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. First introduced by Gilbert N. Lewis in 1916, the concept of a covalent bond formed when two atoms share an electron pair remains as a firm basis of molecular chemistry, giving us a basic understanding of single, double and triple bonds as well as of non-bonding (lone) pairs of electrons on an atom. Evolving from these simple concepts came valence bond theory from Linus Pauling, an early quantum mechanical theory that expressed the concepts of Lewis in terms of wavefunctions. Pauling would later have the unique distinction of being awarded the Nobel Prize in both Chemistry (1954) and Peace (1962). These basic bonding concepts are applicable to both organic and coordination chemistry. The coordinate bond, however, arises not through an equal contribution of electrons from the paired atoms, as occurs in organic chemistry, but from donation of a lone pair of electrons on one atom to an empty orbital on what will become its partner atom.

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:

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

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 clearly understood, simply as A–D. This latter standard representation is entirely appropriate since this bond, once formed, is a two-electron covalent bond like any other (other representations involving an arrow are now discouraged, as they could imply a special character to the covalent bond once it is formed that is inappropriate). The bond formation 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.

Coordination compounds have always been an integral part of chemistry since its recognition as a distinct scientific discipline in the middle of the 18th century, although at that time nothing was known about molecular structure or bonding. Key early developmental work employed the metal cobalt (isolated first only in 1735 by Georg Brandt) and simple reagents such as ammonia and chloride ion. French chemist B.M. Tassaert reported in 1798 the reaction between the mineral

Introduction to Coordination Chemistry, Second Edition. Paul V. Bernhardt and Geoffrey A. Lawrance.

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cobaltite (CoAsS) and excess ammonia, which yielded an uncharacterised yellow compound. With the benefit of hindsight, it is apparent that Tassaert had accidentally prepared the chloride salt of an ammonia complex of cobalt(III), now known to be $[Co(NH_3)_6]^{3+}$ but did not appreciate its significance at the time; Leopold Gmelin reported the oxalate salt of the same complex in 1822. Although many chemists pursued variations of this reaction in the first half of the 19th century, most credit is given to Oliver Wolcott Gibbs and Frederick Augustus Genth for their now classic 1856 review '*Researches on the Ammonia-cobalt Bases*'. This paper describes the synthesis, composition and properties of numerous compounds including the colourfully named, but structurally misunderstood, praseocobaltic chloride (formulated as $CoCl_3{\cdot}4NH_3$), purpureocobaltic chloride ($CoCl_3{\cdot}5NH_3$), roseocobaltic chloride ($CoCl_3{\cdot}5NH_3{\cdot}H_2O$) and luteocobaltic chloride ($CoCl_3{\cdot}6NH_3$) (Figure 1.1). Suffice to say that this nomenclature soon ran out of steam (or at least colours). The French team of Louis Bernard Guyton de Morveau, Antoine-Laurent de Lavoisier, Claude Louis Berthollet and Antoine François Fourcroy had published in 1787 a forward-looking treatise on nomenclature that set under way adoption of a binary notation for salts (such as potassium carbonate, rather than an array of names in existence, including salt of tartar) still in use today. The names used by Gibbs and Genth and other early coordination chemists do follow the binary notation concept in part, but the names of the complex cations, not surprisingly, lack any real precision. An unfortunate tendency to, alternatively, name new compounds after the discoverer only compounded the problem. Modern nomenclature is based on sounder structural bases, demonstrated in Appendix 1.

These coordination compounds are historically important as they provided the impetus for various theories proposed throughout the 1800s to explain their appearance, physical properties and composition, and, in particular, the nature of the attraction between cobalt and ammonia. Thomas Graham had introduced the ammonium theory where ammonia gained a metal substituent instead of a hydrogen ion as in an ammonium salt. Jöns Jacob Berzelius' conjugate theory noted a special pairing (coupling) between metal and ammonia, while Karl Klaus recognised that ammonia once bonded to a metal became 'passive' and lost its basic properties. All these observations contributed to a clearer picture of what we now know as the coordinate bond.

In most coordination compounds, it is possible to identify the 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

Figure 1.1
Four classical coordination compounds reported by Gibbs and Genth in 1856, originally named: (a) praseocobaltic chloride ($CoCl_3{\cdot}4NH_3$); (b) purpureocobaltic chloride ($CoCl_3{\cdot}5NH_3$); (c) roseocobaltic chloride ($CoCl_3{\cdot}5NH_3{\cdot}H_2O$) and (d) luteocobaltic chloride ($CoCl_3{\cdot}6NH_3$).

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 a metalloid (from the *p*-block) 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.

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 monoatomic ion (e.g. F^-) or as large as a protein—the key characteristic is the presence of one or more lone pairs of electrons on an electronegative donor atom (i.e. one with a tendency to draw shared electron density towards itself). Donor atoms often met are heteroatoms like N, O, P and S as well as halide ions, but this is by no means the full range. Moreover, most existing organic molecules can act as ligands or else can be converted into molecules capable of acting as ligands. As mentioned earlier, a classical and well-studied ligand is ammonia, NH_3, which has one lone pair (Figure 1.2). Isoelectronic (same number of electrons) with ammonia is the methyl 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 such as boron, which is also electron deficient, covalent bond formation is invariably associated with an increase in coordination number, and simple electron counting based on the donor–acceptor concept can account for the number of coordinate covalent bonds formed. In this case, boron attains an octet of electrons by coordinate bond formation. With a genuine metal ion (from the *s*-, *p*-, *d*- or *f*-block), this model is less applicable since the metal ion usually carries its preferred number of ligands into a reaction. Consequently, the coordination number tends to remain constant, with an incoming ligand not simply adding to the coordination sphere but replacing an existing ligand in a *substitution* reaction; 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

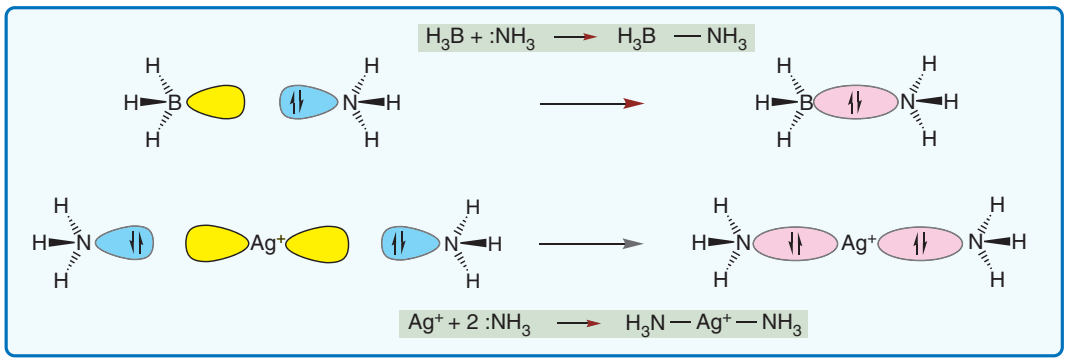

Figure 1.2

A schematic view of ammonia acting as a donor ligand to a metalloid acceptor (boron, shown here with the BH_3 sp^3 hybridised like the ammonia) and to a metal ion acceptor (silver(I), shown here as the 'naked' cation for simplicity) to form coordinate bonds.

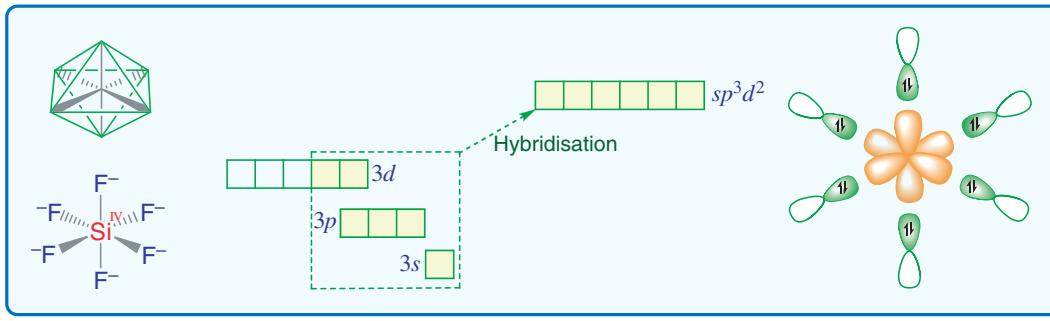

Figure 1.3
The octahedral $[SiF_6]^{2-}$ molecular ion and a simple valence bond approach to explaining its formation. Overlap of a *p*-orbital containing two electrons on each of the six fluoride anions with one of six empty hybrid orbitals on the Si(IV) cation, arranged in an octahedral array, generates the octahedral shape with six equivalent covalent σ-bonds.

complexation—'naked' ions are extremely reactive, 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 1.3), which adopts the shape of a classical octahedron (a polyhedron with eight equilateral triangular faces, sets of four of which meet at each of six vertices) 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, simple valence bond theory and the octet rule that works so well for carbon (and other elements of the second period) cannot deal with a silicon compound exhibiting six equivalent covalent bonds. 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 donating an electron pair ($:F^-$) 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 hybridisation is necessary to accommodate the outcome where all six bonds formed are equivalent (Figure 1.3). The generation of the shape arises through asserting that the silicon arranges a combination of one 3*s*, three 3*p* and two of five available 3*d* valence orbitals into six equivalent sp^3d^2 hybrid orbitals that are directed as far apart as possible and hence towards the six vertices of an octahedron. Each identical empty hybrid orbital then accommodates an electron pair from a fluoride ion, each leading in effect to six covalent (coordinate) σ-bonds with electron density between the two atomic nuclei. The shape depends on the type and number of orbitals that are involved in the hybridisation 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 a tetrahedral array of four sp^3 orbitals. Other examples are linear (*sp* hybrids) and trigonal planar (sp^2 hybrids) shapes. We shall deal with shape and bonding in greater detail in later chapters, although it is worth noting the experimental complexities involved in defining the actual shape of molecules, which draw on an array of modern instrumental methods discussed in Chapter 7. Theories and models of bonding exist to interpret what we 'see' at the molecular level but do not lose sight of the key word—they are models.

A central atom or ion with vacant valence atomic orbitals accepting lone pairs of electrons from ionic or neutral atoms (ligands) 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 really required. Of all the developed approaches, molecular orbital theory is the most sophisticated and is focussed 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 ligands such as ammonia are also bases in the classical Brønsted–Lowry concept of acids and bases (as proton donors or acceptors) 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 donation to 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, $H_3B–NH_3$ 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 1.2). 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 as an assembly of H_3C^+ and $:NH_3$. 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 the metal ions as the electron pair acceptors in forming coordination compounds; perhaps it is not surprising that coordination chemistry is focussed 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, 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 complex, even changing one of a set of ligands will be reflected in readily observable changes 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 exist a large and growing range of compounds where there are two or more metal atoms present either of the same or different types. These metals may be linked together through direct atom-to-atom bonding or else are linked by particular

ligands that as a result are joined to at least two metals 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 *p*-block 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, as discussed earlier. Consequently, in this tale of complexes and ligands, it is with *d*-block 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 periodic table is basically a system of classification, and as such reflects in part the interests and prejudices of the assemblers and the level of acceptance by the scientific community.

John Dalton's proposal in 1806 to classify elements via their relative atomic weights formed a basis for later development of the periodic table. Historically, it has changed over time, and in one of the earliest forms, proposed by John Newlands in 1864, consisted of eight columns. Several other proposals also appeared at around that time (including a remarkable rotatable cylinder carrying a spiral periodic table built by Alexandre-Émile Béguyer de Chancourtois in 1862, which showed the presence of a periodic repetition of chemical properties). Dmitri Mendeleev, in 1869, arranged all the 63 chemical elements known by the late 1860s in order of increasing atomic weight and by chemical groupings, and noticed a recurring pattern (a periodicity) of properties within groups of elements in the resulting table. His periodic table was sophisticated enough that he was able to leave gaps in places where he expected unknown elements should occur and even predicting the properties of some potential elements (two of which, Ga and Sc, were discovered in just the next decade). The later detection of 'missing' elements that he had predicted established Mendeleev as the founder of the modern periodic table, although there have been many approaches and proposals over the years. At essentially the same time as Mendeleev was developing his table, Lothar Meyer also produced a periodic table (eventually published in 1870) reflecting related trends in physical properties and with elements arranged in order of increasing atomic weights. Moreover, post-Mendeleev, development of new proposals did not stop. For example, William Crookes produced a three-dimensional spiral system in 1888, elegant but bulky. In fact, as many as 700 versions of the periodic table appeared in the century or so after 1869 (although many placed the emphasis on artistry rather than chemistry). There is a continuing general interest in the table, with 2019 (150 years after Mendeleev

published his version) declared by UNESCO as the *International Year of the Periodic Table of the Chemical Elements*.

After Mendeleev's first attempt, the periodic table evolved into an arrangement of elements of effectively 18 vertical groups, which became the normal representation by the 1920s as early quantum mechanics was applied to explain the form that had developed from experimentally observed behaviours and similarities. The 18 columns relate to 2 associated with the *s*-block, 6 with the *p*-block and 10 with the *d*-block, reflecting the maximum numbers of electrons that can be accommodated by the orbitals in these sub-shells. Furthermore, the so-called inner transition elements, or *f*-block, are usually arranged as a separate block that is 14 elements wide, associated with the maximum number of electrons that can be accommodated by the set of seven *f*-orbitals. However, there is an expanded 32 column format of the Table that incorporates the *f*-block within the main body of the table along with the rest of the columns (sometimes called the 'long form', for an obvious reason). However, there is still some debate today about the current representation, focussed on Group 3 membership, with one proposal leading to a 15-element wide *f*-block. Various options proposed for *f*-block membership revolve around these elements lying in a part of the Table where assignment of electronic configurations becomes more problematical. The debate reflects a concern of specialist quantum mechanics practitioners rather than general scientists, and are usually put aside in the periodic table that we generally see and use, on the basis that quantum mechanics provides a good but not exact explanation of the Table. Notably, the International Union of Pure and Applied Chemistry (IUPAC) does not officially support any particular form of the periodic table, although their ambivalent approach does not prevent them publishing their version!

Consequently, the position of elements in the traditional form of the periodic table that we use today depends on their basic electronic configuration (Figure 1.4) 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 compounds 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 inherent difficulty in isolating and identifying metallic elements meant that, for most of human history, their chemistry was unknown. Up until around the mid-18th century, only gold, silver, copper, iron, tin, lead and mercury had been isolated in their pure metallic forms. However, in an extraordinary period from 1735 to 1844, all but two of the naturally existing *d*-block elements were isolated in their pure metallic form and characterised. Along with this burst of activity in the identification of new elements came the foundations of modern coordination chemistry, building on this new-found capacity to isolate and identify metallic elements and subsequently explore their reactivity. The especially rare and elusive elements hafnium and rhenium were only isolated in 1922 and 1928, respectively. Nuclear synthesis and isolation of radioactive technetium in 1939 completed the first three rows of the *d*-block. In almost 200 years, what was to become the largest (and arguably most interesting) block of the periodic table was cemented in place. Sustained efforts of scientists in the second half of the 20th century using nuclear fusion created the so-called superheavy (but also short-lived) elements, and a fourth row of transition (*d*-block) elements, and a seventh row of the periodic table, was completed. There are now 118 known elements. Where will it end?

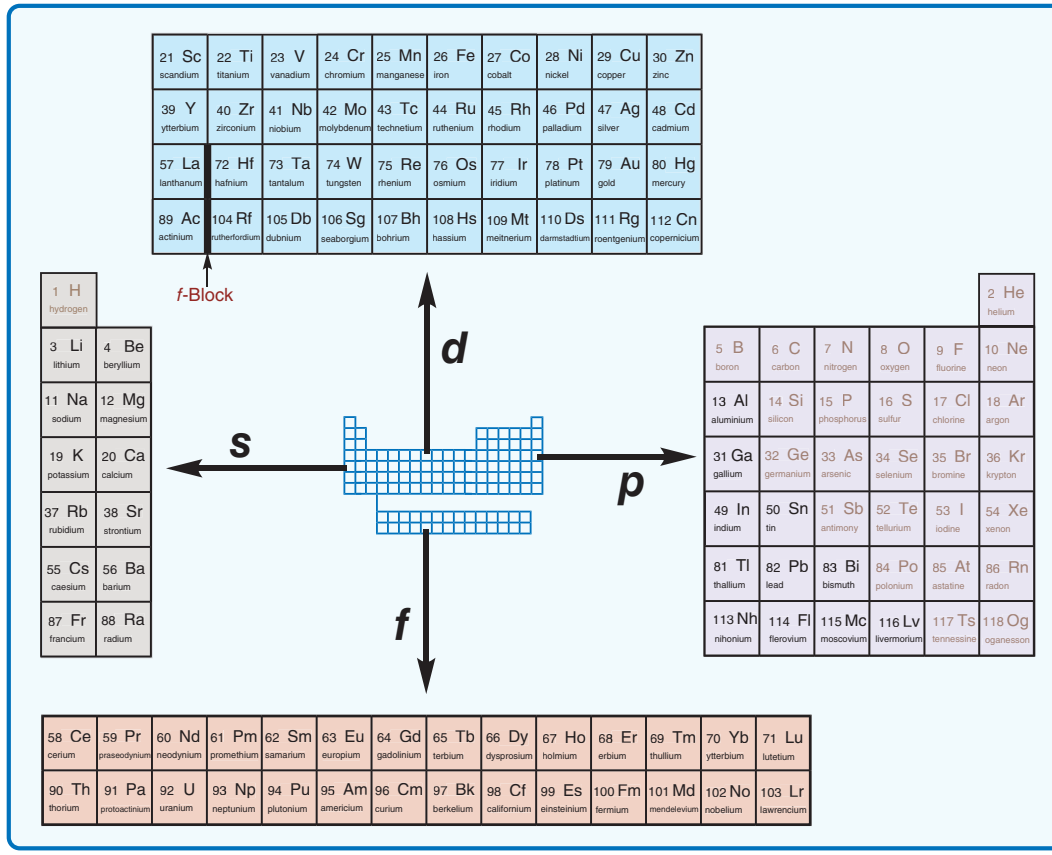

Figure 1.4
The location of metals in the periodic table of the elements. (Non-metallic elements are in faint type to distinguish them from the metals.).

Almost all metals have a commercial value because they have found industrial or medical applications. It is only the more exotic and very short half-life 'superheavy' synthetic elements that have as yet no real commercial valuation. The isolation of a metal in its elemental form can be the starting point for applications, and this is the domain of metallurgy and materials science. The chemistry of metals is overwhelmingly that of their oxidised forms. This is evident even in Nature, where metals are rarely found in their elemental state due to spontaneous oxidation by atmospheric oxygen. There are a few exceptions, of which gold is the standout example, and it was this accessibility in the metallic state that largely governed its adoption and use in antiquity. Dominantly, but not exclusively, a 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 centre of an array of neutral or anionic ligands. Nature employs metal ions in various 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 its periodic table position has a clear impact on its chemistry, such as the reactions it will undergo and the type of coordination compounds 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 recognise 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 place both limitations on, and some structure to, reactions in coordination chemistry.

1.2.1 Common and Uncommon Metals

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, abundance in 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; in any case, it has limited commercial applications at present. Nevertheless, our technology has advanced sufficiently that all metallic elements occurring naturally (on Earth) are commercially available in some amount or form for those wishing to explore their chemistry or for which applications already exist. Even some synthetic elements are available and applicable. Complexes of technetium, the only *d*-block element with no stable isotopes, are now of great significance in medical imaging yet the element itself can only be found in Nature in trace quantities near uranium ores as a daughter product of uranium fission. Even its name is a signal to its general absence, being based on the Greek τεχνητος (technitos, meaning artificial). The once extinct technetium is now making a comeback and is made via nuclear decay of a radioactive isotope of neighbouring element molybdenum (^{99}Mo) produced by neutron bombardment ($^{98}\text{Mo} + n \rightarrow {}^{99}\text{Mo} \rightarrow {}^{99\text{m}}\text{Tc} + \beta^-$). Technetium is a vital component of medical γ-ray imaging (see Chapter 9.2.1). In fact, sufficient technetium is produced so that it may be considered as abundant as its rare naturally available partner element rhenium, although still a radioactive and inherently hazardous element. As another example, an isotope of the synthetic *f*-block actinoid element americium formed, until recently, the core of the ionisation 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 titanium to zinc. Of course, Nature made similar choices much earlier, as most metalloenzymes employ light transition elements at their active sites, although molybdenum and tungsten are interesting outliers that will be mentioned later in Chapter 8.

1.2.2 An Alternative Concept of Common Metals

Apart from availability, discussed in the previous section, 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 found in Nature–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 are highly reactive. With the rare element rhenium, the reverse trend holds true, as the high oxidation state Re(VII) is common but Re(III) and Re(II) are rare. What is apparent from these observations is that each transition metal can display one or more 'usual' oxidation states, a unique feature of the *d*-block elements. The main group (*s*- and *p*-block) and lanthanoid/actinoid (*f*-block) metals are much less capable of existing in more than one stable ionised form.

What allows us to observe different oxidation states in the *d*-block elements is their particular ligand environment, and in general, there is a close relationship between the donor atoms coordinated 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 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 1.5. As is clear from this figure, 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.

Immediately apparent from Figure 1.5 is that most transition metals offer a wealth of oxidation states, with the limit set by simply running out of *d*-electrons (i.e. reaching the $4s^0 3d^0$ arrangement that corresponds to the argon noble gas electron configuration) or else reaching such a high redox 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 spoilt for choice as a coordination chemist!

The standard redox potential (E^o) (formally the reduction–oxidation potential) provides a measure of the stability of a metal in a particular oxidation state. Although this will be covered in greater detail in Chapter 7, the E^o value (in Volts) is an intrinsic property of the coordination compound in its oxidised and reduced forms comprising the so-called redox couple. Put simply, for systems with large positive E^o values, the reduced form of the couple is more stable while a very large negative redox potential indicates the oxidised form is more stable. Most metals in their elemental state undergo spontaneous oxidation by atmospheric oxygen and are found in the Earth's crust as oxide and sulfide minerals. Coordination chemistry underpins

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 1.5
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 red, others in green.]

the mining of many metals, especially some of the more precious metals, as will be shown in Chapter 9.

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 will use and expand on the same example again. Cobalt(III) was shown decades ago to have what was then thought 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 number 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 as four- or six-coordination for another metal ion, Cu(II), illustrating that our definitions of common and uncommon do vary historically. That is 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^{o} value; this leads to the bright surface changing character as it becomes oxidised. Although a highly polished steel surface is attractive and valued, the same surface covered in an oxide layer (better known in the case of iron as rust) is hardly a popular fashion statement. Yet it is the formation of rust that 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. This fact is of great comfort to recipients of titanium metal implants following orthopaedic surgery.

Of course, were the metal ions that exist in the oxidised surface to undergo attack in a different way, through complexation by natural ligands and subsequent dissolution, this would result in fresh metal surface being exposed and hence 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 intervention, 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 an 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, nitrates 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 the more abundant transition metals ions tend to have found vital roles, mediated of course by their chemical and electrochemical properties. Iron is ubiquitous in and essential to all life forms not only because it is common but also due to its versatility. It commonly forms stable complexes with biomolecules in both its oxidised and reduced forms (Fe(III)/(II)) and is arguably the most biologically important transition metal of all.

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; however, as mentioned earlier, their concentrations are in only a very few cases substantial, as is the case with sodium ion in seawater. Complex anions, usually of metals in high oxidation states, also are a component of our oceans. Molybdenum is, perhaps unexpectedly, the most abundant transition metal in surface seawater (although at only about 10 μg/L); vanadium is also relatively abundant, at about 2 μg/L. Molybdenum's unique advantage stems from the fact that it is stable in its highly oxidised and extremely soluble Mo(VI) form as $[MoO_4]^{2-}$; no other transition metal can match this combination of stability in a high oxidation state (low redox potential) and solubility in water. Other more common terrestrial elements such as iron, manganese and titanium in their highly oxidised forms cannot remain in solution and precipitate immediately to soon form charge neutral insoluble oxides, e.g. Fe_2O_3, MnO_2 or TiO_2. 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; one estimate suggests that there are around 5×10^{16} tonnes of minerals dissolved in the oceans.

The other location of metals is within living organisms, where, of the transition metals, iron, zinc and copper predominate in humans and other vertebrates. 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 at up to ~50 mg per gram dry weight. Levels of metal ions in animals and in particular plants vary with species and environment. Generally, the *d*- and *p*-block metals are present in Nature in only trace amounts (Table 1.1), including potentially harmful elements absorbed from our environment (e.g., Cr, Cd and Pb). 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 eventually were recognised 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, other first-row transition elements play some part in the functioning of organisms. Keys to metal ion roles are their high charge (and charge density), capacity to bind organic entities through strong coordinate bonds and ability in many cases to vary their oxidation states. We shall return to look at metals in biological environments in more detail in Chapter 8.

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	1000	2000
K	21,000	1620	28,000	1600
Mg	23,000	1200	2500	40
Ca	41,000	390	12,500	60
Al	82,000	0.0005	50	0.3
Sc	16	0.000006	>0.01	0.008
Ti	5600	0.00048	2.0	0.055
V	160	0.001	0.07	<0.0002
Cr	100	0.00018	0.8	0.008
Mn	950	0.00011	130	0.005
Fe	41,000	0.0001	240	450
Co	20	0.000001	0.6	0.01
Ni	80	0.0001	6.5	0.03
Cu	50	0.00008	9.0	1.0
Zn	75	0.00005	31	7.0
Mo	1.5	0.01	1.1	0.001
Cd	0.11	0.0000011	0.07	0.0052
Pb	14	0.00002	2.0	0.21
Sn	2.2	0.0000023	<0.01	0.38
Ce	68	0.000002	<0.01	<0.001

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 compounds that have been synthesised now number in the tens of 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 ligands at one time, means that the number of potential metal complexes that are not natural species is essentially infinite. Coordination chemistry has altered irreversibly the composition of the world.

It is possible to assign a role for coordination chemistry in some ancient technologies, such as mordants (metal salts) used to fix dyes to fabrics (a technique perhaps 9000 years old), but there was no understanding of the molecular level in the ancient world. Even 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 discovered accidently in the first decade of the 18th century, and developed as a commercial artist's colour within a few years of the discovery (and known to have been used in a 1709 painting); it is still a commercially important pigment today. Preparation and isolation of what we now know are gold(III) and platinum(IV) halide complexes and reaction of the latter with ammonia were reported by W. Lewis in 1763. As we have seen earlier, hexaamminecobalt(III) chloride, discovered serendipitously by Tassaert in 1798, set under way a quest to understand how different combinations of cobalt, ammonia and chloride could lead to such an array

of compounds. 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' green salt* ($PtCl_2 \cdot 2NH_3$) and *Erdmann's salt* ($Co(NO_2)_3 \cdot KNO_2 \cdot 2NH_3$). This early attempt at nomenclature was doomed by profligacy, but as many compounds isolated were coloured, another way of identification arose based on colour (as mentioned above for the series of salts obtained from combination of cobalt, ammonia and chloride and shown in Figure 1.1), prior to the 19th and 20th century development of the systematic nomenclature that is used today.

While some may quail at the outcomes of all the extravagant 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}, isolated by Karl Folkers and a team of researchers at Merck & Co in 1947, and structurally characterised by Dorothy Crowfoot Hodgkin at Oxford University using small bright red crystals supplied by Lester Smith of Glaxo Laboratories, who isolated the compound at about the same time as the Merck group. The structural solution by X-ray crystallography, particularly challenging at this time, took 13 years. Crowfoot Hodgkin, who also was responsible for the structural elucidation of the groundbreaking antibiotic penicillin, was awarded the Nobel Prize in Chemistry in 1964. Vitamin B_{12} is distinguished by being one of a limited number of biomolecules centred on cobalt and was discovered to exist with good stability in three oxidation states, Co(III), Co(II) and Co(I). Moreover, it was found to be one of a rare few natural organometallic (metal–carbon bonded) compounds, involving 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 distinction, 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 quite simple companion 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 embedded within a protein. 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 'extinct' elements such as radioactive technetium and promethium. 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 pH-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 as possible a century ago. These have given rise to applications and technologies that are limited only by our imagination.

1.3.3 Natural or Made-to-Measure Complexes

Metal complexes are natural–expose a metal ion to ligands capable of binding to that ion and complexation almost invariably occurs. Dissolve a metal salt in water, and both cation and anion are surrounded by water molecules, as separate aquated ions. 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 $M^{n+}-OH_2$ bonds results. The coordinate bond exemplified in these aquated cations 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. The array of metalloproteins now offered commercially by chemical companies in gram quantities is evidence of this capacity to isolate biological complexes at scale. Relying on natural sources for some compounds was once both limiting and expensive, but advances in biotechnology have led to large-scale bioreactors being used to produce common drugs like the antibiotic penicillin and the hormone insulin on industrial scales, with Nature doing the complicated chemistry for us. Other designer-made synthetic drugs must be prepared by humans and at a cost that is economically sustainable. Although less sophisticated and potent, 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 pure metals 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. Recovery of the parent metal is then readily achieved electrochemically by reduction to its elemental state. Electrochemical processes are also in regular industrial use; aluminium and sodium are recovered via electrochemical processes from molten salts. Historically, the emergence of electrochemistry as a technique in the early 1800s was the catalyst for the isolation of dozens of new and highly reactive metallic elements from their oxidised forms. Pyrometallurgical (high temperature) processes for isolation of metals, on the other hand, usually rely on reduction reactions of oxide ores at high temperature. An overview of applied coordination chemistry is covered in Chapter 9.

1.4 The Road Ahead

Having identified the important role of metals (usually but not exclusively as cations) as the central atom in coordination chemistry, it is appropriate at this time to recognise that the metal has partners and to reflect on the nature of the partnership. The partners are, of course, the ligands. A coordination compound (or complex) can perhaps be thought of as the product of a molecular marriage—each partner, metal and ligand, brings something to the relationship, and the result involves compromises that, when made, means the product of the union is distinctly different (in terms of chemical and physical properties) from the prior independent parts. While this analogy may be taking anthropomorphism to the extreme, 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, and their preferred shape may change depending in part on the oxidation state and in part on the ligands' preferences. Furthermore, the stability of the metal–ligand assembly is something that we can actually measure experimentally. It is no doubt stretching the analogy to talk of a perfect match, but the concept of fit and misfit between metals and ligands (particularly where the ligand offers more than one donor group) has been developed. These metaphors should alert you to the core aspects of coordination chemistry–partnership, and compromise.

The compounds formed from coordination of ligand molecules and ions to a central atom adopt particular shapes, of which a common shape for complexes with six attached ligands is octahedral, already introduced in Figure 1.3. The early research of Albert Werner and his contemporaries involved a range of metal complexes that adopt this common geometry. An aspect of coordination chemistry that should be addressed at the outset is the 'language' we use, that is how to represent a coordination complex so that others can understand to what you are referring. As mentioned earlier, naming a compound after yourself, or anyone else, is of limited value to the rest of the scientific community. A more productive way forward is to adopt a systematic approach by using a unique chemical name, a formula or a drawing. Naming (nomenclature) is pursued in Appendix 1, and it may soon become apparent that, while formal nomenclature leads to precise identification, interpretating lengthy formal names that often include coordinated organic molecules as components of the full name, as well as devices to identify the mode of coordination of molecules, can be as daunting as compound German nouns are to those with English as a native language. A formula is often simpler but may not be sufficiently clear; for example, it may not define shape or even bonding mode. Consequently, the use of drawings of molecules developed and, if well presented, these pictures provide an unambiguous solution to identity. Chemical structure drawings have grown to play a major role in the field, just as they have in organic chemistry. There are a number of representations commonly met in drawings of coordination compounds, illustrated in Figure 1.6. The space-filling drawing, based on the covalent radii of the components, reflects the space occupied by the electron clouds of each atom within the assembly but lacks clarity due to the bulk of the components. A ball-and-stick representation, where the component atoms are 'shrunk' to yield a more open view, is clearer. The ball-and-stick representation

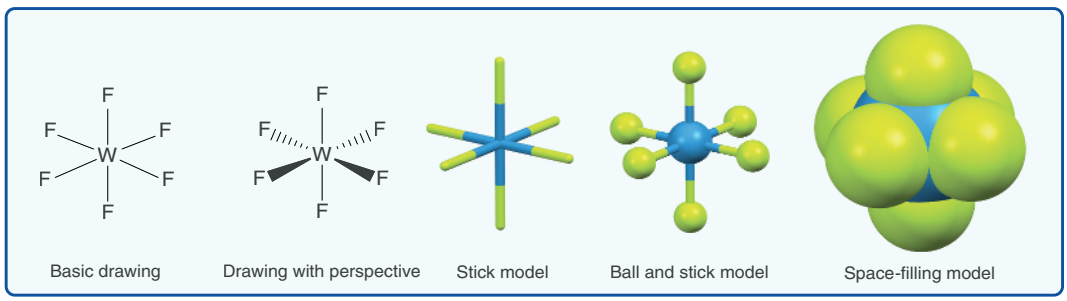

Figure 1.6
Drawings of the tungsten(VI) hexafluoride complex in (from right to left) space-filling, ball-and-stick, stick, perspective line drawing and basic line drawing modes.

shown in Figure 1.6 has two-coloured boundaries that reflect the covalent radii in the space-filling model. However, this is not strictly necessary, and a single-coloured bond is both sufficient and as appropriate in terms of the nature of the coordinate bond, where the bonding electron pair originates from one bond partner. As it happens, this type of drawing has similarities in terms of appearance to the views of complexes shown in structures determined experimentally by X-ray crystallography (see Chapter 7.3.8), where the atomic positions are defined in terms of probabilities (Heisenberg's Uncertainty Principle strikes again); this technique will be addressed in Chapter 7. More commonly, line drawings are used to represent a complex, either drawn with perspective to thus address both molecular bonding and shape, or else drawn as simple representations where bonds are defined but shape must be inferred. You shall meet several approaches to drawing complexes in this book but remember that they are simply conventional and related ways of defining a complex species.

In the rest of this book, we will be examining in more detail ligands, metal–ligand assembly and the consequences. These include molecular shape, bonding models, stability, properties and how we can measure and interpret these. Furthermore, we will look at metal complexes that occur in Nature and find application in commerce and speculate on future developments. 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 covalent 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 may be considered 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 behaviour 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.

Regardless of origin, natural or synthetic, the basic rules of chemistry applying to metal complexes are a constant, supporting measurement, interpretation and modelling of properties and behaviour.

Further Reading

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

Blackman, A., Bottle, S., Schmid, S., Mocerino, M., and Wille, U. (2022). *Chemistry*, 5th ed. Melbourne: Wiley.
An introductory general chemistry textbook appropriate for reviewing basic concepts, that covers all fields of chemistry.

Gillespie, R.J. and Popelier, P.L.A. (2002). *Chemical Bonding and Molecular Geometry*. Oxford: Oxford University Press.

A venerable but still appropriate coverage from the fundamental level upward of various models of molecular bonding.

Housecroft, C.E. and Sharpe, A.G. (2012). *Inorganic Chemistry*, 4th ed. Harlow, UK: Pearson Education.

Of the large and sometimes daunting general advanced textbooks on inorganic chemistry, this is an enduring, finely written and well-illustrated example, useful as a resource book.

Jackson, T. (2020). *The Periodic Table. A Visual Guide to the Elements*. London: Aurum Press.

This is an entertaining and easy-to-read book by a science writer, rather than a scientist, and is an accessible entry level route to basic information.