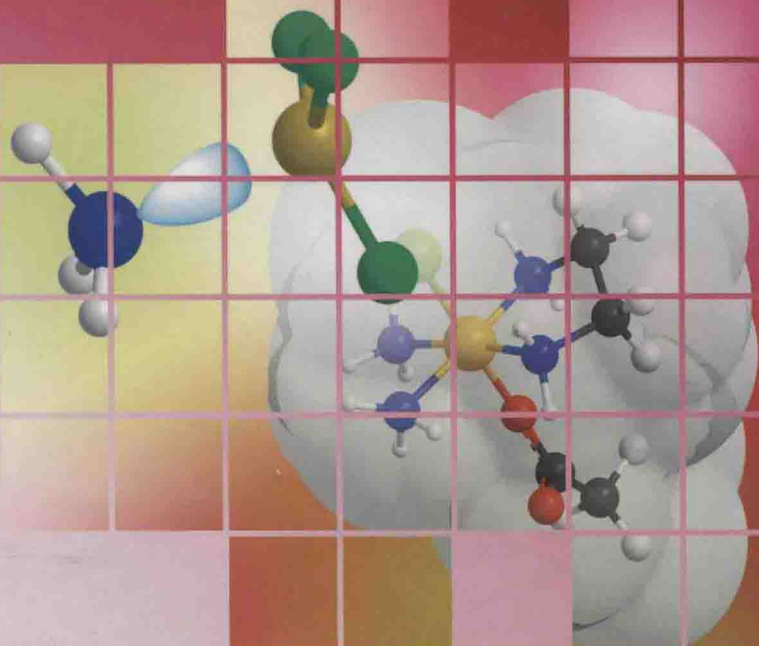


■ GEOFFREY A. LAWRENCE



# INTRODUCTION TO COORDINATION CHEMISTRY

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# INTRODUCTION TO COORDINATION CHEMISTRY



■ **GEOFFREY A. LAWRENCE**, University of Newcastle, Callaghan, Australia

At the heart of coordination chemistry lies the coordinate bond, in its simplest sense arising from donation of a pair of electrons from a donor atom to an empty orbital on a central metalloid or metal. Metals overwhelmingly exist as their cations, but these are rarely met 'naked' – they are clothed in an array of other atoms, molecules or ions that involve coordinate covalent bonds (hence the name coordination compounds). These metal ion complexes are ubiquitous in nature, and are central to an array of natural and synthetic reactions.

Written in a highly readable, descriptive and accessible style *Introduction to Coordination Chemistry* describes properties of coordination compounds such as colour, magnetism and reactivity as well as the logic in their assembly and nomenclature. It is illustrated with many examples of the importance of coordination chemistry in real life, and includes extensive references and a bibliography.

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INTRODUCTION TO COORDINATION CHEMISTRY



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# Introduction to Coordination Chemistry

**Geoffrey A. Lawrance**

*University of Newcastle, Callaghan, NSW, Australia*



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# Preface

This textbook is written with the assumption that readers will have completed an introductory tertiary-level course in general chemistry or its equivalent, and thus be familiar with basic chemical concepts including the foundations of chemical bonding. Consequently, no attempt to review these in any detail is included. Further, the intent here is to avoid mathematical and theoretical detail as much as practicable, and rather to take a more descriptive approach. This is done with the anticipation that those proceeding further in the study of the field will meet more stringent and detailed theoretical approaches in higher-level courses. This allows those who are not intending to specialize in the field or who simply wish to supplement their own separate area of expertise to gain a good understanding largely free of a heavy theoretical loading. While not seeking to diminish aspects that are both important and central to higher-level understanding, this is a pragmatic approach towards what is, after all, an introductory text. Without doubt, there are more than sufficient conceptual challenges herein for a student. Further, as much as is practicable in a chemistry book, you may note a more relaxed style which I hope may make the subject more approachable; not likely to be appreciated by the purists, perhaps, but then this is a text for students.

The text is presented as a suite of sequential chapters, and an attempt has been made to move beyond the pillars of the subject and provide coverage of synthesis, physical methods, and important bioinorganic and applied aspects from the perspective of their coordination chemistry in the last four chapters. While it is most appropriate and recommended that they be read in order, most chapters have sufficient internal integrity to allow each to be tackled in a more feral approach. Each chapter has a brief summary of key points at the end. Further, a limited set of references to other publications that can be used to extend your knowledge and expand your understanding is included at the end of each chapter. Topics that are important but not central to the thrust of the book (nomenclature and symmetry) are presented as appendices.

## Supporting Materials

Self-assessment of your understanding of the material in each chapter has been provided for, through assembly of a set of questions (and answers). However, to limit the size of this textbook, these have been provided on the supporting web site at [www.wiley.com/go/lawrance](http://www.wiley.com/go/lawrance)

This book was written during the depths of the worst recession the world has experienced since the 1930s. Mindful of the times, in which we have seen a decay of wealth, all figures in the text are printed in greyscale to keep the price for the user down. Figures and drawings herein employed mainly ChemDraw and Chem3DPro; where required, coordinates for structures come from the Cambridge Crystallographic Data Base, with some protein views in Chapter Eight drawn from the Protein Data Bank (<http://www.rcsb.org/pdb>). Provision has been made for access to colour versions of all figures, should you as the reader feel these will assist understanding. For colour versions of figures, go to [www.wiley.com/go/lawrance](http://www.wiley.com/go/lawrance). Open access to figures is provided.



## Acknowledgements

For all those who have trodden the same path as myself from time to time over the years, I thank you for your companionship; unknowingly at the time, you have contributed to this work through your influence on my path and growth as a chemist. This book has been written against a background of informal discussions in recent years with a number of colleagues on various continents at various times, and comments on the outline from a panel of reviewers assembled by the publishers. However, the three who have contributed their time most in reading and commenting on draft chapters of this book are Robert Burns, Marcel Maeder and Paul Bernhardt; they deserve particular mention for their efforts that have enhanced structure and clarity. The publication team at Wiley have also done their usual fine job in production of the textbook. While this collective input has led to a better product, I remain of course fully responsible for both the highs and the lows in the published version.

Most of all, I could not possibly finish without thanking my wife Anne and family for their support over the years and forbearance during the writing of this book.

Geoffrey A. Lawrance  
*Newcastle, Australia – October, 2009*

# Preamble

Coordination chemistry in its 'modern' form has existed for over a century. To identify the foundations of a field is complicated by our distance in time from those events, and we can do little more than draw on a few key events; such is the case with coordination chemistry. Deliberate efforts to prepare and characterize what we now call coordination complexes began in the nineteenth century, and by 1857 Wolcott Gibbs and Frederick Genth had published their research on what they termed 'the ammonia-cobalt bases', drawing attention to 'a class of salts which for beauty of form and colour . . . are almost unequalled either among organic or inorganic compounds'. With some foresight, they suggested that 'the subject is by no means exhausted, but that on the contrary there is scarcely a single point which will not amply repay a more extended study'. In 1875, the Danish chemist Sophus Mads Jørgensen developed rules to interpret the structure of the curious group of stable and fairly robust compounds that had been discovered, such as the one of formula  $\text{CoCl}_3 \cdot 6\text{NH}_3$ . In doing so, he drew on immediately prior developments in organic chemistry, including an understanding of how carbon compounds can consist of chains of linked carbon centres. Jørgensen proposed that the cobalt invariably had three linkages to it to match the valency of the cobalt, but allowed each linkage to include chains of linked ammonia molecules and or chloride ions. In other words, he proposed a carbon-free analogue of carbon chemistry, which itself has a valency of four and formed, apparently invariably, four bonds. At the time this was a good idea, and placed metal-containing compounds under the same broad rules as carbon compounds, a commonality for chemical compounds that had great appeal. It was not, however, a great idea. For that the world had to wait for Alfred Werner, working in Switzerland in the early 1890s, who set this class of compounds on a new and quite distinctive course that we know now as coordination chemistry. Interestingly, Jørgensen spent around three decades championing, developing and defending his concepts, but Werner's ideas that effectively allowed more linkages to the metal centre, divorced from its valency, prevailed, and proved incisive enough to hold essentially true up to the present day. His influence lives on; in fact, his last research paper actually appeared in 2001, being a determination of the three-dimensional structure of a compound he crystallized in 1909! For his seminal contributions, Werner is properly regarded as the founder of coordination chemistry.

Coordination chemistry is the study of coordination compounds or, as they are often defined, coordination complexes. These entities are distinguished by the involvement, in terms of simple bonding concepts, of one or more coordinate (or dative) covalent bonds, which differ from the traditional covalent bond mainly in the way that we envisage they are formed. Although we are most likely to meet coordination complexes as compounds featuring a metal ion or set of metal ions at their core (and indeed this is where we will overwhelmingly meet examples herein), this is not strictly a requirement, as metalloids may also form such compounds. One of the simplest examples of formation of a coordination compound comes from a now venerable observation – when  $\text{BF}_3$  gas is passed into a liquid trialkylamine, the two react exothermally to generate a solid which contains

equimolar amounts of each precursor molecule. The solid formed has been shown to consist of molecules  $F_3B-NR_3$ , where what appears to be a routine covalent bond now links the boron and nitrogen centres. What is peculiar to this assembly, however, is that electron book-keeping suggests that the boron commences with an empty valence orbital whereas the nitrogen commences with one lone pair of electrons in an orbital not involved previously in bonding. Formally, then, the new bond must form by the two lone pair valence electrons on the nitrogen being inserted or donated into the empty orbital on the boron. Of course, the outcome is well known – a situation arises where there is an increase in shared electron density between the joined atom centres, or formation of a covalent bond. It is helpful to reflect on how this situation differs from conventional covalent bond formation; traditionally, we envisage covalent bonds as arising from two atomic centres each providing an electron to form a bond through sharing, whereas in the coordinate covalent bond one centre provides both electrons (the donor) to insert into an empty orbital on the other centre (the acceptor); essentially, you can't tell the difference once the coordinate bond has formed from that which would arise by the usual covalent bond formation. Another very simple example is the reaction between ammonia and a proton; the former can be considered to donate a lone pair of electrons into the empty orbital of the proton. In this case, the acid–base character of the acceptor–donor assembly is perhaps more clearly defined for us through the choice of partners. Conventional Brønsted acids and bases are not central to this field, however; more important is the Lewis definition of an acid and base, as an electron pair acceptor and electron pair donor respectively.

Today's coordination chemistry is founded on research in the late nineteenth and early twentieth century. As mentioned above, the work of French-born Alfred Werner, who spent most of his career in Switzerland at Zürich, lies at the core of the field, as it was he who recognized that there was no required link between metal oxidation state and number of ligands bound. This allowed him to define the highly stable complex formed between cobalt(III) (or  $Co^{3+}$ ) and six ammonia molecules in terms of a central metal ion surrounded by six bound ammonia molecules, arranged symmetrically and as far apart as possible at the six corners of an octahedron. The key to the puzzle was not the primary valency of the metal ion, but the apparently constant number of donor atoms it supported (its 'coordination number'). This 'magic number' of six for cobalt(III) was confirmed through a wealth of experiments, which led to a Nobel Prize for Werner in 1913. Whereas his discoveries remain firm, modern research has allowed limited examples of cobalt(III) compounds with coordination numbers of five and even four to be prepared and characterized. As it turns out, Nature was well ahead of the game, since metalloenzymes with cobalt(III) at the active site discovered in recent decades have a low coordination number around the metal, which contributes to their high reactivity. Metals can show an array of preferred coordination numbers, which vary not only from metal to metal, but can change for a particular metal with formal oxidation state of a metal. Thus Cu(II) has a greater tendency towards five-coordination than Mn(II), which prefers six-coordination. Unlike six-coordinate Mn(II), Mn(VII) prefers four-coordination. Behaviour in the solid state may differ from that in solution, as a result of the availability of different potential donors resulting from the solvent itself usually being a possible ligand. Thus  $FeCl_3$  in the solid state consists of Fe(III) centres surrounded octahedrally by six  $Cl^-$  ions, each shared between two metal centres; in aqueous acidic solution, ' $FeCl_3$ ' is more likely to be met as separate  $[Fe(OH_2)_6]^{3+}$  and  $Cl^-$  ions.

Inherently, whether a coordination compound involves metal or metalloid elements is immaterial to the basic concept. However, one factor that distinguishes the chemistry of the majority of metal complexes is an often incomplete d (for transition metals) or f

(for lanthanoids and actinoids) shell of electrons. This leads to the spectroscopic and magnetic properties of members of these groups being particularly indicative of the compound under study, and has driven interest in and applications of these coordination complexes. The field is one of immense variety and, dare we say it, complexity. In some metal complexes it is even not easy to define the formal oxidation state of the central metal ion, since electron density may reside on some ligands to the point where it alters the physical behaviour.

What we can conclude is that metal coordination chemistry is a demanding field that will tax your skills as a scientist. Carbon chemistry is, by contrast, comparatively simple, in the sense that essentially all stable carbon compounds have four bonds around each carbon centre. Metals, as a group, can exhibit coordination numbers from two to fourteen, and formal oxidation states that range from negative values to as high as eight. Even for a particular metal, a range of oxidation states, coordination numbers and distinctive spectroscopic and chemical behaviour associated with each oxidation state may (and usually does) exist. Because coordination chemistry is the chemistry of the vast majority of the Periodic Table, the metals and metalloids, it is central to the proper study of chemistry. Moreover, since many coordination compounds incorporate organic molecules as ligands, and may influence their reactivity and behaviour, an understanding of organic chemistry is also necessary in this field. Further, since spectroscopic and magnetic properties are keys to a proper understanding of coordination compounds, knowledge of an array of physical and analytical methods is important. Of course coordination chemistry is demanding and frustrating – but it rewards the student by revealing a diversity that can be at once intriguing, attractive and rewarding. Welcome to the wild and wonderful world of coordination chemistry – let's explore it.



# Contents

<b>Preface</b> . . . . .	ix
<b>Preamble</b> . . . . .	xi
<b>1 The Central Atom</b> . . . . .	1
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> . . . . .	15
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 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 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 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>	<b>229</b>
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>	<b>251</b>
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>	<b>269</b>
	<b>Appendix B: Molecular Symmetry: The Point Group . . . . .</b>	<b>277</b>
	<b>Index . . . . .</b>	<b>283</b>