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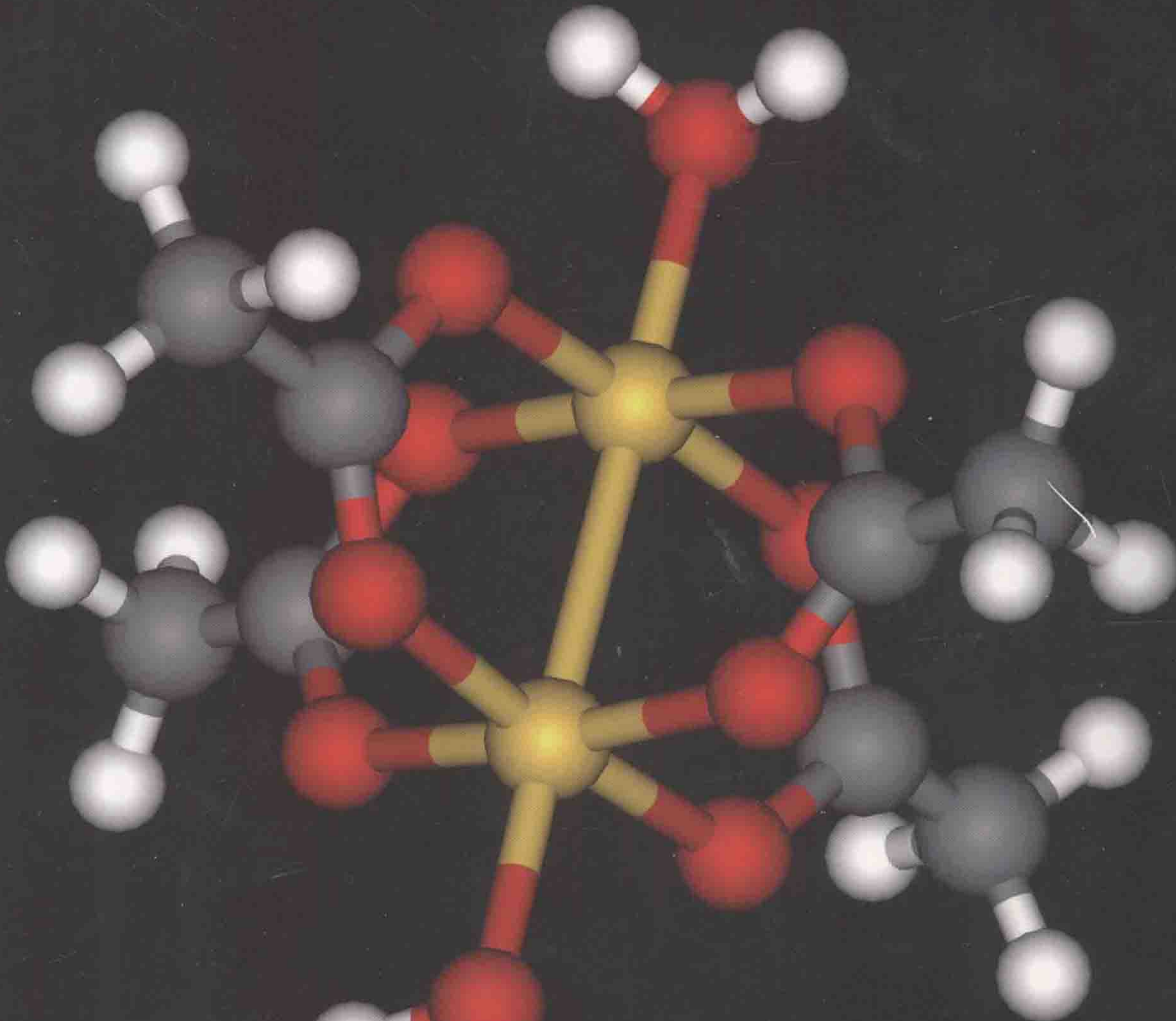
James E. House



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Preface

No single volume, certainly not a textbook, can come close to including all of the important topics in inorganic chemistry. The field is simply too broad in scope and it is growing at a rapid pace. Inorganic chemistry textbooks reflect a great deal of work and the results of the many choices that authors must make as to what to include and what to leave out. Writers of textbooks in chemistry bring to the task backgrounds that reflect their research interests, the schools they attended, and their personalities. In their writing, authors are really saying "this is the field as I see it." In these regards, this book is similar to others.

When teaching a course in inorganic chemistry, certain core topics are almost universally included. In addition, there are numerous peripheral areas that may be included at certain schools but not at others depending on the interests and specialization of the person teaching the course. The course content may even change from one semester to the next. The effort to produce a textbook that presents coverage of a wide range of optional material in addition to the essential topics can result in a textbook for a one semester course that contains a thousand pages. Even a "concise" inorganic chemistry book can be nearly this long. This book is not a survey of the literature or a research monograph. It is a textbook that is intended to provide the background necessary for the reader to move on to those more advanced resources.

In writing this book, I have attempted to produce a concise *textbook* that meets several objectives. First, the topics included were selected in order to provide essential information in the major areas of inorganic chemistry (molecular structure, acid-base chemistry, coordination chemistry, ligand field theory, solid state chemistry, etc.). These topics form the basis for competency in inorganic chemistry at a level commensurate with the one semester course taught at most colleges and universities.

When painting a wall, better coverage is assured when the roller passes over the same area several times from different directions. It is the opinion of the author that this technique works well in teaching chemistry. Therefore, a second objective has been to stress fundamental principles in the discussion of several topics. For example, the hard-soft interaction principle is employed in discussion of acid-base chemistry, stability of complexes, solubility, and predicting reaction products. Third, the presentation of topics is made with an effort to be clear and concise so that the book is portable and user friendly. This book is meant to present in convenient form a readable account of the essentials of inorganic chemistry that can serve as both as a textbook for a one semester course upper level course and as a guide for self study. It is a *textbook* not a review of the literature or a research monograph. There are few references to the original literature, but many of the advanced books and monographs are cited.

Although the material contained in this book is arranged in a progressive way, there is flexibility in the order of presentation. For students who have a good grasp of the basic principles of quantum mechanics and atomic structure, Chapters 1 and 2 can be given a cursory reading but not included in the required course material. The chapters are included to provide a resource for review and self study. Chapter 4 presents an overview structural chemistry early so the reader can become familiar with many types of inorganic structures before taking up the study of symmetry or chemistry of specific elements. Structures of inorganic solids are discussed in Chapter 7, but that material could easily be studied before Chapters 5 or 6. Chapter 6 contains material dealing with intermolecular forces and polarity of molecules because of the importance of these topics when interpreting properties of substances and their chemical behavior. In view of the importance of the topic, especially in industrial chemistry, this book includes material on rate processes involving inorganic compounds in the solid state (Chapter 8). The chapter begins with an overview of some of the important aspects of reactions in solids before considering phase transitions and reactions of solid coordination compounds.

It should be an acknowledged fact that no single volume can present the descriptive chemistry of all the elements. Some of the volumes that attempt to do so are enormous. In this book, the presentation of descriptive chemistry of the elements is kept brief with the emphasis placed on types of reactions and structures that summarize the behavior of many compounds. The attempt is to present an overview of descriptive chemistry that will show the important classes of compounds and their reactions without becoming laborious in its detail. Many schools offer a descriptive inorganic chemistry course at an intermediate level that covers a great deal of the chemistry of the elements. Part of the rationale for offering such a course is that the upper level course typically concentrates more heavily on principles of inorganic chemistry. Recognizing that an increasing fraction of the students in the upper level inorganic chemistry course will have already had a course that deals primarily with descriptive chemistry, this book is devoted to a presentation of the principles of inorganic chemistry while giving an a brief overview of descriptive chemistry in Chapters 12–15, although many topics that are primarily descriptive in nature are included in other sections. Chapter 16 provides a survey of the chemistry of coordination compounds and that is followed by Chapters 17–22 that deal with structures, bonding, spectra, and reactions of coordination compounds. The material included in this text should provide the basis for the successful study of a variety of special topics.

Doubtless, the teacher of inorganic chemistry will include some topics and examples of current or personal interest that are not included in any textbook. That has always been my practice, and it provides an opportunity to show how the field is developing and new relationships.

Most textbooks are an outgrowth of the author's teaching. In the preface, the author should convey to the reader some of the underlying pedagogical philosophy which resulted in the design of his or her book. It is unavoidable that a different teacher will have somewhat different philosophy and methodology. As a result, no single book will be completely congruent with the practices and motivations of all teachers. A teacher who writes the textbook for his or her course should find all of the needed topics in the book. However, it is unlikely that a book written by someone else will ever contain exactly the right topics presented in exactly the right way.

The author has taught several hundred students in inorganic chemistry courses at Illinois State University, Illinois Wesleyan University, University of Illinois, and Western Kentucky University using the materials and approaches set forth in this book. Among that number are many who have gone on to graduate school, and virtually all of that group have performed well (in many cases very well!) on registration and entrance examinations in inorganic chemistry at some of the most prestigious institutions. Although it is not possible to name all of those students, they have provided the inspiration to see this project to completion with the hope that students at other universities may find this book

useful in their study of inorganic chemistry. It is a pleasure to acknowledge and give thanks to Derek Coleman and Philip Bugeau for their encouragement and consideration as this project progressed. Finally, I would like to thank my wife, Kathleen, for reading the manuscript and making many helpful suggestions. Her constant encouragement and support have been needed at many times as this project was underway.

Contents

Part 1

Structure of Atoms and Molecules

Chapter 1

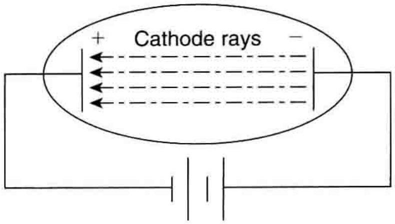
Light, Electrons, and Nuclei

The study of inorganic chemistry involves interpreting, correlating, and predicting the properties and structures of an enormous range of materials. Sulfuric acid is the chemical produced in the largest tonnage of any compound. A greater number of tons of concrete is produced, but it is a mixture rather than a single compound. Accordingly, sulfuric acid is an inorganic compound of enormous importance. On the other hand, inorganic chemists study compounds such as hexaaminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, and Zeise's salt, $K[Pt(C_2H_4)Cl_3]$. Such compounds are known as coordination compounds or coordination complexes. Inorganic chemistry also includes areas of study such as nonaqueous solvents and acid-base chemistry. Organometallic compounds, structures and properties of solids, and the chemistry of elements other than carbon are areas of inorganic chemistry. However, even many compounds of carbon (e.g., CO_2 and Na_2CO_3) are also inorganic compounds. The range of materials studied in inorganic chemistry is enormous, and a great many of the compounds and processes are of industrial importance. Moreover, inorganic chemistry is a body of knowledge that is expanding at a very rapid rate, and a knowledge of the behavior of inorganic materials is fundamental to the study of the other areas of chemistry.

Because inorganic chemistry is concerned with structures and properties as well as the synthesis of materials, the study of inorganic chemistry requires familiarity with a certain amount of information that is normally considered to be physical chemistry. As a result, physical chemistry is normally a prerequisite for taking a comprehensive course in inorganic chemistry. There is, of course, a great deal of overlap of some areas of inorganic chemistry with the related areas in other branches of chemistry. A knowledge of atomic structure and properties of atoms is essential for describing both ionic and covalent bonding. Because of the importance of atomic structure to several areas of inorganic chemistry, it is appropriate to begin our study of inorganic chemistry with a brief review of atomic structure and how our ideas about atoms were developed.

1.1 SOME EARLY EXPERIMENTS IN ATOMIC PHYSICS

It is appropriate at the beginning of a review of atomic structure to ask the question, "How do we know what we know?" In other words, "What crucial experiments have been performed and what do



■ **FIGURE 1.1** Design of a cathode ray tube.

the results tell us about the structure of atoms?" Although it is not necessary to consider all of the early experiments in atomic physics, we should describe some of them and explain the results. The first of these experiments was that of J. J. Thomson in 1898–1903, which dealt with cathode rays. In the experiment, an evacuated tube that contains two electrodes has a large potential difference generated between the electrodes as shown in Figure 1.1.

Under the influence of the high electric field, the gas in the tube emits light. The glow is the result of electrons colliding with the molecules of gas that are still present in the tube even though the pressure has been reduced to a few torr. The light that is emitted is found to consist of the spectral lines characteristic of the gas inside the tube. Neutral molecules of the gas are ionized by the electrons streaming from the cathode, which is followed by recombination of electrons with charged species. Energy (in the form of light) is emitted as this process occurs. As a result of the high electric field, negative ions are accelerated toward the anode and positive ions are accelerated toward the cathode. When the pressure inside the tube is very low (perhaps 0.001 torr), the mean free path is long enough that some of the positive ions strike the cathode, which emits rays. Rays emanating from the cathode stream toward the anode. Because they are emitted from the cathode, they are known as *cathode rays*.

Cathode rays have some very interesting properties. First, their path can be bent by placing a magnet near the cathode ray tube. Second, placing an electric charge near the stream of rays also causes the path they follow to exhibit curvature. From these observations, we conclude that the rays are electrically charged. The cathode rays were shown to carry a negative charge because they were attracted to a positively charged plate and repelled by one that carried a negative charge.

The behavior of cathode rays in a magnetic field is explained by recalling that a moving beam of charged particles (they were not known to be electrons at the time) generates a magnetic field. The same principle is illustrated by passing an electric current through a wire that is wound around a compass. In this case, the magnetic field generated by the flowing current interacts with the magnetized needle of the compass, causing it to point in a different direction. Because the cathode rays are negatively charged particles, their motion generates a magnetic field that interacts with the external magnetic field. In fact, some important information about the nature of the charged particles in cathode rays can be obtained from studying the curvature of their path in a magnetic field of known strength.

Consider the following situation. Suppose a cross wind of 10 miles/hour is blowing across a tennis court. If a tennis ball is moving perpendicular to the direction the wind is blowing, the ball will follow