The starting point is the study of color and its effects on men [Wassily Kandinsky (1912), *Concerning the Spiritual in Art*]

**EARLY DEVELOPMENTS IN INORGANIC CHEMISTRY**

Ask any inorganic chemist just why he or she entered the field and more often than not, the answer will be “color!” People have long been captivated by the magnificent colors of inorganic compounds. As early as 15,000 BC, cave painters used iron oxides for sources of yellows and reds, aluminum silicates for greens, and manganese oxide for browns. By 3000 BC, Egyptian and Syrian artisans and jewelers were staining metal surfaces with inorganic salts derived from ground minerals and alloys. The colors obtained depended mostly on the types of transition metals contained in the minerals and on their combinations. Soon synthetic pigments were developed as well. One of the first, Egyptian Blue, CaCuSi_{4}O_{10}, was prepared by heating malachite/sand (quartz or silica) mixtures to temperatures of 800–900 °C. Later in the fifteenth to eighteenth centuries, metal-containing pigments such as copper carbonate and the brilliant ferric ferrocyanide coordination complex, Prussian Blue, Fe_{4}[Fe(CN)_{6}]_{3}, were synthesized for use in the textile industry (Fig. 1.1). Iron oxides, lead chromates, and the ubiquitous white pigment, titanium dioxide, are just a few of the many inorganic compounds that are still important in this industry today.

The beauty of inorganic chemistry lies in the fact that minute changes in a metal ion environment induce dramatic changes in color. The fact that easily noted changes in color signify chemical and sometimes physical change was critical to the development of the field of chemistry. Even before the establishment of the modern science of chemistry, early metallurgists and alchemists relied on color change as a positive step toward what they believed was the transformation of base metals, primarily into gold. They documented procedures that included the manipulation of mixtures of lead, tin, copper, and iron through a series of black, white, yellow, and purple stages. During the sixteenth and seventeenth centuries, careful quantitative studies of color change brought forth new views on the nature of matter that gave birth to modern chemistry. The heating of mercury metal in the presence of air, for example, forms a red calx (mercury
oxide), which can subsequently be returned to the original metal by heating. In 1778, Antoine Lavoisier showed that this color change was caused by the addition and removal of oxygen at the metal center. In 1788, French chemist Joseph-Louis Proust argued that colors in alloys were a result of constituents in fixed and definite proportions, leading to his law of definite proportions. Between 1790 and 1830 geologists discovered a vast number of naturally occurring inorganic mineral types; and Swedish chemist Jöns Jakob Berzelius alone prepared, purified and analyzed over 2000 inorganic compounds in just 10 years. A few representative inorganic compounds and their colors are given in Table 1.1. Notice how switching the metal from copper to gold in the metal hydroxide \([\text{M(OH)}]_3\) compounds changes the observed color from yellow to dark violet. Likewise, replacing iodides in the yellow \(\text{PbI}_2\) with oxygen or sulfur changes the colors to brown or black, respectively. The colors of these common naturally occurring minerals are earth tones. Chemists have produced their most vibrant colors, however, by manipulating the metal ion environment in compounds known as complex ions.

**TABLE 1.1 Some Inorganic Compounds and Their Colors**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Compound</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Co(OH)}_3)</td>
<td>Black</td>
<td>(\text{PbI}_2)</td>
<td>Yellow</td>
</tr>
<tr>
<td>(\text{Cu(OH)})</td>
<td>Yellow</td>
<td>(\text{PbO}_2)</td>
<td>Brown</td>
</tr>
<tr>
<td>(\text{Cu}_2\text{O})</td>
<td>Red</td>
<td>(\text{PbS})</td>
<td>Black</td>
</tr>
<tr>
<td>(\text{Cu}_2\text{S})</td>
<td>Black</td>
<td>(\text{HgO})</td>
<td>Yellow or red</td>
</tr>
<tr>
<td>(\text{Au(OH)}_3)</td>
<td>Yellow-brown</td>
<td>(\text{Hg}_2\text{O})</td>
<td>Brown-black</td>
</tr>
<tr>
<td>(\text{AuOH})</td>
<td>Dark violet</td>
<td>(\text{Hg}_2\text{I}_2)</td>
<td>Yellow</td>
</tr>
<tr>
<td>(\text{Fe(OH)}_3)</td>
<td>Red-brown</td>
<td>(\text{HgICl})</td>
<td>Red</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{S}_3)</td>
<td>Dark green</td>
<td>(\text{Ag}_3\text{AsO}_4)</td>
<td>Dark red</td>
</tr>
<tr>
<td>(\text{FeS})</td>
<td>Black</td>
<td>(\text{Ag}_3\text{AsO}_3)</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

**COMPLEX IONS**

Although Prussian Blue, synthesized in 1704, was the first officially recognized metal coordination complex to be made, discovery of this group of transition metal complex ions is often credited to Taessert, who in 1798 prepared the first known cobalt ammonia salts. His work inspired a revolution in inorganic chemistry. At the turn of the nineteenth century, amidst the flourishing developments of organic chemistry, the striking colors
of the metal ammines and their unusual characteristics\(^1\) piqued the interest of chemists, resulting in the synthesis of a plethora of metal ammine complexes over the next 50 years. In 1852, French chemist Edmond Frémy put forth a color-based naming scheme for these complexes, shown in Table 1.2. Unfortunately, this scheme has its limitations; for example, the cobalt complexes, Co(NO\(_2\))\(_3\)\(\cdot4\)NH\(_3\) and CoCl\(_3\)\(\cdot6\)NH\(_3\), though both are yellow, bear unrelated names. To further this scheme of confusion, Co(NO\(_2\))\(_3\)\(\cdot4\)NH\(_3\) can be either yellow or brown. One can quickly see the shortcomings of Frémy’s color-based nomenclature.

As new complex ions were synthesized, several bonding theories were postulated and rejected. The two most convincing theories, “the Blomstrand–Jorgensen chain theory” and “coordination theory” proposed by Alfred Werner, were debated extensively (a subject taken up in detail in Chapter 2) and it was coordination theory that eventually proved to be correct, winning Werner the Nobel Prize in 1913.

Thanks to Werner, the nature of complex ions is no longer as complex as it used to seem. A complex ion is a species that contains a central metal ion (M), surrounded by ions or molecules, called ligands (L) (Fig. 1.2). Although partial substitution may take place at the metal center, the complex tends to retain its identity in solution. Werner pointed out that complex ions, now termed metal complexes, have two valences: the primary valence is the charge of the metal ion itself (the oxidation state of the metal, \(n^+\)) and the secondary valence is the number of ligands bound to the metal. Werner noted that, unlike carbon, metal complexes can possess a maximum number of bound ligands beyond their primary valence. The total charge on the metal complex is the sum of the metal ion charge and the ligand charges. If the overall charge is not zero, it is balanced by counterions to give an overall neutral species. Although the early ambiguous formulations for the cobalt ammines in Table 1.2 could be found in texts as late as the mid-1950s, they have since been replaced by modern formulas to reflect the nature of bonding. As an example, consider the yellow croceo complex, Co(NO\(_2\))\(_3\)\(\cdot4\)NH\(_3\). The modern formula, \(\text{trans-[Co(NH}_3)_4(NO_2)_2]NO_2\), gives the spatial relationship of the atoms in this octahedral complex: the complex cation consists of a cobalt ion surrounded by four NH\(_3\) molecules in one plane and two NO\(_2\) ions situated 180° apart from each other (\(\text{trans}\) terminology). Because the counterion balancing the charge on the cation is NO\(_2\), the overall charge on the complex cation is +1; thus the cobalt center contributes +3 charge. The structure of this complex is shown in Figure 1.3(a). The \(\text{cis}\) form of the complex

---

\(^1\)Chemists found it odd that two stable compounds, CoCl\(_3\) and NH\(_3\), with seemingly saturated valences, combined to form a new stable compound. This reactivity was very different from that of carbon.
[Fig. 1.3(b)] places the coordinating NO$_2^-$ ligands orthogonal (90° angles) to each other. This seemingly simple change in ligand arrangement results in a color change from yellow to brown. Color change resulting from such geometric isomerism was critical to Werner’s first predictions of metal complex molecular geometry (Chapter 2).

Ligands bind to the metal center through electron pair donation [Fig. 1.3(b)]. This type of coordinate bonding was first put forth in 1922 by Maurice L. Huggins, an undergraduate student of Gilbert N. Lewis, and was expanded upon by Thomas M. Lowry. In 1927, Nevil V. Sidgwick applied coordinate bonding to metal complexes. Ligands, then, are Lewis bases (electron pair donors) and metals are Lewis acids (electron pair acceptors). This bond type [Fig. 1.3(b)] gives metal complexes their name, coordination complexes, which was a term actually first used by Werner.

The ligand number—or coordination number—varies depending on the nature of the metal ion, as well as on the nature of the ligand. With a given number of ligands, each metal complex adopts one of a number of energetically favorable geometries. A metal complex of coordination number 6, for example, adopts an octahedral shape. The octahedral configuration for a series of hexammonium compounds, first predicted by Werner, was confirmed by X-ray analysis by the early 1920s. The topic of metal complex geometry is explored in Chapter 3 using the geometrically versatile nickel(II) ion.

The robust nature of Werner’s original cobalt(III) ammine complexes enabled him to purify, isolate and study the solution chemistry of these complexes. (Robust complexes have a complex ion—metal and the primary coordination sphere ligands—that remains as one entity in solution.) The ability of a metal complex to resist decomposition by water or dilute acids was recognized early on; it is still a qualitative measure of stability today. One of the first chemists to quantitatively measure metal complex stabilities (stability constants) was Danish chemist Jannik Bjerrum, who published his Ph.D. dissertation on the formation of metal ammines in aqueous solution in 1940. His work suggested that important factors governing stability and coordination number include ligand polarizability and structure, and metal ion electron configuration and size. It was understood that electronegativity differences between the electropositive metal and its electron donating ligand led to an unequal sharing of electrons and a polar covalent bond, yet in his day, the extent of electron sharing was still unknown.

![Figure 1.2](image1.png)

Figure 1.2  (a) Schematic of the octahedral complex and (b) the M–L coordinate bond.

![Figure 1.3](image2.png)

Figure 1.3  Yellow trans- (a) and brown cis-(b) [Co(NH$_3$)$_3$(NO$_2$)$_2$]NO$_2$. 

EXPERIMENTAL INORGANIC CHEMISTRY: A HISTORY OF DAZZLING COLOR!
Valence Bond Theory

Soon after the development of the quantum mechanical model of the atom, physicists such as John H. van Vleck (1928) began to investigate a wave-mechanical concept of the chemical bond. The electronic theories of valency, polarity, quantum numbers, and electron distributions in atoms were described, and the valence bond approximation, which depicts covalent bonding in molecules, was built upon these principles. In 1939, Linus Pauling’s “Nature of the Chemical Bond” offered valence bond theory (VBT) as a plausible explanation for bonding in transition metal complexes. His application of VBT to transition metal complexes was supported by Bjerrum’s work on stability that suggested electrostatics alone could not account for all bonding characteristics.

Although VBT is no longer a popular way to describe bonding in transition metal complexes, its historical importance requires discussion. In this model low-lying, empty $d$ orbitals of transition metals (as with nontransition elements) are combined with appropriate $s$ and $p$ orbitals to form new hybrid orbitals that accept ligand electron pairs to form a coordinate covalent bond. Such a hybridization scheme for Werner’s octahedral, $[\text{Co(NH}_3\text{)}_6]^{3+}$ complex is shown below. Magnetic studies revealed $[\text{Co(NH}_3\text{)}_6]^{3+}$ to be a diamagnetic (having no unpaired electrons) complex and, therefore, the six valence $d$ electrons of cobalt(III) are paired in three $d$ orbitals, leaving the other two $d$ orbitals to form six $d^2sp^3$ hybrids (Fig. 1.4).

The paramagnetic (having unpaired electrons) octahedral cobalt(III) complex, $\text{CoF}_6^{2-}$, however, required hybridization of the $4s$, $4p$, and $4d$ orbitals. VBT could not explain this inconsistency. Further, although VBT accounted for the observed geometry, it could not predict geometry.

Magnetism and geometry were not the only two properties VBT could not predict: metal complex color also eluded this theory. Postulates put forth by Caven and Lander in 1939, which attributed the relationship of color and complex structure to “a looseness or an unsaturation in the electronic structures,” or as Fajans stated, “a constraint or deformation of the electron systems of the co-ordinated molecules,” could not be adequately explained, but because of Pauling’s influence in the field, VBT was used by coordination chemists through the mid-1950s.

Crystal Field Theory

In 1951, chemists trying to make sense of metal complex optical spectra and color returned to an emphasis on the ionic nature of the coordinate covalent bond. Coordination chemists rediscovered physicists Hans Bethe’s and John van Vleck’s crystal field theory (CFT),
which accounted nicely for color and magnetic properties of crystalline solids. In contrast to VBT, CFT is an electrostatic model that ignores covalency in bonding and considers the metal ligand bond to be completely ionic. CFT thus takes a purely electrostatic approach to bonding and—though this is not fully realistic—this model is relatively successful at explaining many transition metal complex properties including color. CFT assumes:

- $d$ electrons do not participate in bonding;
- ligands are point charges;
- metal–ligand bonds are purely electrostatic.

Although the following discussion focuses on CFT as applied to octahedral complexes exclusively, other geometries can be treated similarly. Recall the spatial representations of the five $d$-orbitals (Fig. 1.5). In an isolated gaseous ion (no ligands), these orbitals all have the same energy (i.e., are degenerate) and, when combined, form a spherical field of electron density about the metal ion. Placing ligands (represented as point charges) along the $x$, $y$, and $z$ axes forms an octahedral ligand field around the metal ion. This ligand interaction splits the orbitals into two with higher energy ($d_{x^2-y^2}$, $d_{z^2}$) and three of lower energy ($d_{xy}$, $d_{xz}$, $d_{yz}$). From group theory these are labeled $e_g$ and $t_{2g}$, respectively, as seen in Figure 1.6. The orbitals are separated by an amount of energy, $\Delta_o$ (10 Dq), the crystal field splitting energy. The two $e_g$ orbitals are repelled ($+$) by 0.6$\Delta_o$ while the three $t_{2g}$ orbitals are stabilized ($-$) by 0.4$\Delta_o$ relative to the gas phase isolated ion (see Fig. 1.6). This preservation of the barycenter is common to all metal complexes despite geometry. These values are used to calculate the crystal field stabilization energy (CFSE) for a particular configuration.

For a $d^4t_{2g}^3e_g^1$ configuration in an octahedral field for example, the CFSE is:

$$(3)(-0.4\Delta_o) + (1)(+0.6\Delta_o) = -0.6\Delta_o$$

A $d^4$ metal ion is therefore stabilized by 0.6$\Delta_o$ in this configuration.

![Figure 1.5](image_url)  
**Figure 1.5** Interactions of the metal ion $d$ orbitals with ligands, •, in an octahedral field.
Electrons fill the metal ion orbitals according to Hund’s rule, but for $d^4$, $d^5$, $d^6$, and $d^7$ electronic configurations, electrons may fill the orbitals two different ways, resulting in high and low spin states. For example, in the case of $d^6$ cobalt(III), three electrons are immediately placed in the lower three $t_2g$ orbitals. The fourth electron can either enter the higher energy $e_g$ orbital, or pair with a $t_2g$ orbital electron. Whether the former or latter occurs depends on the relative expense (in terms of overall energy) to pair the electrons (strong field, “low spin” case) vs putting them in the unfavorable $e_g$ orbitals (weak field, “high spin” case). For a $d^6$ ion, the high spin ($t_{2g}^4e_g^2$) case yields:

$$\text{CFSE} = (4)(-0.4\Delta_o) + (2)(+0.6\Delta_o) = -0.4\Delta_o$$

Note that there is no pairing energy, $P$, since the CFSE is the pairing difference between the ground state ion (no ligands) and the ion in the metal complex. Calculating the CFSE for a low spin ($t_{2g}^6$) case yields a stabilization energy of $-2.4\Delta_o + 2P$. When the $\Delta_o$ term is greater than the $P$ term, the low spin state case is very favorable.

One of the factors governing the magnitude of $\Delta_o$ is the nature of the bound ligands. For a metal ion, the field strength increases according to the spectrochemical series:

- **Weak**
  
  $I^- < Br^- < SCN^- < Cl^- < N_3^- < F^- < H_2NC(O)NH_2, OH^- < \text{ox}^{2-}, \text{O}^{2-} < H_2O$
  
  $< \text{NCS}^- < \text{py}, \text{NH}_3 < \text{en} < \text{bpy}, \text{phen} < \text{NO}_2^- < \text{CH}_3^- < C_6H_5^- < \text{CN}^-, \text{CO}$

- **Strong**

Here CO and CN$^-$ are strong field ligands and $I^-$ is the weakest. The spectrochemical series explains why Co(NH$_3$)$_6^{3+}$ is low spin and diamagnetic while CoF$_6^{3-}$ is high spin and paramagnetic. Further, CFT as applied to coordination number 4 also explains nicely why many $d^2$ and $d^8$ complexes adopt a square planar over a tetrahedral geometry. Other factors affecting the crystal field splitting energy are oxidation state and row placement (principle quantum number) in the periodic table.

CFT is powerful in that it can be used to explain thermodynamic properties (Chapter 3), reactivity (Chapters 4 and 5) and color of metal complexes, as we will see below. However, as a model for bonding, it is not fully realistic. The spectrochemical series, for example, indicates that ligands such as CO cause a greater $\Delta_o$ (because of greater repulsion) than the small, negatively charged F$^-$ and suggests that both ionic and covalent forces are important in transition metal bonding.
Molecular orbital theory (MOT), a quantum mechanical treatment of molecules that considers valence orbitals in chemical bonds for the analysis of electronic structural properties, when applied to transition metal complexes, is referred to as ligand field theory (LFT). LFT, unlike CFT, emphasizes the interaction of metal d valence orbitals with appropriate ligand orbitals, accounting for both covalency and ionicity in the bonding interactions and providing a more accurate description of the metal–ligand bond. For example, LFT indicates that pi-bonding capabilities of ligands at the high end of the spectrochemical series (CO) are responsible for the large increase in \( \Delta_\text{o} \). Discussion using LFT is similar to CFT; however, molecular orbital diagrams replace the simplified CFT diagram and the energy of stabilization is then referred to as ligand field stabilization energy (LFSE) instead of CFSE. By the mid-1960s coordination chemists had fully adopted the molecular orbital approach and our present computational methods are based on MOT. Some of these methods will be explored in Chapters 3 and 4 and in select advanced chapters.

**ORIGIN OF COLOR IN TRANSITION METAL COORDINATION COMPLEXES**

Almost every metal ion forms coordination compounds with an accompanying color change (Table 1.3), and one of the great accomplishments of CFT is that it explains the origin of colors in transition metal complexes. We now know that changes in covalency, ligating atoms/molecules, ion packing (structure and impurities), and oxidation state give

<table>
<thead>
<tr>
<th>Aqueous Ion</th>
<th>Color</th>
<th>Aqueous Ion</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(H(_2)O(_6))(^{2+})</td>
<td>Blue</td>
<td>Fe(CN)(_6)(^{3-})</td>
<td>Yellow</td>
</tr>
<tr>
<td>Cr(H(_2)O(_6))(^{3+})</td>
<td>Blue-violet</td>
<td>Fe(CN)(_6)(^{4-})</td>
<td>Red</td>
</tr>
<tr>
<td>Cr(_2)O(_4)(^{2-})</td>
<td>Orange</td>
<td>FeCNS(_2)(^{3+})</td>
<td>Red</td>
</tr>
<tr>
<td>Fe(H(_2)O(_6))(^{2+})</td>
<td>Pale blue-green</td>
<td>FeOH(^{2-})</td>
<td>Yellow</td>
</tr>
<tr>
<td>Fe(H(_2)O(_6))(^{3+})</td>
<td>Pale violet</td>
<td>VO(_2)Cl(^{-})</td>
<td>Yellow</td>
</tr>
<tr>
<td>FeO(_2)(^{2-})</td>
<td>Purple</td>
<td>VS(_2)(^{-})</td>
<td>Black</td>
</tr>
<tr>
<td>Cr(CN)(_6)(^{3-})</td>
<td>Yellow</td>
<td>Ti(H(_2)O(_6))(^{3+})</td>
<td>Purple</td>
</tr>
<tr>
<td>Co(NH(_3))(_6)(^{3+})</td>
<td>Orange-yellow</td>
<td>Co(H(_2)O(_6))(^{2+})</td>
<td>Red</td>
</tr>
<tr>
<td>Co(NH(_3))(_3)H(_2)O(^{3+})</td>
<td>Brick-red</td>
<td>V(H(_2)O(_6))(^{2+})</td>
<td>Violet</td>
</tr>
<tr>
<td>Co(NH(_3))(_3)Cl(^{2+})</td>
<td>Violet-red</td>
<td>V(H(_2)O(_6))(^{3+})</td>
<td>Green</td>
</tr>
<tr>
<td>Ni(NH(_3))(_6)(^{2+})</td>
<td>Violet-blue</td>
<td>VO(^{2+})</td>
<td>Blue</td>
</tr>
<tr>
<td>Ni(NO(_2))(_2)(^{2-})</td>
<td>Yellow</td>
<td>VO(_2)(^{-})</td>
<td>Yellow</td>
</tr>
<tr>
<td>Mn(H(_2)O(_6))(^{2+})</td>
<td>Pale rose</td>
<td>Mn(CN)(_6)(^{5-})</td>
<td>Colorless</td>
</tr>
<tr>
<td>MnO(_2)(^{-})</td>
<td>Blue</td>
<td>Mn(CN)(_6)(^{4-})</td>
<td>Blue</td>
</tr>
<tr>
<td>MnO(_2)(^{2-})</td>
<td>Green</td>
<td>Mn(CN)(_6)(^{3-})</td>
<td>Red</td>
</tr>
<tr>
<td>MnO(_2)(^{-})</td>
<td>Purple</td>
<td>PtCl(_2)(^{-})</td>
<td>Yellow</td>
</tr>
<tr>
<td>Ni(H(_2)O(_6))(^{2+})</td>
<td>Green</td>
<td>PtL(_2)(^{2-})</td>
<td>Black</td>
</tr>
<tr>
<td>Pt(H(_2)O(_4))(^{2+})</td>
<td>Yellow</td>
<td>Pt(NO(_2))(_4)(^{2-})</td>
<td>Colorless</td>
</tr>
</tbody>
</table>

*Denotes denticity refers to the number of atoms that can simultaneously bind to one metal center.*
rise to different colors in transition metal systems because such changes alter the energy gap, $\Delta$, between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in a transition metal complex. The energy gap, $\Delta$, is related to the energy, $E$, in Planck’s equation (1.1):

$$\Delta \approx E = \frac{hc}{\lambda}$$  

Absorption of light of visible wavelength promotes an electronic transition as shown for the $d^1$ case in Figure 1.7. The light that is not absorbed is that which is transmitted and what we observe, giving a metal complex its characteristic color. Using CFT, we can understand just how changes in the environment of a metal ion (including ligands and geometry) can modify the orbital energies and therefore its color. Chapters 2–5 cover aspects of visible spectroscopy more fully.

**COORDINATION COMPLEX REACTIVITY**

**Substitution Reactions**

Even back in 1912, Werner was keenly aware of the need to understand metal complex substitution. Stereochemical changes [e.g., cis–trans conversions, equation (1.2)] in cobalt(III) complexes were critical to the development of his coordination theory and he sought to understand how these occurred.

$$\text{trans-}[\text{Co(en)}_2\text{Cl}_2]^+ \rightarrow \text{cis-}[\text{Co(en)}_2\text{NH}_3\text{Cl}]^{2+}$$  

Werner, in 1912, concluded: “when such a molecule (in the second sphere) gets included in the first sphere an acid group becomes transferred from the first sphere into the second.” Werner’s proposed mechanism for this type of rearrangement is shown in Figure 1.8. The ethylenediamine ligand in the cobalt complex is known as a chelating ligand, which is a molecule that binds the metal using two or more donating atoms.

There are many other reasons why coordination chemists study substitution kinetics, one of the most common being that substitution provides a route for the synthesis of new coordination complexes. The synthesis of $[\text{Co(en)}_3]^3+$ from Werner’s purpureo complex, $[\text{Co(NH}_3)_2\text{Cl}]^+$, by ethylenediamine substitution, equation (1.3), and the synthesis of $[\text{Cu(NH}_3)_4]^{2+}$ by $\text{NH}_3$ substitution of the aqua complex, $[\text{Cu(H}_2\text{O})_4]^{2+}$, equation (1.4), are two notable examples.
The reaction in equation (1.3) involving cobalt(III) is very slow at room temperature (the reaction must be heated to take place), while that in equation (1.4) involving copper(II) is rapid at room temperature, despite similar NH₃ group ligation. The substitution rates depend markedly on the nature of the metal ion.

Nobel prize-winning coordination chemist Henry Taube defined substitution in 1951 as a net process in which one group coordinated to the central ion is replaced by another, without change in oxidation state for any of the atoms participating, and systematically compiled all known rate data. Taube noted how, along with the nature of the central metal ion, variations in the properties of the entering group, the group being replaced, and the remaining groups bound to the central atom affect the rate of reaction.

Years of experience led to a general classification of substitution reactions. The mechanism nomenclature of the 1950s and early 1960s, which was consistent with that of organic chemistry (S_N1, S_N2, etc.), was replaced by stochiometric mechanisms—associative (A), dissociative (D), associative interchange (I_a), and dissociative interchange (I_d)—by Harry Gray and Cooper H. Langford in their 1966 publication, *Ligand Substitution Processes*. General schemes for these mechanisms are noted below in equations (1.5)–(1.7).

\[
\begin{align*}
[\text{Co(NH}_3)_3\text{Cl]}^{2+} + 3\text{en} & \rightarrow [\text{Co(en)}_3]^3+ + 5\text{NH}_3 + \text{Cl}^- & \text{purple} \\
[\text{Cu(H}_2\text{O})_4]^{2+} + 4\text{NH}_3 & \rightarrow [\text{Cu(NH}_3)_4]^{2+} + 4\text{H}_2\text{O} & \text{blue}
\end{align*}
\]

Figure 1.8  Werner’s proposed mechanism for *trans* to *cis* rearrangement upon substitution.

\[
\begin{align*}
\text{MX}_n & \xrightleftharpoons[-X]{+X} \text{MX}_{n-1} \\
\text{MX}_n & \xrightleftharpoons[-Y]{+Y} \text{MX}_{n-1} \text{Y}
\end{align*}
\]

\[
\begin{align*}
\text{Y} \cdots \rightarrow \text{MX}_{n-1} \cdots \rightarrow \text{X}
\end{align*}
\]
The D and A pathways proceed through intermediates of reduced and increased coordination numbers, respectively. The I mechanisms are characterized by the lack of an intermediate with a modified metal ion coordination number in the reaction. When bond breaking is more important than bond making the mechanism is I_d; the transition state has a reduced coordination number. In an I_a mechanism bond making is more important than bond breaking; the transition state has an increased coordination number.

The importance of substitution reactions cannot be overstated. Systematic investigations of coordination compound substitution kinetics, and mechanisms shed light on the electronic structure of compounds and on their interactions. Although formally taken up in Chapter 4, substitution is encountered in all chapters of this book.

**Electron Transfer Reactions**

Valence \( d \) electrons of transition metals impart special properties (e.g., color and substitution reactivity) to coordination complexes. These valence electrons can also be removed completely from (oxidation) or added to (reduction) metal \( d \) orbitals with relative facility. Such oxidation—reduction (redox) reactions, like substitution reactions, are integral to metal complex reactivity. Consider the role of redox chemistry in the synthesis of \([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}\), equation (1.8). In general, the preparation of cobalt(III) complexes (Chapters 2 and 5) starts with substitutionally labile cobalt(II) salts that are combined with appropriate ligands with subsequent oxidation of the metal by \( \text{H}_2\text{O}_2 \) or \( \text{O}_2 \) to the substitutionally inert (robust) \( \text{Co}^{3+} \) state.

\[
\text{[Co(H}_2\text{O})_6]^{2+}_{\text{pink(aq)}} + \text{NH}_3, \text{NH}_4\text{Cl} \rightarrow \text{H}_2\text{O}_2 \text{ or } \text{O}_2 \rightarrow \text{[Co(NH}_3\text{)}_5\text{Cl]}^{2+}_{\text{purple(aq)}} \quad (1.8)
\]

Equation (1.8) also shows how redox reactions are intricately linked to substitution. As Taube stated in his Nobel lecture: “While substitution reactions can be discussed without concern for oxidation reduction reactions, the reverse is not true.” The substitution properties of both cobalt(III) and cobalt(II) metal ions provides the rationale for this synthetic methodology.

The study of electron transfer reactions began in earnest when radioactive isotopes, produced for nuclear research and the atom bomb program during World War II, became accessible. Glen Seaborg, in a 1940 review of artificial radioactivity, noted the first attempt to measure the self-exchange reaction between aqueous iron(III) and iron(II), equation (1.9).†

\[
[\text{Fe(aq)}]^{2+}_{\text{colorless}} + [\text{Fe(aq)}]^{3+}_{\text{yellow}} \rightarrow [\text{Fe(aq)}]^{3+}_{\text{yellow}} + [\text{Fe(aq)}]^{2+}_{\text{colorless}} \quad (1.9)
\]

By 1950, such isotopic tracer methods began to revolutionize the study of redox reactions as color alone could not always be used to distinguish product formation; see equation (1.9). The importance of \( \text{H}^+ \) and other ions on electron transfer rates was soon discovered. A symposium on electron transfer took place in 1951 at the University of Notre Dame, during which a distinction between outer- and inner-sphere electron transfer was made.

---

†Equation (1.9) is an example of a “self-exchange” electron transfer reaction for which \( \Delta G^o = 0 \). One cannot tell the difference between reactant and product by color alone, hence the need for isotopic labeling indicated by the asterisk.
In 1954, King and Taube published the 1980 Nobel Prize winning work that defined these two different types of electron transfer reactions. In an inner-sphere mechanism, the atoms undergoing redox form bonds to a common atom (or small group of atoms), which then serves as a bridge for electron transfer (ISPC = inner-sphere precursor complex and $k_{et} =$ electron transfer rate constant).

\[
\begin{align*}
A_{\text{red}} - X + B_{\text{ox}}^0 & \rightleftharpoons A_{\text{red}}^{0} - X - B_{\text{red}}^0 \quad \text{ISPC} \\
A_{\text{red}} - X - B_{\text{ox}}^0 & \rightarrow A_{\text{ox}} - X - B_{\text{red}}^0 \\
A_{\text{ox}}^0 - X - B_{\text{red}}^0 & \rightarrow A_{\text{ox}}^0 + X - B_{\text{red}}^0 \\
\text{or } A_{\text{ox}}^0 + B_{\text{red}}^0
\end{align*}
\]

The bridging group, X, does not necessarily transfer from A to B; however, if this happens, it is strong evidence that an inner-sphere reaction has taken place. Indeed, this sort of evidence was how Taube first solved the puzzle. In the reduction of $[\text{Co(NH}_3)_5\text{Cl}]^{2+}$ by $[\text{Cr(H}_2\text{O}_6]^3^+$, the $\text{Cl}^-\text{Cl}^2^+$ on the inert cobalt(III) complex readily displaces a $\text{H}_2\text{O}$ molecule at the labile chromium(II) center to form the bridged species:

\[
[(\text{H}_3\text{N})_5\text{Co}^-\text{Cl}^-\text{Cr(OH}_2)^5]^{4+}
\]

Electron transfer from the chromium(II) center to the cobalt(III) center within this inner-sphere precursor complex results in a labile cobalt(II) center and inert chromium(III) center. Concurrent with electron transfer, atom transfer ($\text{Cl}^-\text{Cl}^2^+$) also takes place as $\text{Cl}^-$ remains bound to the inert chromium(III) center to yield $[\text{ClCr(OH}_2)^5]^2^+$ and \"$[(\text{H}_3\text{N})_5\text{Co}]^{2+}$\" decomposes to $[\text{Co(H}_2\text{O}_6]^2^+$, respectively. In 1961, Norman Sutin was able to provide direct mechanistic proof of atom transfer in the inner-sphere process by his introduction of the stopped-flow (rapid mixing) technique. The transition state in the inner-sphere process is relatively well defined, and because the kinetics are complex, the overall mechanism is also well defined.

The outer-sphere pathway is obtained when electron transfer is much faster than substitution, and electron transfer takes place through the intact coordination spheres of the reaction partners (OSPC = outer-sphere precursor complex):

\[
\begin{align*}
A_{\text{ox}}^0 + B_{\text{red}}^0 & \rightleftharpoons [A_{\text{ox}}^0, B_{\text{red}}^0] \quad \text{OSPC or ion pair} \\
[A_{\text{ox}}^0, B_{\text{red}}^0] & \rightarrow [A_{\text{ox}}^0, B_{\text{ox}}^0] \\
[A_{\text{red}}^0, B_{\text{ox}}^0] & \rightarrow A_{\text{red}}^0 + B_{\text{ox}}^0
\end{align*}
\]

Unlike the inner-sphere reaction, the kinetic simplicity of outer-sphere reactions makes it difficult to obtain mechanistic details about the reactants in the electron transfer process. Experimental investigations using optically active metal complexes, along with theoretical calculations pioneered by Rudolph Marcus, have shed light on factors governing outer-sphere electron transfer processes.

The rates of many electron transfer reactions have now been measured and, as new coordination complexes are prepared, characterized, and their solution properties studied, our understanding of fundamental structure (both geometric and electronic)–reactivity relationships continues to grow. Both inner- and outer-sphere reactions will be explored in Chapter 5.
APPLICATIONS OF COORDINATION COMPLEXES

As the fundamentals of coordination complex structure and reactivity were realized, new and exciting applications were discovered. In 1955, Ziegler and Natta and their coworkers developed a titanium-based catalyst, Figure 1.9, which catalyzes the polymerization of alkenes at atmospheric pressure and ambient temperature. The open coordination site allows an alkene ligand such as ethylene or propylene to bind to the Ti center, initiating the polymerization. Their work sparked tremendous interest in the field and garnered them the Nobel Prize in 1963.

In 1962 Max Perutz and John Kendrew earned the Nobel Prize for solving the crystal structures of metalloproteins myoglobin and hemoglobin. Central to function of these proteins is their iron heme coordination complex shown in Figure 1.10. The iron center serves to bind dioxygen, transporting and delivering this important life-sustaining molecule to all parts of the body.

Barnett Rosenberg, in 1969, serendipitously discovered the cytotoxic effects of cis-platin, Figure 1.11, a complex studied in Chapter 6. The area of metals in medicine has grown so rapidly that new journals and conferences dedicated solely to this topic now flourish.

Figure 1.9 The Ziegler–Natta TiCl₄ catalyst.

Figure 1.10 An iron heme complex.
Applications and roles for new metal coordination complexes continue to be discovered daily. Coordination complexes in the development of new architectural materials such as nanostructures and in environmental applications (e.g., “green” catalysts and bioremediation; Chapter 7) are on the frontiers of inorganic chemistry in the twenty-first century; however, even these exciting and splashy new systems remain governed by the fundamentals of metal ion chemistry. Advancements in applied fields cannot be fully realized without the knowledge imparted by pure and basic research, especially as metal ions are placed in novel environments.

ASPECTS OF INORGANIC SYNTHESIS—GOVERNING FACTORS

Why do inorganic chemists prepare new compounds? One reason is simple curiosity! The synthesis of the many fascinating borohydrides (B_xH_y), for example, came about when, in 1912, Alfred Stock speculated whether boron could form a variety of compounds similar to carbon, its neighbor on the periodic table. New syntheses also emerge by accident or chance coupled with astute observation. The anticancer agent, cis-platin (Chapter 6), discovered by Rosenberg in 1969, is such an example. Other complexes are designed and synthesized to fulfill a particular need. Many metal coordination complex catalysts have been designed to carry out specific organic reactions (Chapter 9), and other metal systems have been designed to recognize and bind specific biological targets (Chapter 8). Chemists sometimes synthesize new compounds to test theories. Alfred Werner synthesized many new metal complexes in support of his coordination complex bonding theory, including an optically active complex free of carbon. In fact, a combination of curiosity and desire to test theory is what inspired both Alfred Werner and Danish chemist, Sophus Jørgensen, the chemist who laid down the groundwork for Werner’s contributions, to study metal ammine complexes (Chapter 2).

Synthesis: An Interplay Between Thermodynamics and Kinetics

Just like any other chemical reactions, synthetic reactions adhere to the principles of thermodynamics: the study of energy and its interconversions. Is your desired product thermodynamically stable (can it be made and will it exist at room temperature and atmosphere)? Will it be stable under your given synthetic conditions, including during and after isolation? Gibb’s free energy, ΔG, is our measure of the driving force for reactions, equation (1.10).

\[ \Delta G = -RT \ln Q = \Delta H - T \Delta S = -nFE \] (1.10)
When the reactants and products are at unit activity, equation (1.10) is expressed with standard state functions, equation (1.11):

$$
\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ = -nFE^\
$$

(1.11)

A general expression for metal complex formation is given in equation (1.12). The formation constant, $K_f$, reflects the thermodynamic feasibility of complex formation.

$$
M + L \rightleftharpoons ML \quad K_f = [ML]/[M][L] \quad (1.12)
$$

For example, the reaction of aqueous iron(III) with the hexadentate ligand, EDTA$^{4-}$, equation (1.13), has a log $K_f = 25.0$ (25 °C, 0.1 M ionic strength). The large equilibrium constant tells us that the reaction as written is expected to favor the FeEDTA$^{-}$ product (i.e., the product should be very stable under these conditions in solution)—and it does!

$$
Fe^{3+}(aq) + EDTA^{4-}(aq) \longrightarrow FeEDTA^- \quad K_f = 10^{25} \quad (1.13)
$$

Formation constants for many metal complexes have been compiled by Ramunas Motekaitis and Art Martell, and these as well as techniques for measuring them in the laboratory will be covered in Chapters 3 and 8. One can, however, predict the relative stability of a desired complex based on simple bonding theories. Crystal field theory, as well as the Irving–Williams series and Pearson’s hard–soft–acid–base theory (see the next section) enable us to predict what might happen in solution.

Knowing and understanding standard reduction potentials, $E^0$, also helps determine whether a particular oxidation state will be stable and appropriate oxidants and reductants to use in a synthetic scheme. In reviewing the cobalt complex syntheses in Chapters 2 and 6, for example, complex ions are formed by oxidizing cobalt(II) salts to the more stable $\text{+3}$ state.

Thermodynamic data only suggest whether a reaction is able to take place (i.e., if $\Delta G < 0$): They do not reveal how long it will take for the reaction to occur. Consequently, both thermodynamic and kinetic factors must be considered when devising a synthesis. Consider an example pertinent to the synthesis in Chapter 2. Thermodynamics predicts that $[\text{Co(NH}_3\text{)}_3\text{Cl}]^{2+}$ should be thermodynamically favorable compared with $[\text{Co(NH}_3\text{)}_6]^{3+}$, equation (1.14):

$$
[\text{Co(NH}_3\text{)}_3\text{]}^{3+} + \text{Cl}^- \rightleftharpoons [\text{Co(NH}_3\text{)}_3\text{Cl}]^{2+} + \text{NH}_3 \quad K = 2 \times 10^4 \quad (1.14)
$$

Although this reaction is thermodynamically favorable (large $K$), sluggish substitution at the cobalt(III) center of $[\text{Co(NH}_3\text{)}_3\text{]}^{3+}$ makes this reaction almost nonexistent under the given laboratory conditions. Vigorous conditions must be used, reinforcing the rule that simply knowing a reaction is thermodynamically favorable does not ensure that the reaction will be complete in a reasonable time frame. Alternatively, consider a metal complex that is thermodynamically stable but kinetically labile with respect to substitution at the metal center. Such a situation may hinder product isolation. The formation and rapid breakdown of the violeto complex, $cis$-[Co(NH$_3$)$_3$Cl$_2$]$^{+}$, for example, caused Werner considerable problems during his early defense of coordination theory, equation (1.15).
A successful synthesis may require careful manipulation of reaction temperature. The rate of a reaction depends on the activation energy, $E_a$ (the energy to reach the transition state) and this energy barrier, in turn, depends on temperature. The Arrhenius expression, equation (1.16), shows that the rate constant and, therefore, for most instances the rate, for a reaction will increase with an increase in temperature.

$$k = Ae^{-E_a/RT}$$

$$\ln k = -E_a/RT + \ln(A)$$

However, if a reaction is exothermic ($\Delta H < 0$), Le Chatelier’s principle states that increasing the temperature during the reaction will push the thermodynamic equilibrium towards reactants. The classic example of this dilemma is seen in the Haber synthesis of ammonia, equation (1.17).

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H^\circ = -92 \text{ kJ}$$

Although the equilibrium lies far to the right ($K \approx 10^6$), a large amount of energy ($E_a$) is required to break the $N_2$ triple bond. Because of the exothermicity, however, $K$ decreases significantly when the temperature is increased. The Haber process requires the use of an iron-based catalyst at 250 atm and $\sim 400 \degree C$.

**Acid–Base Chemistry (Hard–Soft–Acid–Base Theory)**

One of the simplest ways to predict the formation and stability of metal–ligand bonds is by using hard–soft–acid–base theory. In 1968, Ralph Pearson noted that some Lewis acids prefer first row donors (bases). These “class a” acids (or hard acids) include all ions from the $s$ block, other cations with charge $\geq +3$, and lighter transition metals with charges $\geq +1$ (Table 1.4). Other Lewis acids, “class b” acids, were shown to prefer second and third row donors. These soft acids include lower oxidation state metals (di- and monovalent metals), cations from the $p$ block with a charge $< +3$ and heavier transition metals with a charge $< +3$. The soft bases are characterized by high polarizability and low charge density. In general, hard acids prefer hard bases and are stabilized by ionic-type interactions while and soft acids prefer soft bases, stabilized by covalent-like bonds. As seen in Table 1.4, metal ions are potent Lewis acids.

Because most coordination complex syntheses are carried out in aqueous solution, the formation of metal hydroxides, equation (1.18), which are less substitutionally labile and are often insoluble, can pose substantial problems.

$$\text{M(H}_2\text{O)}^{n+} \rightarrow \text{M(OH)}^{(n-1)+} + \text{H}^+$$

†R. Bruce Martin (Inorg. Chim. Acta 1998, 283, 30–36) points out the limitations of HSAB theory, showing that metal ion stabilities correlate better with electron affinities than with hardness and softness. Still, this is a good qualitative general rule.
TABLE 1.4 Examples of Hard, Intermediate and Soft Acids and Bases

<table>
<thead>
<tr>
<th>Acids</th>
<th>Hard</th>
<th>Intermediate</th>
<th>Soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺, Li⁺, Na⁺, K⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Mn²⁺, Al³⁺, Sc³⁺, Ga³⁺, In³⁺, La³⁺, Ga³⁺, Cr³⁺, Co³⁺, Fe³⁺, Ni³⁺, As³⁺, Si⁴⁺, Ti⁴⁺, U⁴⁺, Ce³⁺, Sn⁴⁺, VO²⁺</td>
<td>Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Sn²⁺, Sb³⁺, Bi³⁺, Rh³⁺, Ir³⁺, Ru³⁺, Os³⁺</td>
<td>Cu⁺, Ag⁺, Au⁺, Ti⁺, Hg⁺, Pd⁺, Cd²⁺, Pt²⁺, Hg²⁺, Co(CN)₂⁻, Pt⁴⁺, Te⁴⁺</td>
<td></td>
</tr>
<tr>
<td>Bases</td>
<td>H₂O, OH⁻, F⁻, CH₃COO⁻, PO₄³⁻, SO₄²⁻, Cl⁻, ClO₄⁻, NO₃⁻, NH₃, RNH₂</td>
<td>C₂H₅NH₂, C₃H₇N, N₃⁻, R₂S, RSH, RS⁻, I⁻, SCN⁻, R₂P, CN⁻, RNC, CO, C₂H₄, C₆H₆, H⁺, R⁻</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 1.5 Acid Hydrolysis Constants (pKₐs) for Some Aquo Ions and Complex Metal Ions at 25 °C (Selected from Basolo and Pearson²² and pH Precipitation Ranges of Hydroxides or Hydrous Oxides (Adapted from Walton²³)

<table>
<thead>
<tr>
<th>Ion</th>
<th>pKₐ</th>
<th>Ppt Range</th>
<th>Ion</th>
<th>pKₐ</th>
<th>Ppt Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl⁺</td>
<td>13.2</td>
<td></td>
<td>Tl³⁺</td>
<td>2.2</td>
<td>0–2</td>
</tr>
<tr>
<td>Hg₂⁺</td>
<td>5.0</td>
<td></td>
<td>Cr³⁺</td>
<td>3.8</td>
<td>4–6</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>11.4</td>
<td>&gt;10</td>
<td>Co³⁺</td>
<td>0.7⁴</td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>12.6</td>
<td></td>
<td>Fe³⁺</td>
<td>2.2</td>
<td>2–4</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>13.2</td>
<td>(pKₐ₂ = 3.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>10.6</td>
<td>8–10</td>
<td>Co(NH₃)₅H₂O₃⁺</td>
<td>6.6⁴</td>
<td></td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>9.5</td>
<td>6–8</td>
<td>cis-Co(NH₃)₅(H₂O)₂⁻</td>
<td>6.0⁴</td>
<td></td>
</tr>
<tr>
<td>Co³⁺</td>
<td>8.9</td>
<td>6–8</td>
<td>Ru(NH₃)₅H₂O₃⁺</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>10.6</td>
<td>6–8</td>
<td>Rh(NH₃)₅H₂O₃⁺</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>6.8</td>
<td>4–6</td>
<td>Cr(NH₃)₅H₂O₃⁺</td>
<td>5.3⁴</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>8.8</td>
<td>6–8</td>
<td>cis-Co(en)₂(H₂O)₂⁻</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>9.0</td>
<td></td>
<td>trans-Co(en)₂(H₂O)₂⁻</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>3.7</td>
<td>(pKₐ₂ = 2.6)</td>
<td></td>
<td>(pKₐ₂ = 8.2)</td>
<td>115</td>
</tr>
<tr>
<td>Sn²⁺</td>
<td>3.9</td>
<td>cis-Cr(en)₂(H₂O)₂⁻</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>7.8</td>
<td></td>
<td>cis-Cr(en)₂(H₂O)₂⁻</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Al³⁺</td>
<td>5.1</td>
<td>2–4</td>
<td>trans-Co(en)₂(H₂O)₂⁻</td>
<td>(pKₐ₂ = 7.2)</td>
<td>115</td>
</tr>
<tr>
<td>Sc³⁺</td>
<td>5.1</td>
<td></td>
<td>trans-Co(en)₂(H₂O)₂⁻</td>
<td>(pKₐ₂ = 7.5)</td>
<td>115</td>
</tr>
<tr>
<td>In³⁺</td>
<td>4.4</td>
<td>(pKₐ₂ = 3.9)</td>
<td></td>
<td>(pKₐ₂ = 7.3)</td>
<td>115</td>
</tr>
<tr>
<td>Tl³⁺</td>
<td>1.1</td>
<td>(pKₐ₂ = 1.5)</td>
<td></td>
<td>(pKₐ₂ = 7.4)</td>
<td>115</td>
</tr>
<tr>
<td>Bi³⁺</td>
<td>1.6</td>
<td></td>
<td>trans-Pt(NH₃)₂(H₂O)₂⁺⁻</td>
<td>4.3</td>
<td>Strong acid</td>
</tr>
<tr>
<td>V³⁺</td>
<td>2.8</td>
<td></td>
<td>Pt(NH₃)₄H₂O⁺⁻</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt(en)₂(H₂O)₄⁺⁺</td>
<td>Strong acid</td>
<td></td>
</tr>
</tbody>
</table>

Systems are dilute unless indicated with *³ M NaClO₄ or ³¹ M NaNO₃. a Reaction at 20 °C.
Most metal ions effectively reduce the $pK_a$ ($-\log$ of the acid dissociation constant, $K_a$) of a solvent water molecule, so knowing the $pK_a$ values of metal aquo complexes can be useful. Some values are given in Table 1.5.

As with syntheses that occur at relatively high pH, acid–base reactions must be considered for those taking place at low pH. Being such strong Lewis acids, metal ions compete effectively for hydrogen ions bound to a ligand, LH. However, depending on the acid–base chemistry of the ligand and of the metal ion, placing a metal complex under very acidic conditions may result in a loss of the ligand through protonation, equation (1.19).

$$ML + H^+ \rightarrow M^+ + LH$$ \hfill (1.19)

As you become familiar with the metal ion with which you are working, designing and manipulating experimental conditions for synthesis and further application will become more straightforward.

**Stoichiometry**

Once a synthetic route for preparing a complex has been designed, the stoichiometry of the reaction will help to determine the minimum amount of reagents needed. Often, excess reagents are used to maximize the yield of a desired product, in compliance with Le Chatelier’s principle. A move towards “greener” approaches, however, asks chemists to think of a new definition of maximizing yield, one in terms of total atoms rather than just the desired product. This new approach asks synthetic chemists to adhere as closely as possible to the stoichiometric amounts.

**The Art of Precipitation: Properties of Precipitates**

Most often, synthetic products are obtained by precipitation from the reactant solution and purified by recrystallization. This section introduces some aspects of these processes.

**Product Solubility** Precipitates vary widely in solubility. Metal complexes in particular are often polar and charged. This fact taken with the consideration that most syntheses are carried out in polar aqueous media, can lead to high solubility losses in the desired material. Careful control of precipitation and washing is necessary.

Simple general chemistry principles can be used to help maximize precipitation and product yield. The first is the *common ion effect*, formally defined as making a weak acid or weak base weaker by the addition of a salt that contains a common ion, a direct consequence of Le Chatlier’s principle. The common ion effect can also be used to understand metal complex precipitation. Consider a saturated solution of $[\text{Co(NH}_3\text{)}_6\text{]}\text{Cl}_3$, equation (1.20).

$$\frac{1}{2}\text{Co(NH}_3\text{)}_6\text{]}\text{Cl}_3(\text{s}) \rightleftharpoons [\text{Co(NH}_3\text{)}_6\text{]}\text{Cl}_3^{3+} + 3\text{Cl}^-_{(\text{aq})}$$ \hfill (1.20)

According to the solubility product relationship, equation (1.21), if the concentration of one ion is raised, the other must drop. Doubling the chloride ion concentration by addition of NaCl(s) for example, will divide the concentration of $[\text{Co(NH}_3\text{)}_6\text{]}^{3+}$ in equilibrium with the solid by a factor of 8, maximizing precipitation.

$$[\text{Co(NH}_3\text{)}_6\text{]}^{3+}[\text{Cl}^-]^3 = K_{sp} = 1.2 \times 10^{-1}$$ \hfill (1.21)
Another important factor for coordination chemists is the general principle stated simply by Basolo: “solid salts separate from aqueous solution easiest for combinations of either small cation–small anion or large cation–large anion, preferably with systems having the same but opposite charges on the counter ions.” Other factors governing solubility of salts are pH, interionic attraction, and the diverse ion effect, which will not be covered in detail here.

Particle Size of Precipitates and Product Isolation Three types of precipitates you may encounter are: crystalline, 0.1–1 μm (e.g., BaSO₄), curdy, approximately 0.02 ≤ x ≤ 0.1 μm (e.g., AgCl), and gelatinous, ≤ 0.02 μm (e.g., hydrous Fe₂O₃). The more slowly a precipitate forms, the more effective the crystal packing and the larger and purer are the particles. Thus controlling the speed of precipitation (or particle size control) is often important in inorganic synthesis. The rate of crystal growth is influenced by several factors, including temperature, metal complex character and concentration, solvent, and nature of the counter ion.

The more concentrated a solution is, the greater the speed of precipitation. This is known as von Weimarn’s rule: the rate of precipitation can be slowed down by lowering the concentrations of the reactants and raising the solubility of the precipitate. The solubility of the precipitate can be altered using a cosolvent as well as by controlling temperature and taking into consideration the factors mentioned above and by the nature of the counter ion. If the smallest, curdy or gelatinous precipitates form, they can pass through normal filters and special procedures (e.g., multiple filter papers and/or multiple filtering) must be taken to trap these precipitates. These precipitates should be washed with an electrolyte solution to avoid dispersion of aggregates.

Crystal packing of a precipitate (particle size) also influences the color of a precipitate. For example, large crystals of solid NaFeEDTA are dark brown in color, while powder precipitate is yellow. Do not be fooled by comparing the color of your product with a lab-mate’s color!

Impurities in Precipitates Coprecipitation is the process by which soluble impurities become incorporated into precipitates during their formation by either incorporation into the crystal lattice or by surface adsorption. In the former, less common process, the coprecipitates interlace. Once this occurs the impurity cannot be simply washed out of a desired product. An undesired coprecipitate may be converted into another form (e.g., a more soluble salt) prior to precipitation. Impurities due to surface adsorption are more common. For an impure crystalline substance, again the contaminant cannot just be washed out. The impure product should be redissolved and reprecipitated in a process called “Ostwald ripening,” the dissolving of small particles followed by a redeposition of the material on the larger particles. If coprecipitated impurities are sensitive to pH, recrystallization in alkali or acid can be used to remove these. For curdy and gelatinous precipitates, because of the difference in precipitate size, coprecipitate impurities can often be washed out using a dilute electrolyte (e.g., HNO₃) that can then be removed by volatilization upon drying.

Postprecipitation is the precipitation of an impurity after the main product precipitate has been formed. With postprecipitation, contamination increases the longer the precipitate is in contact with its mother liquor. Contamination is faster at higher temperatures and can amount to even 100% by weight of the desired precipitate. Timing, temperature,
and pH are often critical factors in minimizing postprecipitation problems. A challenging example of this process is encountered with the synthesis of Ca[Co(ox)₂en] in Chapter 5.

**Purification by Recrystallization** Most impurities can be removed by the process of recrystallization. Recrystallization involves several steps that you should commit to memory:

- dissolving crude solid product in a minimum amount of solvent in which the product is slightly soluble, preferentially at a mild but elevated temperature;
- filtering the saturated solution by vacuum filtration to remove any insoluble particulates;
- allowing the product to crystallize from solution at room or reduced temperature (scratching the sides of the beaker often helps by providing a surface nucleation site for crystallization);
- filtering the purified product.

This section alerts you to only a few important considerations that should be kept in mind during synthesis. Keep a log in your notebook of others you may discover along the way.

One of the most exciting and challenging aspects for the experimental inorganic coordination chemist today is the need to draw on knowledge from all areas of chemistry: physical, organic, analytical, instrumental, and biochemistry. We hope this text convinces you of this. Although synthetic routes are outlined for you throughout the text, you should pay close attention to fundamental chemical principles governing a successful synthesis. Thinking scientifically about a synthesis will help you remain calm should mistakes occur during your procedure, as well as provide flexibility in modifying conditions during more advanced or first-time syntheses.

**REFERENCES**