

Inorganic Chemistry

SECOND EDITION

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Inorganic Chemistry

Second Edition

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Preface

A new edition of a text can mean many things. To authors, it is a chance to try again to get it right and readable, and to revise outdated sections. To teachers and students, the new edition is potentially a more readable and useful text. For the author's family and friends, it is a chance to reclaim the attention that was devoted to the revising process. And finally, it means that the first edition was successful enough that a revision is necessary. We hope potential users will agree that this second edition retains the best features of the first edition and corrects any flaws.

As in the first edition of *Inorganic Chemistry*, we have chosen to emphasize molecular orbitals and symmetry in many aspects of bonding and reactivity. For example, we have devoted an early chapter, Chapter 4, to a discussion of molecular symmetry and introductory group theory, with examples of applications to molecular vibrations and chirality. In later chapters, we have used group theory in a variety of other applications, including molecular orbitals of main group compounds (Chapter 5) and coordination complexes (Chapter 10), and infrared spectra of organometallic compounds (Chapter 13). Additional applications of group theory are included in problems at the end of these and other chapters.

The early chapters provide a review of atomic theory (Chapter 2) and simple concepts of chemical bonding (Chapter 3). Following the introduction to group theory in Chapter 4, this theory is applied to the construction of molecular orbitals in Chapter 5. Chapter 6 provides a discussion of various acid–base concepts, emphasizing applications of molecular orbitals to acid–base interactions. Following the advice of many, we have added a chapter on solid state inorganic chemistry (Chapter 7). Chapter 8 summarizes some of the most important aspects of main group elements and their compounds. The rapid development of chemistry of the fullerenes has been recognized in a discussion of these molecules in Chapter 8 and of fullerene complexes in Chapter 13.

Chapters 9 through 14 are directed to the chemistry of the transition elements. The first four of these chapters deal, respectively, with the structures, bonding, electronic spectra, and reactions of classical transition metal complexes. We have followed reviewers' advice in reorganizing these chapters into this sequence. For this edition we have moved the discussion of terms and microstates into Chapter 11 so it immediately precedes its most common use, interpretation of spectra of coordination complexes. [We have written the section on terms and microstates so it can still be used with the discussion of atomic spectra (Chapter 2) for those who might wish to follow the organization of the first edition.]

Chapters 13 and 14 provide an introduction to organometallic compounds, their spectra, and reactions. Special attention has been given to catalytic cycles and their application to problems of chemical and industrial significance.

We believe that seeking similarities in the chemistry of different types of compounds can be an extremely valuable exercise, and we have therefore discussed some of these important parallels in Chapter 15, placing particular emphasis on the isolobal analogy developed by Roald Hoffmann and on similarities between main group and transition metal clusters.

Finally, no text would be complete without a discussion of the role of inorganic compounds in biological processes and in the environment. We have therefore devoted the final chapter, Chapter 16, to selected aspects of bioinorganic and environmental inorganic chemistry.

We have chosen the topics and the level of treatment that works well for us. Every teacher has favorite topics, as well as least-favorite ones. We hope that our choice of topics allows potential users to tailor the contents to their own courses. We welcome suggestions for improvements in future editions.

In addition to selecting the most appropriate topics, we have attempted to make our text as accessible to students as possible. We have therefore increased the number of examples and exercises within the chapters, with answers to examples included in the chapters and answers to exercises in Appendix A. To encourage use of the literature in inorganic chemistry, we have retained the extensive references in the first edition and have also increased the number of end-of-chapter problems taken from the chemical literature. We hope that these will be useful to both faculty and students using this text. At the end of each chapter is a list of suggested supplemental readings, with brief comments on each.

We want to express special appreciation to our students, who have submitted many suggestions for improving the clarity and accuracy of this edition. We especially appreciate one student, Beth Truesdale (now a Rhodes Scholar), who reviewed every chapter in detail and made hundreds of valuable suggestions. Thanks also to those from other schools who reviewed this book in preparation and offered many helpful suggestions:

Christopher W. Allen, University of Vermont	Robert M. Kren, University of Michigan, Flint
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We are responsible for the final result, but it has been improved by their comments, even when we did not follow their suggestions.

At Prentice Hall, John Challice was instrumental in starting the revision and Matthew Hart in keeping it moving. And Celeste Clingan at Accu-color, Inc. shepherded us through the production process with grace and understanding.

Most of all, we thank Becky, Naomi, Rachel, and Marge for their patience, help, and love throughout this process.

Gary L. Miessler
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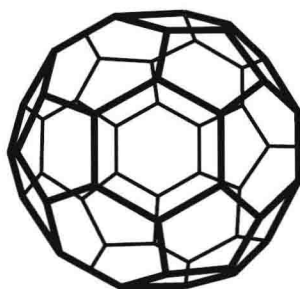
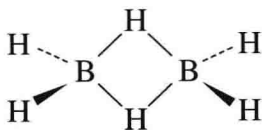
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Introduction to Inorganic Chemistry

 C_{60}

1-1 WHAT IS INORGANIC CHEMISTRY?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of “everything else.” This includes all the remaining elements in the periodic table, as well as carbon, which plays a major role in many inorganic compounds. Organometallic chemistry, a very large and rapidly growing field, bridges both areas by considering compounds containing direct metal–carbon bonds. As can be imagined, the inorganic realm is extremely broad, providing essentially limitless areas for investigation.

1-2 CONTRASTS WITH ORGANIC CHEMISTRY

Some comparisons between organic and inorganic compounds are in order. In both areas, single, double, and triple covalent bonds are found, as shown in Figure 1-1; for inorganic compounds, these include direct metal–metal bonds and metal–carbon bonds. However, while the maximum number of bonds between two carbon atoms is three, there are many compounds containing quadruple bonds between metal atoms. In addition to the sigma and pi bonds common in organic chemistry, quadruply bonded metal atoms contain a delta (δ) bond (Figure 1-2); a combination of one sigma bond, two pi bonds, and one delta bond makes up the quadruple bond. The delta bond is possible in these cases because metal atoms have *d* orbitals to use in bonding, whereas carbon has only *s* and *p* orbitals available.

In organic compounds, hydrogen is nearly always bonded to a single carbon. In inorganic compounds, especially of the Group 13 (IIIA) elements, hydrogen is frequently encountered as a bridging atom between two or more other atoms. Bridging hydrogen atoms can also occur in metal cluster compounds. In these clusters, hydrogen atoms form bridges across edges or faces of polyhedra of metal atoms. Alkyl groups may also act as bridges in inorganic compounds, a function rarely encountered in organic chemistry (except in reaction intermediates). Examples of terminal and bridging hydrogen atoms and alkyl groups in inorganic compounds are shown in Figure 1-3.

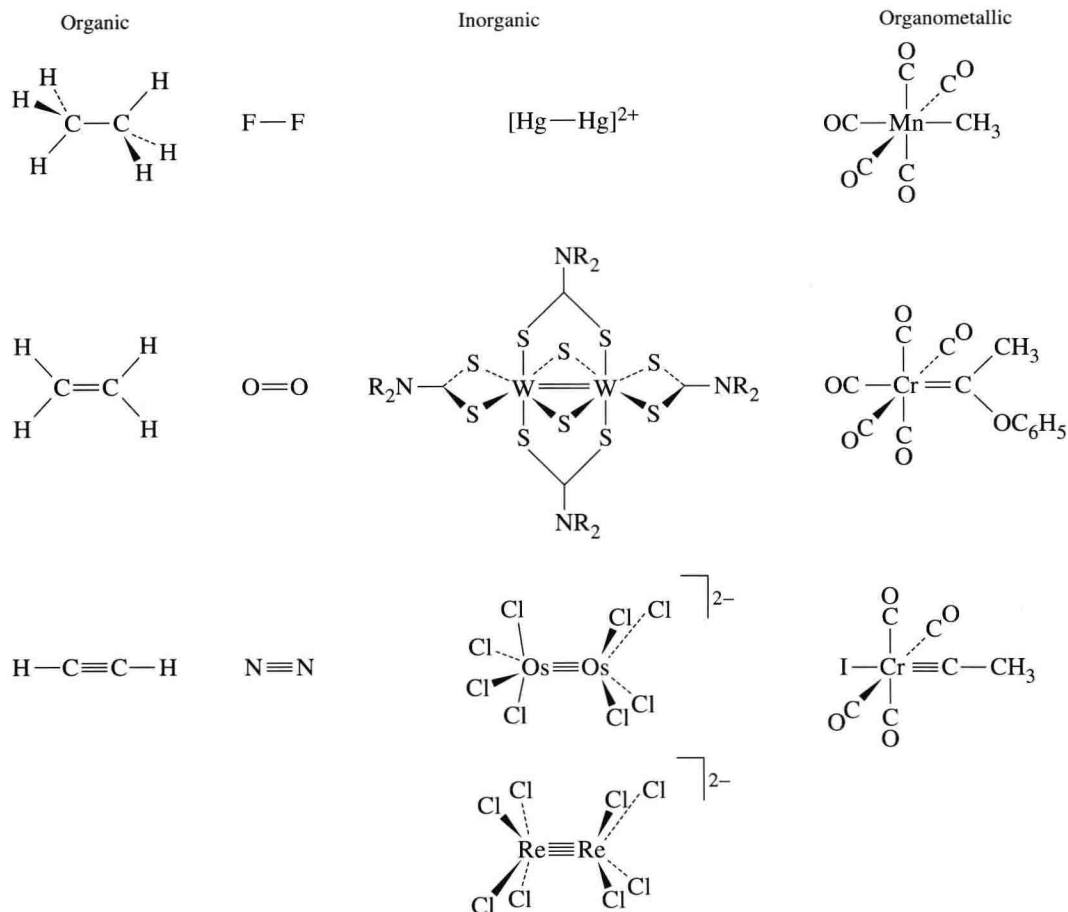


FIGURE 1-1 Single and Multiple Bonds in Organic and Inorganic Molecules.

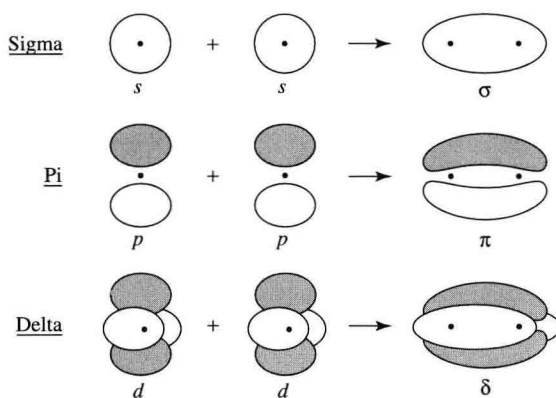


FIGURE 1-2 Examples of Bonding Interactions.

Some of the most striking differences between the chemistry of carbon and that of many other elements are in coordination number and geometry. Although carbon is usually limited to a maximum coordination number of four (a maximum of four atoms bonded to carbon, as in CH_4), inorganic compounds having coordination numbers of five, six, seven, and more are very common; the most common coordination geometry is an octahedral arrangement around a central atom, as shown for $[\text{TiF}_6]^{3-}$ in Figure 1-4.

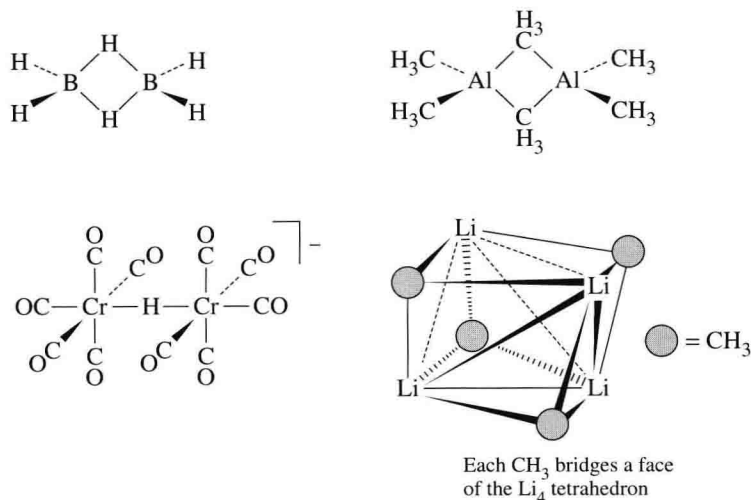


FIGURE 1-3 Examples of Inorganic Compounds Containing Terminal and Bridging Hydrogens and Alkyl Groups.

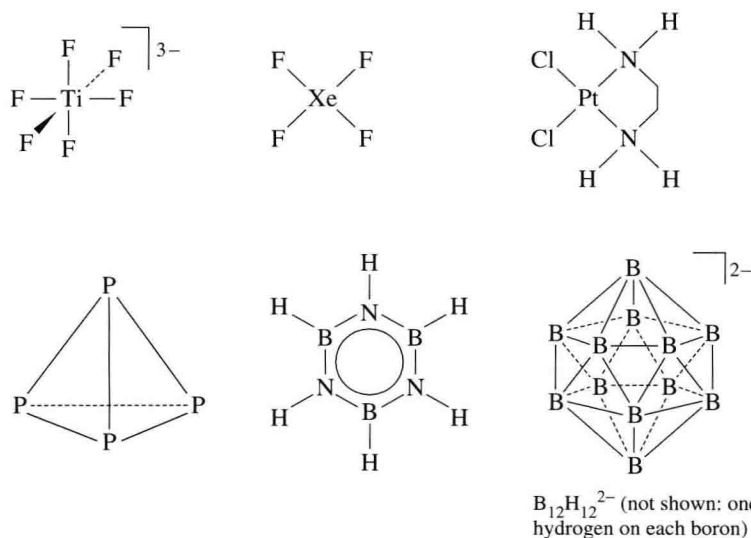


FIGURE 1-4 Examples of Geometries of Inorganic Compounds.

Furthermore, inorganic compounds present coordination geometries different from those found for carbon. For example, while 4-coordinate carbon is nearly always tetrahedral, both tetrahedral and square planar shapes occur for 4-coordinate compounds of both metals and nonmetals. When metals are the central atoms, with anions or neutral molecules bonded to them (frequently through N, O, or S), these are called coordination complexes; when carbon is the element directly bonded to a metal atom or ion, they are called organometallic compounds.

The tetrahedral geometry usually found in 4-coordinate compounds of carbon also occurs in a different form in some inorganic molecules. Methane contains four hydrogens in a regular tetrahedron around carbon. Elemental phosphorus is tetratomic (P_4) and also is tetrahedral, but with no central atom. Examples of some of the geometries found for inorganic compounds are shown in Figure 1-4.

Aromatic rings are common in organic chemistry, and aryl groups can also form sigma bonds to metals. However, aromatic rings can also bond to metals in a dramatically different fashion using their pi orbitals, as shown in Figure 1-5. The result is a metal atom bonded above the center of the ring, almost as if suspended in space. In many

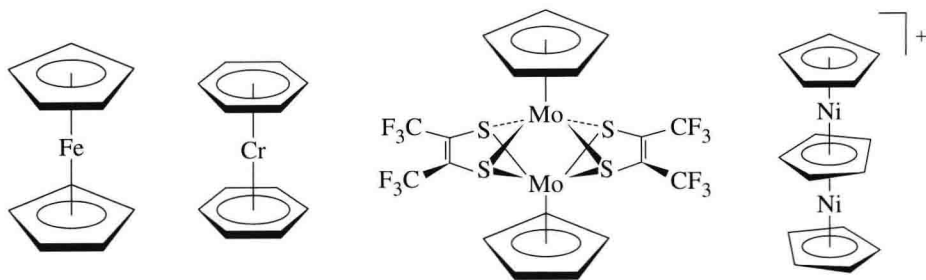


FIGURE 1-5 Inorganic Compounds Containing Pi-bonded Aromatic Rings.

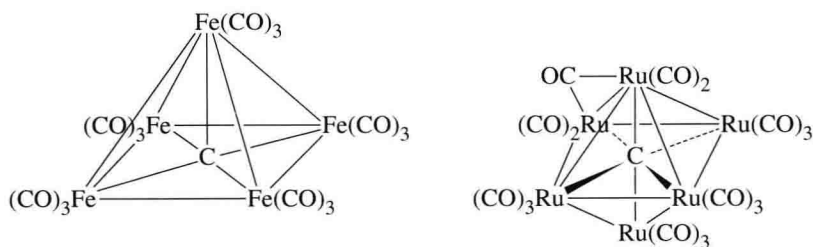


FIGURE 1-6 Carbon-centered Metal Clusters.

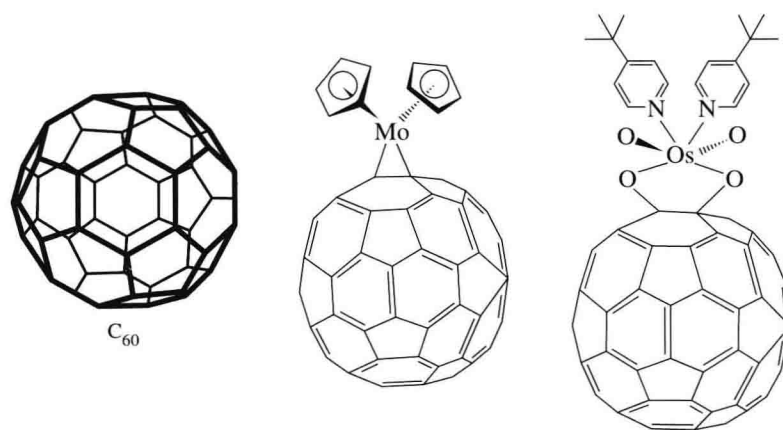


FIGURE 1-7 Fullerene Compounds.

cases, metal atoms are sandwiched between two aromatic rings. Multiple-decker sandwiches of metals and aromatic rings are also known.

Carbon plays an unusual role in a number of metal cluster compounds, in which a carbon atom is at the center of a polyhedron of metal atoms. Examples of carbon-centered clusters of five, six, or more metals are known; two of these are shown in Figure 1-6. The contrast of the role that carbon plays in these clusters to its usual role in organic compounds is striking, and attempting to explain how carbon can form bonds to the surrounding metal atoms in clusters has provided an interesting challenge to theoretical inorganic chemists. A molecular orbital picture of bonding in these clusters is discussed in Chapter 15.

In addition, during the past decade the realm of a new class of carbon clusters, the fullerenes, has flourished. The most common of these clusters, C_{60} , has been labeled “buckminsterfullerene” after the developer of the geodesic dome and has served as the core of a variety of derivatives (Figure 1-7).

There are no sharp dividing lines between subfields in chemistry. Many of the subjects in this book, such as acid-base chemistry and organometallic reactions, are of vital interest to organic chemists. Others, such as oxidation–reduction reactions, spectra, and