Introduction to Coordination Chemistry

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University of Newcastle, Callaghan, NSW, Australia

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Geoffrey A. Lawrance
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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

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. Open access to figures is provided.

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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 $CoCl_3{\cdot}6NH_3$. 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, Jorgensen 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 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.

1 The Central Atom

1.1 Key Concepts in Coordination Chemistry

The simple yet distinctive concept of the *coordinate bond* (also sometimes called a *dative bond*) lies at the core of coordination chemistry. Molecular structure, in its simplest sense, is interpreted in terms of covalent bonds formed through shared pairs of electrons. The coordinate bond, however, arises not through the sharing of electrons, one from each of two partner atoms, as occurs in a standard covalent bond, but from the donation of a pair of electrons from an orbital on one atom (a lone pair) to occupy an empty orbital on what will become its partner atom.

First introduced by G.N. Lewis almost a century ago, the concept of a covalent bond formed when two atoms share an electron pair remains as a firm basis of chemistry, giving us a basic understanding of single, double and triple bonds, as well as of a lone pair of electrons on an atom. Evolving from these simple concepts came valence bond theory, an early quantum mechanical theory which expressed the concepts of Lewis in terms of wavefunctions. These concepts still find traditional roles in coordination chemistry. However, coordination chemistry is marked by a need to employ the additional concept of coordinate bond formation, where the bond pair of electrons originates on one of the two partner atoms alone. In coordinate bond formation, the bonding arrangement between electron-pair acceptor (designated as A) and electron-pair donor (designated as :D, where the pair of dots represent the lone pair of electrons) can be represented simply as Equation (1.1):

$$\mathrm{A} + :\mathrm{D} \rightarrow \mathrm{A}:\mathrm{D} \tag{1.1}$$

The product alternatively may be written as A←:D or A←D, where the arrow denotes the direction of electron donation, or, where the nature of the bonding is understood, simply as A—D. This latter standard representation is entirely appropriate since the covalent bond, once formed, is indistinguishable from a standard covalent bond. The process should be considered reversible in the sense that, if the A—D bond is broken, the lone pair of electrons originally donated by :D remains entirely with that entity.

In most coordination compounds it is possible to identify a central or core atom or ion that is bonded not simply to one other atom, ion or group through a coordinate bond, but to several of these entities at once. The central atom is an acceptor, with the surrounding species each bringing (at least) one lone pair of electrons to donate to an empty orbital on the central atom, and each of these electron-pair donors is called a *ligand* when attached. The central atom is a metal or metalloid, and the compound that results from bond formation is called a coordination compound, coordination complex or often simply a *complex*. We shall explore these concepts further below.

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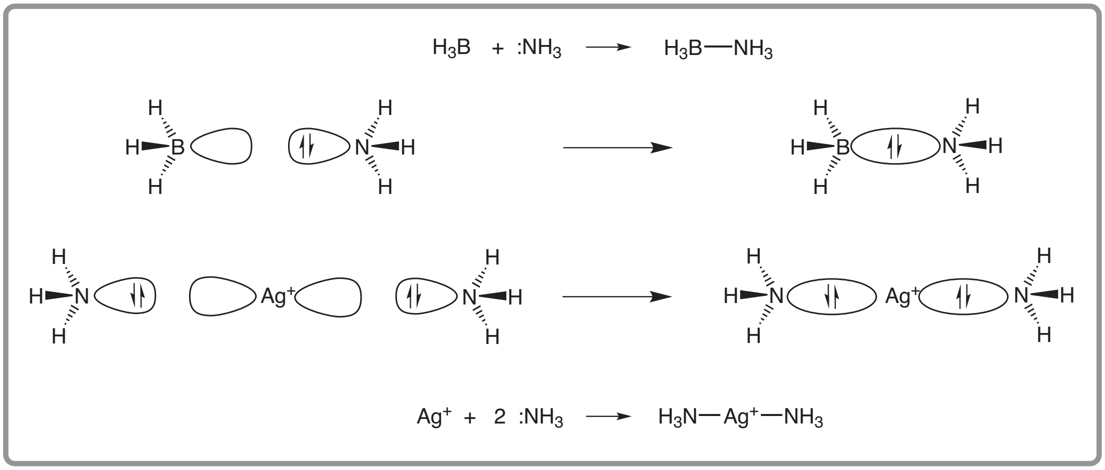


Figure 1.1
A schematic view of ammonia acting as a donor ligand to a metalloid acceptor and to a metal ion acceptor to form coordinate bonds.

The species providing the electron pair (the electron-pair donor) is thought of as being coordinated to the species receiving that lone pair of electrons (the electron-pair acceptor). The coordinating entity, the *ligand*, can be as small as a monatomic ion (e.g. F^-) or as large as a polymer – the key characteristic is the presence of one or more lone pairs of electrons on an electronegative donor atom. Donor atoms often met are heteroatoms like N, O, S and P as well as halide ions, but this is by no means the full range. Moreover, the vast majority of existing organic molecules can act as ligands, or else can be converted into molecules capable of acting as ligands. A classical and successful ligand is ammonia, NH_3, which has one lone pair (Figure 1.1). Isoelectronic with ammonia is the carbanion $^-CH_3$, which can also be considered a ligand under the simple definition applied; even hydrogen as its hydride, H^-, has a pair of electrons and can act as a ligand. It is not the type of donor atom that is the key, but rather its capacity to supply an electron pair.

The acceptor with which a coordinate covalent bond is formed is conventionally either a metal or metalloid. With a metalloid, covalent bond formation is invariably associated with an increase in the number of groups or atoms attached to the central atom, and simple electron counting based on the donor–acceptor concept can account for the number of coordinate covalent bonds formed. With a metal ion, the simple model is less applicable, since the number of new bonds able to be generated through complexation doesn't necessarily match the number of apparent vacancies in the valence shell of the metal; a more sophisticated model needs to be applied, and will be developed herein. What is apparent with metal ions in particular is the strong drive towards complexation – 'naked' ions are extremely rare, and even in the gaseous state complexation will occur. It is a case of the whole being better than the sum of its parts, or, put more appropriately, coordinate bond formation is energetically favourable.

A more elaborate example than those shown above is the anionic compound SiF_6^{2-} (Figure 1.2), which adopts a classical octahedral shape that we will meet also in many metal complexes. Silicon lies below carbon in the Periodic Table, and there are some limited similarities in their chemistry. However, the simple valence bond theory and octet rule that

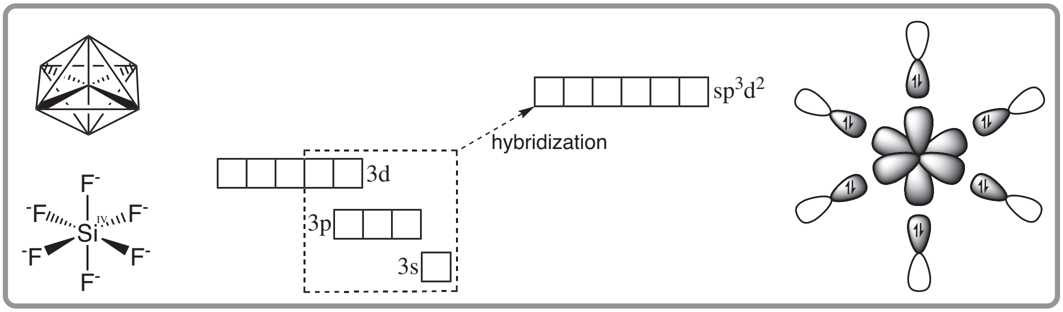


Figure 1.2
The octahedral $[SiF_6]^{2-}$ molecular ion, and a simple valence bond approach to explaining its formation. Overlap of a p orbital containing two electrons on each of the six fluoride anions with one of six empty hybrid orbitals on the Si(IV) cation, arranged in an octahedral array, generates the octahedral shape with six equivalent covalent σ bonds.

works so well for carbon cannot deal with a silicon compound with six bonds, particularly one where all six bonds are equivalent. One way of viewing this molecular species is as being composed of a Si^{4+} or Si(IV) centre with six F^- anions bound to it through each fluoride anion using an electron pair ($:F^-$) to donate to an empty orbital on the central Si(IV) ion, which has lost all of its original four valence electrons in forming the Si^{4+} ion. Using traditional valence bond theory concepts, a process of hybridization is necessary to accommodate the outcome (Figure 1.2). The generation of the shape arises through asserting that the silicon arranges a combination of one 3s, three 3p and two of five available 3d valence orbitals into six equivalent sp^3d^2 hybrid orbitals that are directed as far apart as possible and towards the six corners of an octahedron. Each empty hybrid orbital then accommodates an electron pair from a fluoride ion, each leading in effect to a coordinate covalent bond that is a σ bond because electron density in the bond lies along the line joining the two atomic centres. The shape depends on the type and number of orbitals that are involved in the hybridization process. Above, a combination resulting in an octahedral shape (sp^3d^2 hybrids) is developed; however, different combinations of orbitals yield different shapes, perhaps the most familiar being the combination of one s and three p orbitals to yield tetrahedral sp^3; others examples are linear (sp hybrids) and trigonal planar (sp^2 hybrids) shapes.

A central atom or ion with vacant or empty orbitals and ionic or neutral atoms or molecules joining it, with each bringing lone pairs of electrons, is the classic requirement for formation of what we have termed coordinate bonds, leading to a coordination compound. The very basic valence bonding model described above can be extended to metal ions, as we will see, but with some adjustments due to the presence of electrons in the d orbitals; more sophisticated models are required. Of developed approaches, molecular orbital theory is the most sophisticated, and is focused on the overlap of atomic orbitals of comparable energy on different atoms to form molecular orbitals to which electrons are allocated. While providing accurate descriptions of molecules and their properties, it is relatively complicated and time-consuming, and somewhat difficult to comprehend for large complexes; consequently, simpler models still tend to be used.

In the simple theory based on Lewis' concepts exemplified above, the key aspects are an empty orbital on one atom and a filled orbital (with a pair of electrons present, the lone pair) on the other. Many of the ligand species providing the lone pair are considered bases in the classical Brønsted–Lowry concept of acids and bases (which has as its focus the transfer of a proton), since these species are able to accept a proton. However, in the description we have developed here, no proton is involved, but the concept of accepting an electron-deficient species does apply. The broader and more general concept of an electron-pair donor as a base and an electron-pair acceptor as the acid evolved, and these are called a *Lewis base* (electron-pair donor) and a *Lewis acid* (electron-pair acceptor). Consequently, an $H_3B{-}NH_3$ compound is traditionally considered a coordination compound, arising through coordination of the electron deficient (or Lewis acid) H_3B and the electron lone-pair-containing (or Lewis base) compound $:NH_3$ (Figure 1.1). It is harder, in part as a result of entrenched views of covalent bonding in carbon-based compounds, to accept $[H_3C{-}NH_3]^+$ in similar terms purely as a H_3C^+ and $:NH_3$ assembly. This need to consider and debate the nature of the assembly limits the value of the model for non-metals and metalloids. With metal ions, however, you tend to know where you stand – almost invariably, you may start by considering them as forming coordination compounds; perhaps it is not surprising that coordination chemistry is focused mainly on compounds of metals and their ions.

Coordination has a range of consequences for the new assembly. It leads to structural change, seen in terms of change in the number of bonds and/or bond angles and distances. This is inevitably tied to a change in the physical properties of the assembly, which differ from those of its separate components. With metal atoms or ions at the centre of a coordination complex, even changing one of a set of ligands will be reflected in readily observable change in physical properties, such as colour. With growing sophistication in both synthesis and our understanding of physical methods, properties can often be ‘tuned’ through varying ligands to produce a particular result, such as a desired reduction potential.

It should also be noted that a coordination compound adopts one of a limited number of basic shapes, with the shape determined by the nature of the central atom and its attached ligands. Moreover, the physical properties of the coordination compound depend on and reflect the nature of the central atom, ligand set and molecular shape. Whereas only one central atom occurs in many coordination compounds (a compound we may thus define as a monomer), it should also be noted that there exists a large and growing range of compounds where there are two or more ‘central atoms’, either of the same or different types. These ‘central atoms’ are linked together through direct atom-to-atom bonding, or else are linked by ligands that as a result are joined to at least two ‘central atoms’ at the same time. This latter arrangement, where one or even several ligands are said to ‘bridge’ between central atoms, is the more common of these two options. The resulting species can usually be thought of as a set of monomer units linked together, leading to what is formally a polymer or, more correctly when only a small number of units are linked, an oligomer. We shall concentrate largely on simple monomeric species herein, but will introduce examples of larger linked compounds where appropriate.

Although, as we have seen, the metalloid elements can form molecular species that we call coordination compounds, the decision on what constitutes a coordination compound is perhaps more subtle with these than is the case with metals. Consequently, in this tale of complexes and ligands, it is with metals and particularly their cations as the central atom that we will almost exclusively meet examples.

1.2 A Who’s Who of Metal Ions

The Periodic Table of elements is dominated by metals. Moreover, it is a growing majority, as new elements made through the efforts of nuclear scientists are invariably metallic. If the Periodic Table was a parliament, the non-metals would be doomed to be forever the minority opposition, with the metalloids a minor third party who cannot decide which side to join. The position of elements in the Periodic Table depends on their electronic configuration (Figure 1.3), and their chemistry is related to their position. Nevertheless, there are common features that allow overarching concepts to be developed and applied. For example a metal from any of the s, p, d or f blocks behaves in a common way – it usually forms cations, and it overwhelmingly exists as molecular coordination complexes through combination with other ions or molecules. Yet the diversity of behaviour underlying this commonality is both startling and fascinating, and at the core of this journey.

The difficulty inherent in isolating and identifying metallic elements meant that, for most of human history, very few were known. Up until around the mid-eighteenth century, only gold, silver, copper and iron of the d-block elements were known and used as isolated metals. However, in an extraordinary period from around 1740 to 1900, all but two of the naturally existing elements from the d block were firmly identified and characterized, and it was the synthesis and identification of technetium in 1939, the sole 'missing' element in the core of this block because it has no stable isotopes, that completed the series. In almost exactly 200 years, what was to become a large block of the Periodic Table was cemented in place; this block has now been expanded considerably with the development of higher atomic number synthetic elements. Along with this burst of activity in the identification of elements came, in the late nineteenth century, the foundations of modern coordination chemistry, building on this new-found capacity to isolate and identify metallic elements.

Almost all metals have a commercial value, because they have found commercial applications. It is only the more exotic synthetic elements made as a result of nuclear reactions that have, as yet, no real commercial valuation. The isolation of the element can form the starting point for applications, but the chemistry of metals is overwhelmingly the chemistry of metals in their ionic forms. This is evident even in Nature, where metals are rarely found in their elemental state. There are a few exceptions, of which gold is the standout example, and it was this accessibility in the metallic state that largely governed the adoption and use in antiquity of these exceptions. Dominantly, but not exclusively, the metal is found in a positive oxidation state, that is as a cation. These metal cations form, literally, the core of coordination chemistry; they lie at the core of a surrounding set of molecules or atoms, usually neutral or anionic, closely bound as ligands to the central metal ion. Nature employs metal ions in a variety of ways, including making use of their capacity to bind to organic molecules and their ability to exist, at least for many metals, in a range of oxidation states.

The origins of a metal in terms of it Periodic Table position has a clear impact on its chemistry, such as the reactions it will undergo and the type of coordination complexes that are readily formed. These aspects are reviewed in Chapter 6.2, after important background concepts have been introduced. At this stage, it is sufficient to recognize that, although each metallic element is unique, there is some general chemical behaviour, that relates to the block of the Periodic Table to which it belongs, that places both limitations on and some structure into chemical reactions in coordination chemistry.

1.2.1 Commoners and 'Uncommoners'

Because we meet them daily in various forms, we tend to think of metals as common. However, 'common' is a relative term – iron may be more common than gold in terms of availability in the Earth's crust, but gold is itself more common than rhenium. Even for the fairly well-known elements of the first row of the d block of the Periodic Table, abundance in

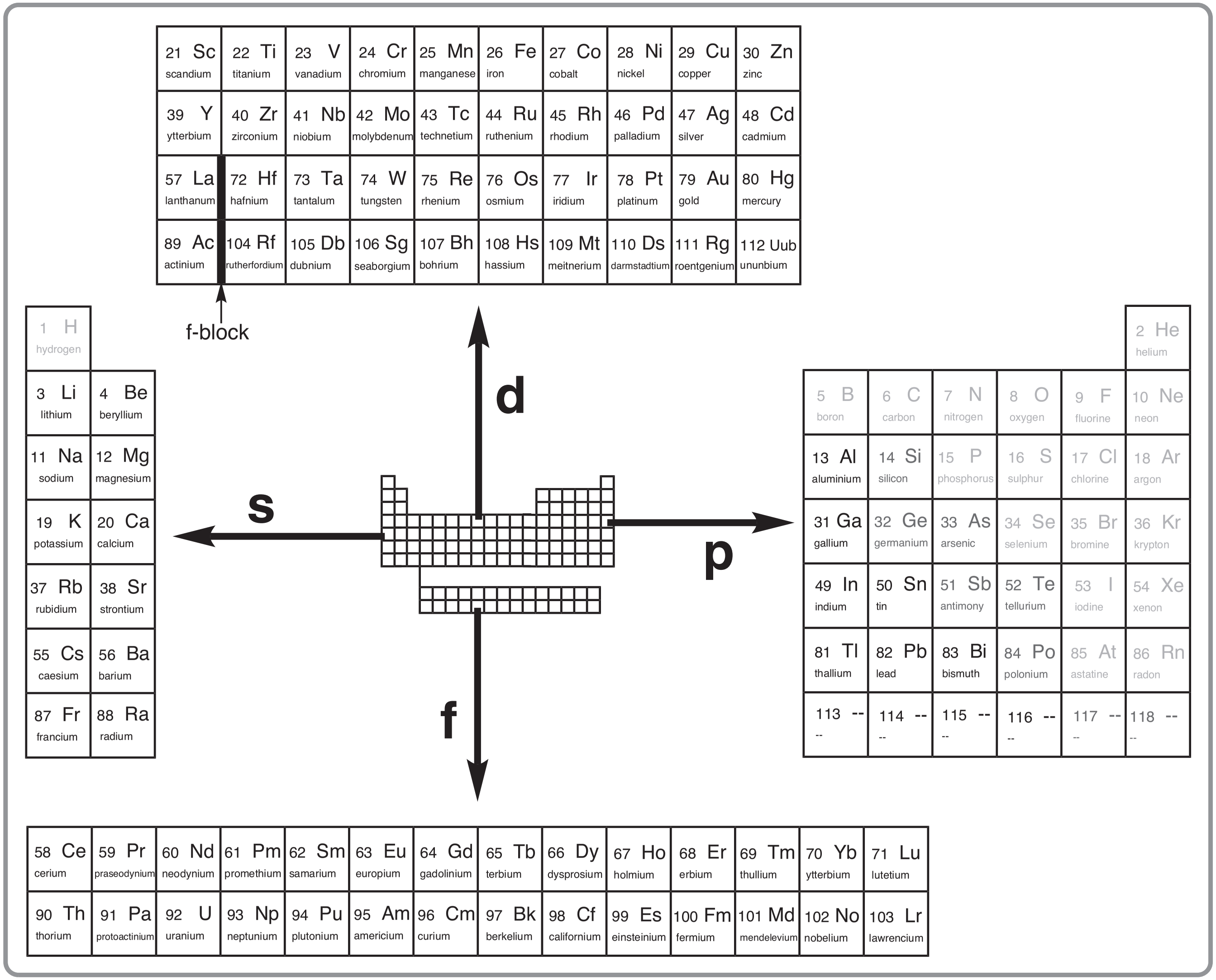

21 Sc scandium
22 Ti titanium
23 V vanadium
24 Cr chromium
25 Mn manganese
26 Fe iron
27 Co cobalt
28 Ni nickel
29 Cu copper
30 Zn zinc
39 Y ytterbium
40 Zr zirconium
41 Nb niobium
42 Mo molybdenum
43 Tc technetium
44 Ru ruthenium
45 Rh rhodium
46 Pd palladium
47 Ag silver
48 Cd cadmium
57 La lanthanum
72 Hf hafnium
73 Ta tantalum
74 W tungsten
75 Re rhenium
76 Os osmium
77 Ir iridium
78 Pt platinum
79 Au gold
80 Hg mercury
89 Ac actinium
104 Rf rutherfordium
105 Db dubnium
106 Sg seaborgium
107 Bh bohrium
108 Hs hassium
109 Mt meitnerium
110 Ds darmstadtium
111 Rg roentgenium
112 Uub ununbium
f-block
1 H hydrogen
3 Li lithium
4 Be beryllium
11 Na sodium
12 Mg magnesium
19 K potassium
20 Ca calcium
37 Rb rubidium
38 Sr strontium
55 Cs caesium
56 Ba barium
87 Fr francium
88 Ra radium
d
s
p
f
2 He helium
5 B boron
6 C carbon
7 N nitrogen
8 O oxygen
9 F fluorine
10 Ne neon
13 Al aluminium
14 Si silicon
15 P phosphorus
16 S sulphur
17 Cl chlorine
18 Ar argon
31 Ga gallium
32 Ge germanium
33 As arsenic
34 Se selenium
35 Br bromine
36 Kr krypton
49 In indium
50 Sn tin
51 Sb antimony
52 Te tellurium
53 I iodine
54 Xe xenon
81 Tl thallium
82 Pb lead
83 Bi bismuth
84 Po polonium
85 At astatine
86 Rn radon
113 -- --
114 -- --
115 -- --
116 -- --
117 -- --
118 -- --
58 Ce cerium
59 Pr praseodynium
60 Nd neodynium
61 Pm promethium
62 Sm samarium
63 Eu europium
64 Gd gadolinium
65 Tb terbium
66 Dy dysprosium
67 Ho holmium
68 Er erbium
69 Tm thullium
70 Yb ytterbium
71 Lu lutetium
90 Th thorium
91 Pa protoactinium
92 U uranium
93 Np neptunium
94 Pu plutonium
95 Am americium
96 Cm curium
97 Bk berkelium
98 Cf californium
99 Es einsteinium
100 Fm fermium
101 Md mendelevium
102 No nobelium
103 Lr lawrencium

Figure 1.3
The location of metals in the Periodic Table of the elements.

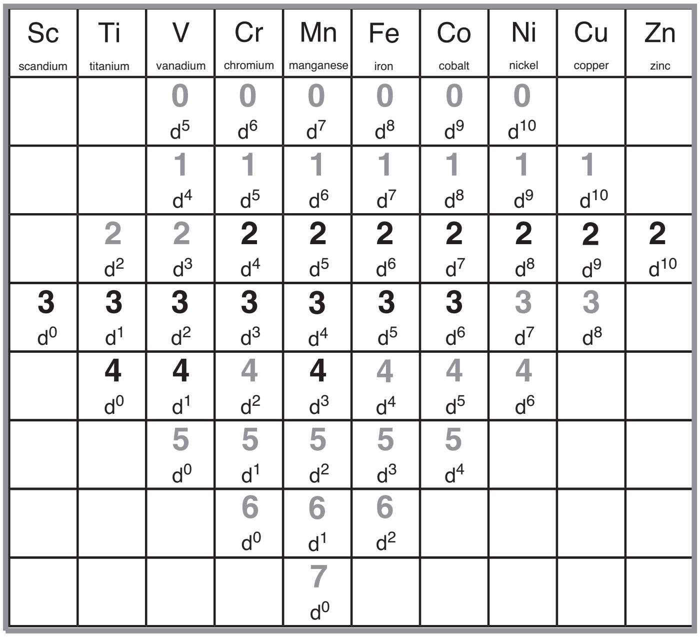
the Earth's crust varies significantly, from iron (41 000 ppm) to cobalt (20 ppm); moreover, what we think of as 'common' metals, like copper (50 ppm abundance) and zinc (75 ppm abundance), are really hardly that. Availability of an element is not driven by how much is present on average in the Earth's crust, of course, but by other factors such as its existence in sufficiently high concentrations in accessible ore bodies and its commercial value and applicability (see Chapter 9). Iron, more abundant than the sum of all other d-block elements, is mined from exceedingly rich ore deposits and is of major commercial significance. Rhenium, the rarest transition metal naturally available, is a minor by-product of some ore bodies where other valuable metals are the primary target, and in any case has limited commercial application. Nevertheless, our technology has advanced sufficiently that there is not one metal available naturally on Earth that is not isolated in some amount or form, and for which some commercial applications do not now exist. Even synthetic elements are available and applicable. Complexes of an isotope of technetium, the only d-block element with no stable isotopes that consequently does not exist in the Earth's crust and must be made in a nuclear reactor, are important in medical γ-ray imaging; in fact, sufficient technetium is produced so that it may be considered as accessible as its rare, naturally available, partner element rhenium. As another example, an isotope of the synthetic f-block actinoid element americium forms the core of the ionization mechanism operating in the sensor of household smoke detectors.

These observations have one obvious impact on coordination chemistry – every metallic element in the Periodic Table is accessible and in principle able to be studied, and each offers a suite of unique properties and behaviour. As a consequence, they are in one sense all now 'common'; what distinguishes them are their relative cost and the amounts available. In the end, it has been such commercially-driven considerations that have led to a concentration on the coordination chemistry of the more available and applicable lighter elements of the transition metals, from vanadium to zinc. Of course Nature, again, has made similar choices much earlier, as most metalloenzymes employ light transition elements at their active sites.

1.2.2 Redefining Commoners

Apart from availability (Section 1.2.1), there is another more chemical approach to commonality that we should dwell on, an aspect that we have touched upon already. This is a definition in terms of oxidation states. With the most common of all metals in the Earth's crust, the main group element aluminium, only one oxidation state is important – Al(III). However, for the most common transition metal (iron), both Fe(II) and Fe(III) are common, whereas other higher oxidation states such as Fe(IV) are known but very uncommon. With the rare element rhenium, the reverse trend holds true, as the high oxidation state Re(VI) is common but Re(III) and Re(II) are rare. What is apparent from these observations is that each metal can display one or more 'usual' oxidation states and a range of others met much more rarely, whereas some are simply not accessible.

What allows us to see the uncommon oxidation states is their particular environment in terms of groups or atoms bound to the metal ion, and in general there is a close relationship between the groups that coordinate to a metal and the oxidation states it can sustain, which we will explore later. The definition of 'common' in terms of metal complexes in a particular oxidation state is an ever-changing aspect of coordination chemistry, since it depends in part on the amount of chemistry that has been performed and reported; over time, a metal in a particular oxidation state may change from 'unknown' to 'very rare' to 'uncommon' as more chemists beaver away at extending the chemistry of an element. At



Sc scandium	Ti titanium	V vanadium	Cr chromium	Mn manganese	Fe iron	Co cobalt	Ni nickel	Cu copper	Zn zinc
		0 d^5	0 d^6	0 d^7	0 d^8	0 d^9	0 d^{10}		
		1 d^4	1 d^5	1 d^6	1 d^7	1 d^8	1 d^9	1 d^{10}	
	2 d^2	2 d^3	**2** d^4	**2** d^5	**2** d^6	**2** d^7	**2** d^8	**2** d^9	**2** d^{10}
3 d^0	**3** d^1	**3** d^2	**3** d^3	**3** d^4	**3** d^5	**3** d^6	3 d^7	3 d^8	
	4 d^0	**4** d^1	4 d^2	**4** d^3	4 d^4	4 d^5	4 d^6		
		5 d^0	5 d^1	5 d^2	5 d^3	5 d^4			
			6 d^0	6 d^1	6 d^2				
				7 d^0					

Figure 1.4
Oxidation states met amongst complexes of transition metal elements; *d*-electron counts for the particular oxidation states of a metal appear below each oxidation state. [Oxidation states that are relatively common with a range of known complexes are in black, others in grey.]

this time, a valid representation of the status of elements of the first row of the d block with regard to their oxidation states is shown in Figure 1.4. Clearly, oxidation states two and three are the most common. Notably, hydrated transition metal ions of charge greater than 3+ (that is, oxidation state over three) are not stable in water, so higher oxidation state species invariably involve other ligands apart from water. Differences in the definition of what amounts to a common oxidation state leads to some variation, but the general trends remain constant.

What is immediately apparent from Figure 1.4 is that most metals offer a wealth of oxidation states, with the limit set by simply running out of d electrons (i.e. reaching the d^0 arrangement) or else reaching such a high reduction potential that stability of the ion is severely compromised (that is it cannot really exist, because it involves itself immediately in oxidation–reduction reactions that return the metal to a lower and more common stable oxidation state). Notably, it gets harder to ‘use up’ all d electrons on moving from left to right across the Periodic Table, associated with both the rising number of d electrons and lesser screening from the charge on the nucleus. Still, you are hardly spoilt for choice as a coordination chemist!

The standard reduction potential (E^0) provides a measure of the stability of a metal in a particular oxidation state. The E^0 value is the voltage generated in a half-cell coupled with the standard hydrogen electrode (SHE), which itself has a defined half-cell potential of 0.0 V. Put simply, the more positive is E^0 the more difficult is it for metal oxidation to a hydrated metal ion to occur. Alternatively, we could express it by saying that the less positive is E^0, the more stable is the metal in the higher oxidation state of its couple and consequently the less easily is it reduced to the lower oxidation state. Metal activity can be related to reactivity with a protic solvent (like water) or hydrogen ions, and correlates with electronegativity. Very electropositive metals (reduction potentials of cations <-1.6 V) have low electronegativities; these include the s block and all lanthanide metals. Electropositive metals display cation reduction potentials up to ~0 V, and include the first row of the d-block and some p-block elements. Electronegative metals have positive cation reduction potentials; these include most of the second and third rows of the d block. Reactivities in redox processes differ for these different classes; electronegative metals are not corroded by oxygen, for example, unlike electropositive metals.

Yet another way of defining commonality with metal ions relates to how many ligand donor groups may be attached to the central metal. This was touched on in the Preamble, and we'll use and expand on the same example again. Cobalt(III) was shown decades ago to have what was then thought to be invariably six donor groups or atoms bound to the central metal ion, or a *coordination number* of six. While this is still the overwhelmingly common coordination number for cobalt in this oxidation state, there are now stable examples for Co(III) of coordination numbers of five and even four. In its other common oxidation state, as Co(II), there are two 'common' coordination numbers, four and six; it is hardly a surprise, then, that more and more examples of the intermediate coordination number five have appeared over time. Five-coordination has grown to be almost as common for another metal ion, Cu(II), as four or six, illustrating that our definitions of common and uncommon do vary historically. That's a problem with chemistry generally – it never stands still. The number of research papers published with a chemical theme each year continues to grow at such a rate that it is impossible to read a single year's complete offerings in a decade, let alone that year.

1.3 Metals in Molecules

Metals in the elemental form typically exhibit bright, shiny surfaces – what we tend to expect of a 'metallic' surface. In the atmosphere, rich with oxygen and usually containing water vapour, these surfaces may be prone to attack, depending on the E^0 value; this leads to the bright surface changing character as it becomes oxidized. Although a highly polished steel surface is attractive and valued, the same surface covered in an oxide layer (better known in this particular case as rust) is hardly a popular fashion statement. Yet it is the formation of rust which is perfectly natural, with the shiny metal surface the unnatural form that needs to be carefully and regularly maintained to retain its initial condition. What we are witnessing with rust formation is a chemical process governed by thermodynamics (attainment of an equilibrium defined by the stability of the reaction products compared to the reactants) and kinetics (the rate at which change, or the chemical reaction, proceeds to equilibrium under the conditions prevailing). While the outcome may not be aesthetically appealing (unless one wants to make a virtue of rusted steel as a 'distressed' surface with character), chemistry is not given to making allowances for the sake of style or commerce – it is a demanding task to 'turn off' the natural chemistry of a system. Some metals, such as titanium, are less wilful than iron; they undergo surface oxidation, but form a tight monolayer of oxide that is difficult to penetrate and thus is resistant to further attack.

Of course, were the metal ions that exist in the oxidized surface to undergo attack in a different way, through complexation by natural ligands and subsequent dissolution, fresh metal surface would be exposed and available for attack. Such a process, occurring over long periods, would suggest that free active metals would increasingly end up dissolved as their ions in the ocean, and this is clearly not so – most metal ion concentrations in the ocean are very low (apart from alkali metal ions, being <0.001 ppm). In reality, because reactive elemental-state metals are made mainly through human action, the contribution to the biosphere even by reversion to ionic forms will be small. Most metals are locked up as ions in rocks – particularly as highly insoluble oxides, sulfides, sulfates or carbonates that will dissolve only with human interception, through reaction with strong acids or ligands. Even if they enter the biosphere as soluble complex ions, they are prone to chemistry that leads to re-precipitation. The classic example is dissolved iron(II), which readily undergoes aerial oxidation to Fe(III) and precipitation as a hydroxide, followed by dehydration to an oxide, all occurring below neutral pH.

Thus in the laboratory we tend to meet almost all metals in a pure form as synthetic cationic salts of common anions. These tend to be halides or sulfates, and it is these metal salts, hydrated or anhydrous, that form the entry point to almost all of metal coordination chemistry. In nature, it is no accident that metal ions that are relatively common tend to find roles, mediated of course by their chemical and electrochemical properties. Thus iron is heavily used not only because it is common, but also because it forms strong complexes with available biomolecules and has an Fe(II)/(III) redox couple that is accessible by biological oxidants and reductants and thus useful to drive some biochemical processes.

1.3.1 Metals in the Natural World

Most metals in the Earth's crust are located in highly inorganic environments – as components of rocks or soils on land or under water. Where metals are aggregated in local high concentrations through geological processes, these may be sufficient in amount and concentration to represent an ore deposit, which is really an economic rather than a scientific definition. In addition, metals are present in water bodies as dissolved cations; their concentrations can be in a very few cases substantial, as is the case with sodium ion in seawater. However, even if present in very low concentration, as for gold in seawater, the size of the oceans means that there is a substantial amount of gold (and other metals) dispersed in the aquatic environment. The other location of metals is within living organisms, where, of the transition metals, iron, zinc and copper predominate. On rare occasions the concentration of another metal may be relatively high; this is the case in some plants that tolerate and concentrate particular metal ions, such as nickel in *Hybanthus floribundus*, native to Western Australia, which can be hyper-accumulated up to $\sim$50 mg per gram dry weight. Levels of metal ions in animals and in particular plants vary with species and environment. However, generally metals are present in nature in only trace amounts (Table 1.1). High levels of most metal ions are toxic to living species; for example ryegrass displays a toxicity order Cu $>$ Ni $>$ Mn $>$ Pb $>$ Cd $>$ Zn $>$ Al $>$ Hg $>$ Cr $>$ Fe, with each species displaying a unique trend.

Metals were eventually recognized as having a presence in a range of biomolecules. Where metal cations appear in living things, their presence is rarely if ever simply fortuitous. Rather, they play a particular role, from simply providing an ionic environment through to being at the key active site for reactions in a large enzyme. Notably, it is the lighter alkali, alkaline earth and transition elements that dominate the metals present in living organisms. Of transition metals, although iron, copper and zinc are most dominant, almost all of the first row transition elements play some part in the functioning of organisms. Nevertheless, even heavier elements such as molybdenum and tungsten are found to have some roles.

Table 1.1 Typical concentrations (ppm) of selected metals ions in nature.

Metal	Earth's crust	Oceans	Plants (ryegrass)	Animals (human blood)
Na	23 000	10 500	1 000	2 000
K	21 000	1 620	28 000	1 600
Mg	23 000	1 200	2 500	40
Ca	41 000	390	12 500	60
Al	82 000	0.000 5	50	0.3
Sc	16	0.000 000 6	>0.01	0.008
Ti	5 600	0.000 48	2.0	0.055
V	160	0.001	0.07	<0.000 2
Cr	100	0.000 18	0.8	0.008
Mn	950	0.000 11	130	0.005
Fe	41 000	0.000 1	240	450
Co	20	0.000 001	0.6	0.01
Ni	80	0.000 1	6.5	0.03
Cu	50	0.000 08	9.0	1.0
Zn	75	0.000 05	31	7.0
Mo	1.5	0.01	1.1	0.001
Cd	0.11	0.000 001 1	0.07	0.0052
Pb	14	0.000 02	2.0	0.21
Sn	2.2	0.000 002 3	<0.01	0.38
Ce	68	0.000 002	<0.01	<0.001

Keys to metal ion roles are their high charge (and surface charge density), capacity to bind organic entities through strong coordinate bonds, and ability in many cases to vary oxidation states. We shall return to look at metals in biological environments in more detail in Chapter 8.

1.3.2 Metals in Contrived Environments

What defines chemistry over the past century has been our growing capacity to design and construct molecules. The number of new molecules that have been synthesized now number in the millions, and that number continues to grow at an astounding pace, along with continuing growth in synthetic sophistication; we have reached the era of the 'designer' molecule. Many of the new organic molecules prepared can bind to metal ions, or else can be readily converted to other molecules that can do so. This, along with the diversity caused by the capacity of a central metal ion to bind to a mixture of molecules at one time, means that the number of potential metal complexes that are not natural species is essentially infinite. Chemistry has altered irreversibly the composition of the world, if not the universe.

Discovering when the first synthetic metal complex was deliberately made and identified is not as easy as one might expect, because so much time has passed since that event. One popular candidate is *Prussian blue*, a cyanide complex of iron, developed as a commercial artist's colour in the early eighteenth century. A more reliable candidate is what we now know as hexaamminecobalt(III) chloride, discovered serendipitously by Tassaert in 1798, which set under way a quest to interpret its unique properties, such as how separately stable species NH_3 and $CoCl_3$ could produce another stable species $CoCl_3{\cdot}6NH_3$, and to discover similar species. As new compounds evolved, it was at first sufficient to identify them simply through their maker's name. Thus came into being species such as *Magnus's green salt* ($PtCl_2{\cdot}2NH_3$) and *Erdmann's salt* ($Co(NO_2)_3{\cdot}KNO_2{\cdot}2NH_3$). This first attempt at nomenclature was doomed by profligacy, but as many compounds isolated were coloured, another way of identification arose based on colour; thus Tasseart's original yellow compound $CoCl_3{\cdot}6NH_3$ became luteocobaltic chloride, and the purple analogue $CoCl_3{\cdot}5NH_3$ was named purpureocobaltic chloride. This nomenclature also dealt with isomers, with two forms of $CoCl_3{\cdot}4NH_3$ identified and recognized – green praseocobaltic chloride and violet violeocobaltic chloride. Suffice to say that this nomenclature soon ran out of steam (or at least colours) also, and modern nomenclature is based on sounder structural bases, demonstrated in Appendix 1.

While some may quail at the outcomes of all this profligate molecule building, what remains a constant are the basic rules of chemistry. A synthetic metal complex obeys the same basic chemical 'rules' as a natural one. 'New' properties result from the character of new assemblies, not from a shift in the rules. As a classic example of how this works, consider the case of Vitamin B_{12}, distinguished by being one of a limited number of biomolecules centred on cobalt, and one of a rare few natural organometallic (metal–carbon bonded) compounds. This was discovered to exist with good stability in three oxidation states, Co(III), Co(II) and Co(I). Moreover, it was found to involve a C—Co(III) bond. At the time of these discoveries, examples of low molecular weight synthetic cobalt(III) complexes also stable in both Co(II) and Co(I) oxidation states were few if any in number, nor had the Co(III)–carbon bond been well defined. Such observations lent some support to a view that metals in biological entities were 'special'. Of course, time has removed the discrepancy, with synthetic Co complexes stable in all of the (III), (II) and (I) oxidation states well established, and examples of the Co(III)–carbon bond reported even with very simple ligands in other sites around the metal ion. The 'special' nature of metals in biology is essentially a consequence of their usually very large and specifically arranged macromolecular environments. While it is demanding to reproduce such natural environments in detail in the laboratory, it is possible to mimic them at a sufficient level to reproduce aspects of their chemistry.

Of course, the synthetic coordination chemist can go well beyond nature, by making use of facilities that don't exist in Earth's natural world. This can include even re-making elements that have disappeared from Earth. Technetium is radioactive in all its isotopic forms, and consequently has been entirely transmuted to other elements over time. However, it can be made readily enough in a nuclear reactor, and is now widely available. All of its chemistry, consequently, is synthetic or contrived. The element boron has given rise to a rich chemistry based on boron hydrides, most of which are too reactive to have any geological existence. Some boron hydrides as well as mixed carbon–boron compounds (carboranes) can bind to metal ions. Nitrogen forms a vast array of carbon-based compounds (amines) that are excellent at binding to metal ions; Nature also makes wide use of these for binding metal ions, but the construction of novel amines has reached levels that far exceed the limitations of Nature. After all, most natural chemistry has evolved at room temperature and pressure in near-neutral aqueous environments – limitations that do not apply in a chemical laboratory. What the vast array of synthetic molecules for binding metal ions provides is a capacity to control molecular shape and physical properties in metal-containing compounds not envisaged possible a century ago. These have given rise to applications and technologies that seem to be limited only by our imagination.

1.3.3 Natural or Made-to-Measure Complexes

Metal complexes are natural – expose a metal ion to molecules capable of binding to that ion and complexation almost invariably occurs. Dissolve a metal salt in water, and both cation and anion are hydrated through interaction with water. In particular, the metal ion acts as a

Lewis acid and water as a Lewis base, and a structure of defined coordination number with several $M^{n+} \leftarrow :OH_2$ bonds results; an experimentally-determined M—O—H angle of $\sim 130^\circ$ is consistent with involvement of a lone pair on the approximately tetrahedral oxygen. The coordinate bond is at the core of all natural and synthetic complexes.

While metals are usually present in minute amounts in living organisms, techniques for isolation and concentration have been developed that allow biological complexes to be recovered. An array of metalloproteins now offered commercially by chemical companies is evidence of this capacity. However, relying on natural sources for some compounds is both limiting and expensive. Many drugs and commercial compounds of natural origins are now prepared reliably and cheaply synthetically. Drugs originally from natural sources are made synthetically because the amount required to satisfy global demand makes isolation from natural sources impractical. This can also apply both to molecules able to attach to metal ions, and to their actual metal complexes. Simple across-the-counter compounds of metals find regular medical use; zinc supplements, for example, are actually usually supplied as a simple synthetic zinc(II) amino acid complex. Aspects of biological coordination chemistry are covered in Chapter 8.

Isolation of metal ions from ores by hydrometallurgical (water-based) processing often relies on complexation as part of the process. For example gold recovery from ore currently employs oxygen as oxidant and cyanide ion as ligand, leading selectively to a soluble gold(I) cyanide complex. Copper(II) ion dissolved from ore is recovered from an aqueous mixture by solvent extraction as a metal complex into kerosene, followed by decomposition and back extraction into aqueous acid, from which it is readily isolated by reduction to the metal. Pyrometallurgical (high temperature) processes for isolation of metals, on the other hand, usually rely on reduction reactions of oxide ores at high temperature. Electrochemical processes are also in regular industrial use; aluminium and sodium are recovered via electrochemical processes from molten salts. An overview of applied coordination chemistry is covered in Chapter 9.

1.4 The Road Ahead

Having identified the important role of metals as the central atom in coordination chemistry, it is appropriate at this time to recognize that the metal has partners and to reflect on the nature of the partnership. The partners are of course the ligands. A coordination complex can be thought of as the product of a molecular marriage – each partner, metal and ligand, brings something to the relationship, and the result of the union involves compromises that, when made, mean the union is distinctly different from the prior independent parts. While this analogy may be taking anthropomorphism to the extreme (unless one wants to carry it below even the atomic level), it is nevertheless not a bad analogy and not so unreasonable an outlook to think of a complex as a 'living' combination. After all, as we shall touch on later, it is not a totally inert combination. Metal complexes undergo ligand exchange (dare we talk of divorce and remarriage?) and can change their shape depending in part on their oxidation state and in part on their partner's preferences (shades of molecular-level compromise here?). With the right partner, the union will be strong, something that we can actually measure experimentally. It's no doubt stretching the analogy to talk of a perfect match, but the concept of fit and misfit between metals and ligands has been developed. What all of this playing with common human traits is about, is alerting you to core aspects of coordination chemistry – partnership and compromise.

In the rest of this book we will be examining in more detail ligands, metal–ligand assembly and the consequences. These include molecular shape, stability, properties and how we can measure and interpret these. Further, we will look at metal complexes in place – in nature and in commerce, and speculate on the future. Overall, the intent is to give as broad and deep an overview as is both reasonable and proper in an introductory text. Pray continue.

Concept Keys

A coordination complex consists of a central atom, usually a metal ion, bound to a set of ligands by coordinate bonds.

A coordinate covalent bond is distinguished by the ligand donor atom donating both electrons (of a lone pair) to an empty orbital on the central atom to form the bond.

A ligand is a *Lewis base* (electron-pair donor), the central atom a *Lewis acid* (electron-pair acceptor).

A 'common' metal may be defined simply by its geo-availability, but from a coordination chemistry perspective it is more appropriate to define 'common' in terms of aspects such as preferred oxidation state, number of coordinated donors or even preferred donor types.

Metal ions may exist and form complexes in a number of oxidation states; this is particularly prevalent in the d block.

First row d-block metal ions are found dominantly in the M(II) or M(III) oxidation states. Heavier members of the d block tend to prefer higher oxidation states.

Further Reading

Atkins, P. and Jones, L. (2000) *Chemistry: Molecules, Matter and Change*, 4th edn, Freeman, New York, USA. An introductory general chemistry textbook appropriate for reviewing basic concepts.

Beckett, M. and Platt, A. (2006) *The Periodic Table at a Glance*, Wiley-Blackwell, Oxford, UK. This short undergraduate-focussed book gives a fine, well-illustrated introductory coverage of periodicity in inorganic chemistry.

Gillespie, R.J. and Popelier, P.L.A. (2002) *Chemical Bonding and Molecular Geometry*, Oxford University Press. A coverage from the fundamental level upward of various models of molecular bonding.

Housecroft, C.E. and Sharpe, A.G. (2008) *Inorganic Chemistry*, 3rd edn, Pearson Education. Of the large and sometimes daunting general advanced textbooks on inorganic chemistry, this is a finely-written and well-illustrated current example, useful as a resource book.