209
8.1 Introduction	209
8.2 Stabilization of less common oxidation states	210
8.3 Reactions involving change of ligand unsaturation	219
8.4 Concluding remarks	223
<b>9 The natural macrocycles</b>	224
9.1 Cyclic antibiotics and related systems	224
9.2 Natural corrin, porphyrin and related systems	231
<b>References</b>	245
<b>Index</b>	265