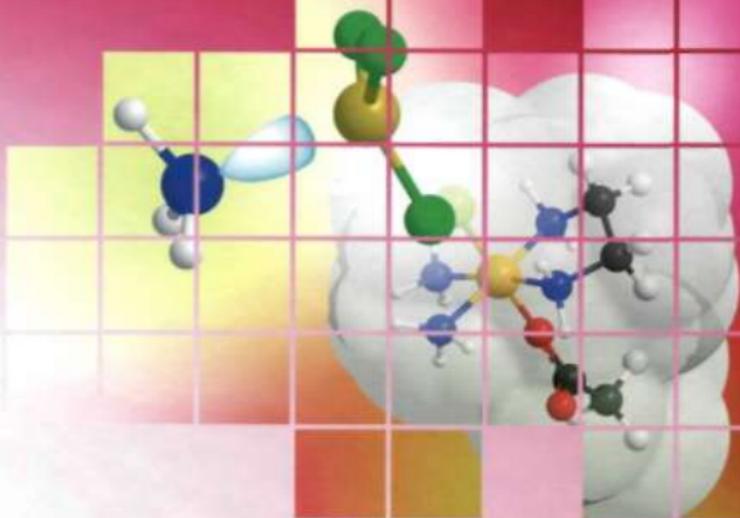


■ GEOFFREY A. LAWRENCE



# INTRODUCTION TO COORDINATION CHEMISTRY

 WILEY

INORGANIC  
CHEMISTRY  
A WILEY  
TEXTBOOK  
SERIES

# Contents

Preface . . . . .	ix
Preamble . . . . .	xi
<b>1 The Central Atom . . . . .</b>	<b>1</b>
1.1 Key Concepts in Coordination Chemistry . . . . .	1
1.2 A Who's Who of Metal Ions . . . . .	4
1.2.1 Commoners and 'Uncommoners' . . . . .	5
1.2.2 Redefining Commoners . . . . .	7
1.3 Metals in Molecules . . . . .	9
1.3.1 Metals in the Natural World . . . . .	10
1.3.2 Metals in Contrived Environments . . . . .	11
1.3.3 Natural or Made-to-Measure Complexes . . . . .	12
1.4 The Road Ahead . . . . .	13
Concept Keys . . . . .	14
Further Reading . . . . .	14
<b>2 Ligands . . . . .</b>	<b>15</b>
2.1 Membership: Being a Ligand . . . . .	15
2.1.1 What Makes a Ligand? . . . . .	15
2.1.2 Making Attachments – Coordination . . . . .	16
2.1.3 Putting the Bite on Metals – Chelation . . . . .	17
2.1.4 Do I Look Big on That? – Chelate Ring Size . . . . .	22
2.1.5 Different Tribes – Donor Group Variation . . . . .	23
2.1.6 Ligands with More Bite – Denticity . . . . .	24
2.2 Monodentate Ligands – The Simple Type . . . . .	26
2.2.1 Basic Binders . . . . .	26
2.2.2 Amines Ain't Ammines – Ligand Families . . . . .	27
2.2.3 Meeting More Metals – Bridging Ligands . . . . .	27
2.3 Greed is Good – Polydentate Ligands . . . . .	29
2.3.1 The Simple Chelate . . . . .	29
2.3.2 More Teeth, Stronger Bite – Polydentates . . . . .	31
2.3.3 Many-Armed Monsters – Introducing Ligand Shape . . . . .	32
2.4 Polynucleating Species – Molecular Bigamists . . . . .	33
2.4.1 When One is Not Enough . . . . .	33
2.4.2 Vive la Difference – Mixed-metal Complexation . . . . .	34
2.4.3 Supersized – Binding to Macromolecules . . . . .	36
2.5 A Separate Race – Organometallic Species . . . . .	36
Concept Keys . . . . .	38
Further Reading . . . . .	39

<b>3</b>	<b>Complexes</b>	41
3.1	The Central Metal Ion	41
3.2	Metal–Ligand Marriage	42
3.2.1	The Coordinate Bond	42
3.2.2	The Foundation of Coordination Chemistry	42
3.2.3	Complex Shape – Not Just Any Which Way	45
3.3	Holding On – The Nature of Bonding in Metal Complexes	49
3.3.1	An Ionic Bonding Model – Introducing Crystal Field Theory	53
3.3.2	A Covalent Bonding Model – Embracing Molecular Orbital Theory	57
3.3.3	Ligand Field Theory – Making Compromises	62
3.3.4	Bonding Models Extended	63
3.4	Coupling – Polymetallic Complexes	73
3.5	Making Choices	75
3.5.1	Selectivity – Of all the Molecules in all the World, Why This One?	75
3.5.2	Preferences – Do You Like What I Like?	75
3.5.3	Complex Lifetimes – Together, Forever?	77
3.6	Complexation Consequences	80
	Concept Keys	81
	Further Reading	82
<b>4</b>	<b>Shape</b>	83
4.1	Getting in Shape	83
4.2	Forms of Complex Life – Coordination Number and Shape	86
4.2.1	One Coordination (ML)	86
4.2.2	Two Coordination (ML <sub>2</sub> )	87
4.2.3	Three Coordination (ML <sub>3</sub> )	88
4.2.4	Four Coordination (ML <sub>4</sub> )	89
4.2.5	Five Coordination (ML <sub>5</sub> )	93
4.2.6	Six Coordination (ML <sub>6</sub> )	96
4.2.7	Higher Coordination Numbers (ML <sub>7</sub> to ML <sub>9</sub> )	98
4.3	Influencing Shape	101
4.3.1	Metallic Genetics – Metal Ion Influences	101
4.3.2	Moulding a Relationship – Ligand Influences	103
4.3.3	Chameleon Complexes	105
4.4	Isomerism – Real 3D Effects	105
4.4.1	Introducing Stereoisomers	106
4.4.2	Constitutional (Structural) Isomerism	106
4.4.3	Stereoisomerism: in Place – Positional Isomers; in Space – Optical Isomers	109
4.4.4	What’s Best? – Isomer Preferences	113
4.5	Sophisticated Shapes	115
4.5.1	Compounds of Polydentate Ligands	116
4.5.2	Encapsulation Compounds	117
4.5.3	Host–Guest Molecular Assemblies	121
4.6	Defining Shape	123
	Concept Keys	123
	Further Reading	124

<b>5</b>	<b>Stability</b>	125
5.1	The Makings of a Stable Relationship	125
5.1.1	Bedded Down – Thermodynamic Stability	125
5.1.2	Factors Influencing Stability of Metal Complexes	127
5.1.3	Overall Stability Constants	138
5.1.4	Undergoing Change – Kinetic Stability	141
5.2	Complexation – Will It Last?	143
5.2.1	Thermodynamic and Kinetic Stability	143
5.2.2	Kinetic Rate Constants	144
5.2.3	Lability and Inertness in Octahedral Complexes	145
5.3	Reactions	146
5.3.1	A New Partner – Substitution	147
5.3.2	A New Body – Stereochemical Change	155
5.3.3	A New Face – Oxidation–Reduction	160
5.3.4	A New Suit – Ligand-centred Reactions	169
	Concept Keys	170
	Further Reading	170
<b>6</b>	<b>Synthesis</b>	173
6.1	Molecular Creation – Ways to Make Complexes	173
6.2	Core Metal Chemistry – Periodic Table Influences	173
6.2.1	s Block: Alkali and Alkaline Earth Metals	173
6.2.2	p Block: Main Group Metals	174
6.2.3	d Block: Transition Metals	175
6.2.4	f Block: Inner Transition Metals (Lanthanoids and Actinoids)	176
6.2.5	Beyond Natural Elements	178
6.3	Reactions Involving the Coordination Shell	179
6.3.1	Ligand Substitution Reactions in Aqueous Solution	179
6.3.2	Substitution Reactions in Nonaqueous Solvents	184
6.3.3	Substitution Reactions without using a Solvent	186
6.3.4	Chiral Complexes	189
6.3.5	Catalysed Reactions	190
6.4	Reactions Involving the Metal Oxidation State	190
6.5	Reactions Involving Coordinated Ligands	194
6.5.1	Metal-directed Reactions	194
6.5.2	Reactions of Coordinated Ligands	197
6.6	Organometallic Synthesis	203
	Concept Keys	206
	Further Reading	207
<b>7</b>	<b>Properties</b>	209
7.1	Finding Ways to Make Complexes Talk – Investigative Methods	209
7.2	Getting Physical – Methods and Outcomes	210
7.3	Probing the Life of Complexes – Using Physical Methods	214
7.3.1	Peak Performance – Illustrating Selected Physical Methods	216
7.3.2	Pretty in Red? – Colour and the Spectrochemical Series	220

7.3.3	A Magnetic Personality? – Paramagnetism and Diamagnetism	223
7.3.4	Ligand Field Stabilization	225
	Concept Keys	227
	Further Reading	227
<b>8</b>	<b>A Complex Life</b>	229
8.1	Life's a Metal Ion	229
8.1.1	Biological Ligands	229
8.1.2	Metal Ions in Biology	231
8.1.3	Classes of Metallobiomolecules	233
8.2	Metalloproteins and Metalloenzymes	233
8.2.1	Iron-containing Biomolecules	234
8.2.2	Copper-containing Biomolecules	240
8.2.3	Zinc-containing Biomolecules	242
8.2.4	Other Metal-containing Biomolecules	243
8.2.5	Mixed-Metal Proteins	244
8.3	Doing What Comes Unnaturally – Synthetic Biomolecules	245
8.4	A Laboratory-free Approach – <i>In Silico</i> Prediction	247
	Concept Keys	249
	Further Reading	250
<b>9</b>	<b>Complexes and Commerce</b>	251
9.1	Kill or Cure? – Complexes as Drugs	251
9.1.1	Introducing Metallodrugs	252
9.1.2	Anticancer Drugs	252
9.1.3	Other Metallodrugs	255
9.2	How Much? – Analysing with Complexes	256
9.2.1	Fluoroimmunoassay	256
9.2.2	Fluoroionophores	258
9.3	Profiting from Complexation	259
9.3.1	Metal Extraction	259
9.3.2	Industrial Roles for Ligands and Coordination Complexes	261
9.4	Being Green	263
9.4.1	Complexation in Remediation	264
9.4.2	Better Ways to Synthesize Fine Organic Chemicals	264
9.5	Complex Futures	264
9.5.1	Taking Stock	265
9.5.2	Crystal Ball Gazing	265
	Concept Keys	266
	Further Reading	266
	<b>Appendix A: Nomenclature</b>	269
	<b>Appendix B: Molecular Symmetry: The Point Group</b>	277
	<b>Index</b>	283