CHAPTER 1

Experimental Inorganic Chemistry: A History of Dazzling Color!

> 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[1–4]

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, $CaCuSi_4O_{10}$, 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

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Integrated Approach to Coordination Chemistry: An Inorganic Laboratory Guide. By Rosemary A. Marusak, Kate Doan, and Scott D. Cummings

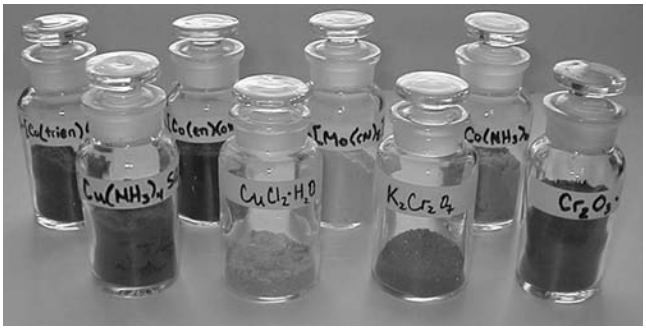

Figure 1.1 Vials of different metal-containing compounds and complexes.

TABLE 1.1 Some Inorganic Compounds and Their Colors

Compound	Color	Compound	Color
$Co(OH)_3$	Black	PbI_2	Yellow
$Cu(OH)$	Yellow	PbO_2	Brown
Cu_2O	Red	PbS	Black
Cu_2S	Black	HgO	Yellow or red
$Au(OH)_3$	Yellow-brown	Hg_2O	Brown-black
$AuOH$	Dark violet	Hg_2I_2	Yellow
$Fe(OH)_3$	Red-brown	$HgICl$	Red
Fe_2S_3	Dark green	Ag_3AsO_4	Dark red
FeS	Black	Ag_3AsO_3	Yellow

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 occuring 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 [M(OH)] compounds changes the observed color from yellow to dark violet. Likewise, replacing iodides in the yellow 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.

COMPLEX IONS[3,7,8]

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

TABLE 1.2 Color Names Given by Edmond Frémy (Adapted from Brock[3])

Compound	Color	Original Name	Formula
$Co(NO_2)_3 \cdot 4NH_3$	Brown	*Flavo* complex	*cis*-$[Co(NH_3)_4(NO_2)_2]NO_2$
$Co(NO_2)_3 \cdot 4NH_3$	Yellow	*Croceo* complex	*trans*-$[Co(NH_3)_4(NO_2)_2]NO_2$
$CoCl_3 \cdot 6NH_3$	Yellow	*Luteo* complex	$[Co(NH_3)_6]Cl_3$
$CoCl(H_2O) \cdot 5NH_3$	Rose-red	*Roseo* complex	$[Co(NH_3)_5(H_2O)]Cl_3$
$CoCl_3 \cdot 5NH_3$	Purple	*Purpureo* complex	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	Green	*Praseo* complex	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4NH_3$	Violet	*Violeto* complex	*cis*-$[Co(NH_3)_4Cl_2]Cl$

of the metal ammines and their unusual characteristics[†] 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, $Co(NO_2)_3 \cdot 4NH_3$ and $CoCl_3 \cdot 6NH_3$, though both are yellow, bear unrelated names. To further this scheme of confusion, $Co(NO_2)_3 \cdot 4NH_3$ 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 valency. 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, $Co(NO_2)_3 \cdot 4NH_3$. The modern formula, *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 (*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 *cis* form of the complex

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[†] 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.

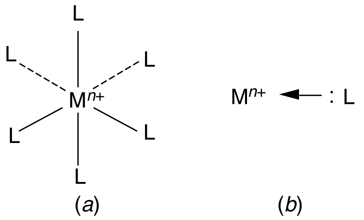

Figure 1.2 (*a*) Schematic of the octahedral complex and (*b*) the M–L coordinate bond.

[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.

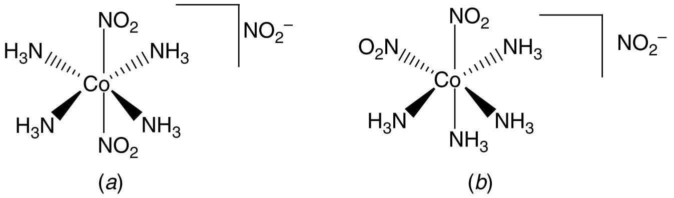

Figure 1.3 Yellow *trans*- (*a*) and brown *cis*-(*b*) $[Co(NH_3)_4(NO_2)_2]NO_2$.