INORGANIC CHEMISTRY
A Unified Approach

Porterfield

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William W. Porterfield

Hampden-Sydney College

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For everybody who has ever taught a course or written a text:

SONG OF A MAN WHO HAS COME THROUGH

Not I, not I, but the wind that blows through me!
A fine wind is blowing the new direction of Time.
If only I let it bear me, carry me, if only it carry me!
If only I am sensitive, subtle, oh, delicate, a winged gift!
If only, most lovely of all, I yield myself and am borrowed
By the fine, fine wind that takes its course through the chaos of the world
Like a fine, an exquisite chisel, a wedge-blade inserted;
If only I am keen and hard like the sheer tip of a wedge
Driven by invisible blows,
The rock will split, we shall come at the wonder, we shall find the Hesperides.

Oh, for the wonder that bubbles into my soul
I would be a good fountain, a good well-head,
Would blur no whisper, spoil no expression.

What is the knocking?
What is the knocking at the door in the night?
It is somebody wants to do us harm.

No, no, it is the three strange angels.
Admit them, admit them.

—D. H. Lawrence (1931)

Preface

A preface gives an author a chance to explain to the dubious reader why he went to all the trouble of writing another book about an area already treated by experts. Well, why did I? It has seemed to me that as inorganic chemistry has grown over the last twenty or thirty years the textbooks that have attempted to cope with this growth have tended to add the new classes of compounds and new theoretical structures to a pre-existing framework. But I think that some of the most exciting developments have tended to integrate previously separated areas (for example, boron clusters and metal clusters), and that a whole new organizational principle may be needed, one that takes advantage of the growing integration and unity of perspective that have come to the field of inorganic chemistry. I have tried to do that here—partly in the broad general layout of the book and partly in the details of the treatment within each chapter.

After a short introduction that gives some geological and historical background for our ideas of elements, atomic structure, and periodicity, two chapters describe the structures and preparation of main-group compounds, not in periodic table order but in terms of the way inorganic chemists think about bonding in ionic and covalent systems. These are followed by a chapter on the structures of acids and bases, then a section on principles of reactivity of main-group compounds beginning with a chapter on acid-base reactivity in thermodynamic terms, and continuing with a thermodynamic organization: enthalpy-driven redox reactions and entropy-driven reactions in general. A fourth section uses three chapters to describe the underlying bonding theory and structures of transition-metal compounds, and the last section uses three chapters to describe the patterns of reactivity of transition-metal compounds, both in mechanistic terms and by describing the catalytic and bioinorganic roles of transition-metal systems. An important feature of this last section is the emphasis given to photochemical reactions, which constitute a particularly active area of inorganic research. Discussions of reactivity inevitably rely on structural and electronic arguments, and the chapter sequence here develops both main-group and transition-metal reactivities with extensive reference to previously developed bonding concepts. This is a fairly tight integration, and it accounts for the "Unified Approach" subtitle of this textbook.

A casual inspection of the table of contents suggests that some important material is alarmingly missing—but, except for group theory, it's all there, and in what I think will prove to be a logical and teachable format. For example, the word *bonding* does not appear in any chapter title. That's accidental; inorganic chemists hardly talk about anything else! Ionic lattice energies and solvation energies are treated in Chapters 3 and 5, and qualitative MO models are discussed in Chapters 4 and 9. No chapters describe the alkaline-earth metals, or the chalcogens, or any other periodic table group, but I believe that honest-to-goodness descriptive chemistry is best presented in terms of unifying bonding concepts, and that Chapters 3 through 8 provide a great deal of main-group descriptive chemistry and Chapters 10 through 14 provide a great deal of transition-metal descriptive chemistry on that basis. If they didn't, it wouldn't be an inorganic chemistry textbook. There is no chapter (or chapters) on bioinorganic systems, because the principles underlying their structures and reactivity are no different from those for other metal complexes, and it makes sense to discuss them together. The VSEPR model for *p*-block molecular geometries is used fairly extensively throughout the book but not explicitly developed, because most general-chemistry textbooks now do that; but it is presented in Appendix B for those who need to review it. The only genuine "missing topic" is a development of group theory to accompany spectroscopic arguments for metal complexes. After considerable reflection and comment from reviewers, group theory was deliberately omitted from Chapter 9 in the interest of brevity—but point-group nomenclature is used, and the discussion is compatible with a group-theory-based presentation if the instructor wishes to add it. All things considered, I think that even though the organization may be unfamiliar to an instructor examining the book for the first time, so that topics appear to have been ignored, careful inspection—perhaps with use of the index—will show that this format allows a compact but reasonably comprehensive treatment.

This approach is, I think, uniquely my own—but many friends and colleagues have contributed to it over a number of years, in many ways: S. Y. Tyree, Jr., who got me interested in inorganic chemistry; speakers at many Gordon Research Conferences on inorganic chemistry who have presented new and sometimes dramatic insights into the unfolding pattern of our discipline; reviewers of the manuscript, particularly Russell Grimes, who corrected several (but assuredly not all) of my misconceptions; students at Hampden-Sydney College who used a preliminary version, suffered through it, and improved it by their advice (Ryan Anderson, Trey Campbell, Mark Deaton, Neil Huffman, Tim Lass, Richard Leggett, Rick Morrisett, and Paul Nelson); and the staff at Addison-Wesley, particularly Bob Rogers and Marilee Sorotskin, who tried to be sure the good ideas made a good book. Unfortunately, none of these can be held responsible for the shortcomings, misconceptions, and errors the book undoubtedly still contains; the buck will have to stop here. I want particularly, too, to acknowledge grant support from Hampden-Sydney College for the writing of this book, and moral support from Dorothy, who was convinced I could do it.

Hampden-Sydney, Virginia W. W. P.
June 1983

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PART I

Introduction

CHAPTER 1

The Inorganic Chemist's Domain

Inorganic chemists are relatively few in number, but they have a good time. Their research is the most varied of any field of chemistry. They study the chemistry of at least 105 elements, finding them and their compounds all the way from the earth's core to the farthest reaches of the universe. They observe physical properties ranging all the way from the superfluid liquid helium at temperatures so low that quantum effects become important in the thermal behavior of matter to the incredibly stable lattices of refractory carbides that scratch diamond and cannot be melted at the temperature of an oxyacetylene torch. They deal with chemical reactivities ranging from molecules so unstable that they must be isolated on an individual basis in a crystal of frozen argon to systems that require hours to react at white heat. They model inorganic structures as isolated molecules that are completely covalent, as crystals in which ions are almost completely electrostatically bound, and as metallic crystals with almost complete electron delocalization. And they use literally every experimental technique ever devised by chemists to prepare and to study the species of their research, ranging in age and sophistication from gravimetric analysis to ion cyclotron resonance.

It is a challenging task to bring order and comprehensibility to the rich diversity suggested here. This short introductory chapter is intended to provide some background for inorganic systems and to give historical perspective to the scheme we shall use to categorize the wealth of experimental knowledge and theoretical modeling that form the basis for today's research in inorganic chemistry.

1.1 THE OCCURRENCE OF INORGANIC SYSTEMS

The most obvious source of inorganic materials for study is the earth. It is almost entirely inorganic: Of the earth's total mass of about 6×10^{24} kg, only about one part in ten billion is in the biosphere or is otherwise organic. Most of the inorganic mass, of course, is in the solid part of the earth, the lithosphere. Figure 1.1 is a drawing, approximately to scale, of the earth's lithosphere. It is about one-third core (by mass) and two-thirds mantle; the crust is less than 0.5% of the earth's total mass. We have