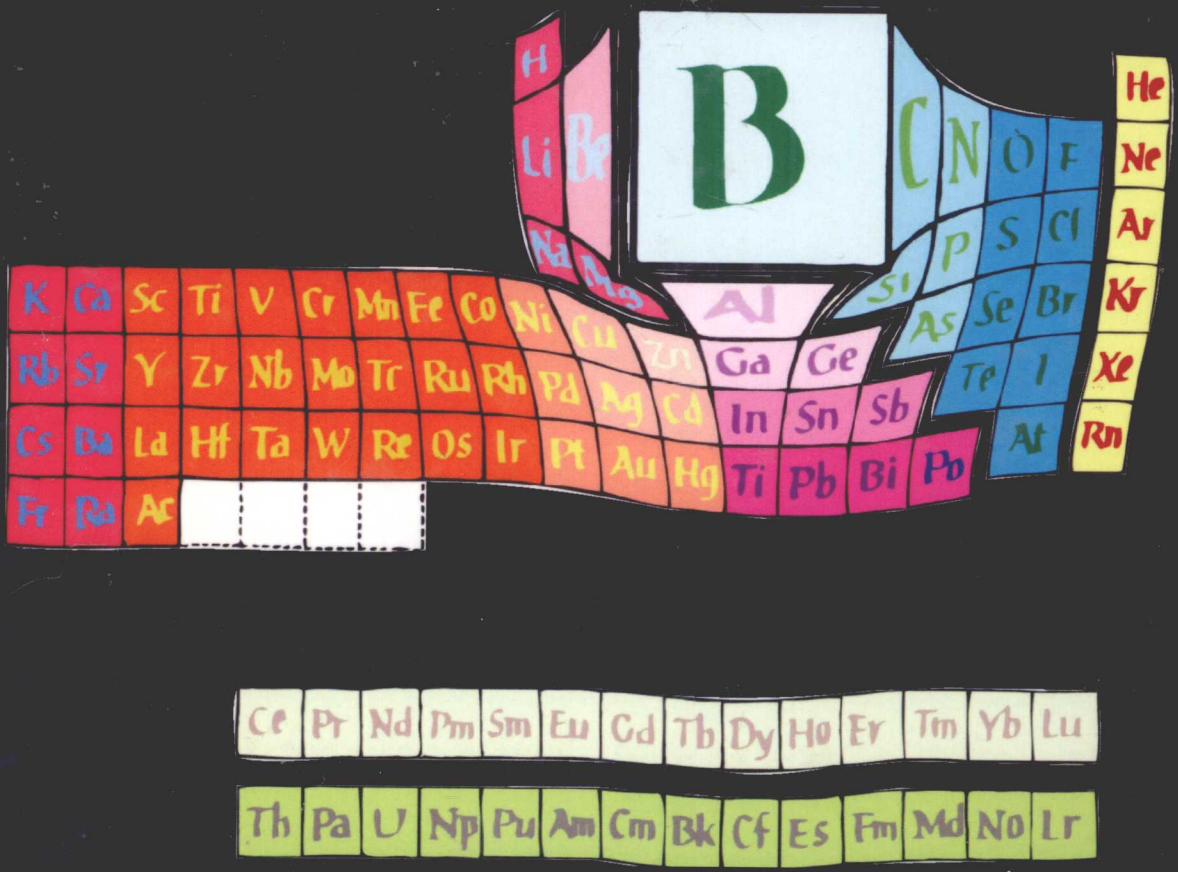
Boron Science

New Technologies and Applications



EDITED BY

NARAYAN S. HOSMANE

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Description of the Cover Figure: Lipscomb's Perception of the Element Boron in the Modern Periodic Table.

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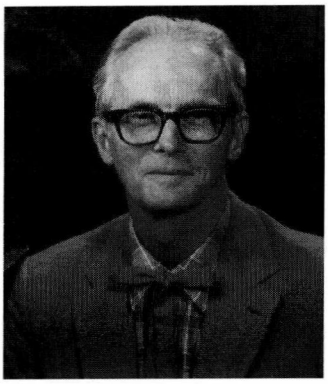

This book is dedicated to William N. Lipscomb Jr. (December 9, 1919–April 14, 2011), Emeritus Professor at Harvard University and the winner of the 1976 Nobel Prize for Chemistry. Professor Lipscomb, one of the founders of theoretical and structural polyhedral boron chemistry, had dedicated much of his career to promoting boron science, which is the subject of this book. Much of the progress in these endeavors rests on Professor Lipscomb's original work on bonding in boranes. His dedication to our global society is hereby recognized and saluted. We miss him.

Foreword

It has been observed many times but bears repeating: boron is a unique element. Of course, in a sense the same can be said of other elements, such as carbon and hydrogen, but the capacity of boron to confound established notions of structure and bonding—at times seeming to write its own rules—has fascinated and exasperated generations of workers. This seemingly innocuous element, tucked into the top of the periodic table between beryllium and carbon, appeared normal—even boring—for a century following its isolation in 1808 by Humphrey Davy and, independently, Gay-Lussac and Thenard. It behaved exactly as expected, forming trivalent compounds such as the boron trihalides, trialkylboranes, $B(OH)_3$, and borates, and everyone, including the eminent William Ramsey, a Nobel Laureate and discoverer of the noble gases, believed that its simplest hydride had to be BH_3 (what else could it be?). It took the great German chemist Alfred Stock to uncover the truth about the boron hydrides and, even he, working in the early twentieth century, had little notion of their incredible structures and assumed they must be similar to hydrocarbons despite their inconvenient shortage of electrons. Not until another half-century had passed did another towering scientist, William Nunn Lipscomb, finally crack the mystery of the three-center-bonded polyboranes, proving many of their structures with his ingenious apparatus that enabled the collection of x-ray diffraction data at ultracold temperatures and developing a theoretical foundation based on the concept of the three-center two-electron bond. For these achievements, Lipscomb was awarded the 1976 Nobel Prize in Chemistry.

It is highly appropriate that the editor of this volume highlighting recent advances in boron science across an amazingly broad spectrum of applications, with contributions by leading experts in their respective fields, has chosen to dedicate it to Lipscomb, a Kentuckian known as "the Colonel" to generations of his students, coworkers, and colleagues. I first met the Colonel in 1958 as a new graduate student in inorganic chemistry at the University of Minnesota, when it was suggested that I talk with him about joining his research group. I almost didn't go—after all, he was not a member of the inorganic faculty, in fact serving as physical chemistry division chair, and I had no interest in boranes (or so I thought). But I went anyway, and after an hour in his office I was hooked. The borane structures and bonding diagrams that filled several blackboards were exotic and strange to me, but there was something about this man and his mission that was irresistible, and I signed on. Only later did I discover that I was to be his first student who was neither a crystallographer nor a theoretician—it would be my job to learn how to build vacuum lines and manipulate such lovely materials as diborane and pentaborane. With the invaluable help of a summer in Riley Schaeffer's lab at Indiana University just prior to moving with the Colonel to Harvard in early 1960, I eventually managed to acquire these skills. But what struck me most forcefully about the Colonel, and still does, was his unconventional approach to research. In group discussions in which we were encouraged to think outside the box—the further outside, the better—I seldom, if ever, heard him dismiss an idea out of hand. Vacuum line explosions and other setbacks were shrugged off as the price of progress. (There were rare exceptions to his usual good humor, including an incident in which an expensive piece of x-ray diffraction equipment was dropped while being unloaded by crane from the second story of Gibbs Hall, gouging a large crater in the front lawn.)

Reflecting on the Lipscomb research philosophy after all these years, I think that a central attribute has been his uncommon willingness to risk error, as he acknowledged in an early classic paper on three-center bonding with Eberhardt and Crawford. This is not a universal attitude these days, as research funding agencies have little tolerance for false starts and dead ends, and pure exploratory synthesis is practically extinct. Moreover, it must be admitted that a free-wheeling approach is more likely to produce success when coupled with a consummate scientific imagination like the Colonel's.

To me, this book represents more than a fine up-to-date compilation of progress in the applied chemistry and physics of boron. It is, as well, a tribute to the groundbreaking studies of legions of workers over many years led by some truly inspired scientists including not only the late Lipscomb but Fred Hawthorne (who is still at it, full force, directing his new International Institute of Nano and Molecular Medicine at the University of Missouri), the late Herbert C. Brown, and their scientific protégés who together transformed boron science from a boring area to a compelling, exciting, vibrant, and growing one. One of the latter-day scientific descendants of these pioneers, Narayan Hosmane (a postdoc in my own laboratory over 30 years ago, and a major contributor in his own right) has performed a major service in bringing together this excellent fount of information in a rapidly moving field.

Russell N. Grimes
Charlottesville, Virginia

Preface

What is boron? The question itself may not seem very significant to many people. Their introduction to the word "boron" could come as the butt of a joke. Conan O'Brien made jokes about boron (http://www.wired.com/wiredscience/2009/02/conanchemistry/) by calling it either "Boring Boron" or "Boron Moron." Many people may connect boron to borax, which is one of its natural sources. Some of us with longer memories might recall a popular television show called *Death Valley Days*, aired in the 1950s, narrated by a young Ronald Reagan and sponsored by 20 Mule Team Borax. Although boron is one of the closest neighbors to carbon in the periodic table, it has neither gained the importance nor the popularity of carbon. But boron is not just about borax. How many of us know that a regular intake of boron can lessen the chance of prostate cancer? How many of us know that boron plays a direct and critical role in combating cancer through a treatment called boron neutron capture therapy (BNCT)?

If you were among those fortunate attendees of Professor M. Frederick Hawthorne's lecture at UCLA titled "From Mummies to Rockets and on to Cancer Therapy," you had the opportunity to explore the power of boron chemistry. Boron has made a significant impact in our lives through its use in fertilizers, fungicides, soaps, and detergents as well as many household glassware utensils; thus boron is silently present everywhere. Those involved in boron chemistry are beginning to realize that this silence needs to be broken. This book, titled *Boron Science: New Technologies and Applications*, attempts to do just that.

To illustrate the versatility of boron in all areas of applications, the 29 chapters of this book are divided into seven major sections, Boron for Living: Medicine (Part I); Boron for Living: Health and Nutrition (Part II); Boron for Living: Radioisotope (Part III); Boron for Living: Boron Neutron Capture Therapy (Part IV); Boron for Electronics: Optoelectronics (Part V); Boron for Energy: Energy Storage, Space, and Other Applications (Part VI); and Boron for Chemistry and Catalysis: Catalysis and Organic Transformations (Part VII). Each chapter has been rigorously reviewed by at least three reviewers. In order to maintain high quality, reviews were solicited not only from the expert authors of other chapters but also from renowned scientists who willingly shared their expertise and help in improving the quality of the chapters. The invaluable reviews from the following scientists are hereby gratefully acknowledged.

Didier Astruc, University of Bordeaux, France
S. Thomas Autrey, Pacific Northwest National Laboratory, USA
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Russell N. Grimes, University of Virginia, USA
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Kung K. Wang, West Virginia University, USA
Lars Wesemann, Universität Tübingen, Germany
Alexander Wlodawer, National Cancer Institute at Frederick, USA

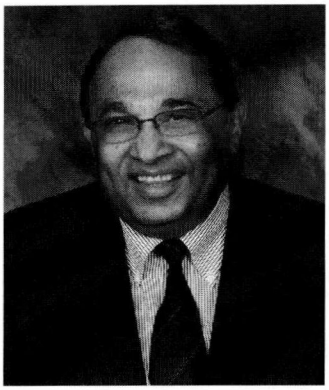
While I would take this opportunity to thank all of the contributors for their timely submission and valuable input, the immense help from the senior project coordinator, Kari Budyk, and persuasive ability of Lance Wobus, the scientific editor of CRC Press, in making me edit this unique book will always be remembered, appreciated, and acknowledged.

Since the contributing authors are all renowned scientists in their respective disciplines, they truly deserve all of the credit for the success of this book. However, it would be a great mistake if I forgot to thank three most important individuals, Dr. Amartya Chakrabarti, his undergraduate research assistant Hiren Patel, and my wife, Sumathy Hosmane, for their immense support, patience, and help throughout the editing process, from drawing the figures to proofreading to contributing chapters.

We sincerely hope that the chapters in this book will make your reading more intriguing and fascinating than those derived from other elements, as they illuminate the multifaceted nature of the boron compounds beyond their normal place as chemical curiosities.

For the authors,
Narayan S. Hosmane

Editor



Narayan S. Hosmane was born in Gokarn near Goa, Karnatak state, Southern India, and is a BS and MS graduate of Karnatak University, India. He obtained a PhD degree in inorganic/organometallic chemistry in 1974 from the University of Edinburgh, Scotland, under the supervision of Professor Evelyn Ebsworth. After a brief postdoctoral research training in Professor Frank Glockling's laboratory at the Queen's University of Belfast, he joined the Lambeg Research Institute in Northern Ireland, and then moved to the United States to study carboranes and metallacarboranes. After postdoctoral work with Russell Grimes at the University of Virginia, in 1979 he joined the faculty at the Virginia Polytechnic Institute and State University. In 1982 he joined the faculty at the Southern Methodist University, where he became professor of chemistry in 1989. In 1998 he moved to Northern Illinois University and is currently a distinguished research professor and inaugural board of trustees professor. Dr. Hosmane is widely acknowledged to have an international reputation as "one of the world leaders in an interesting, important, and very active area of boron chemistry that is related to cancer research" and as "one of the most influential boron chemists practicing today." Hosmane has received numerous international awards that include but are not limited to the Alexander von Humboldt Foundation's Senior U.S. Scientist Award twice; the BUSA Award for Distinguished Achievements in Boron Science; the Pandit Jawaharlal Nehru Distinguished Chair of Chemistry at the University of Hyderabad, India; and the Gauss Professorship of the Göttingen Academy of Sciences in Germany. While his recent lecture at the Kishwaukee Community Hospital in DeKalb, Illinois, on "Boron and Gadolinium Neutron Capture Therapy: A New Perspective in Cancer Treatment" has resulted in the initiation of collaborative research efforts between NIU and the oncologists/surgeons at Kish Hospital, his featured lecture at the recent American Chemical Society's special symposium on nanomaterials, held in Philadelphia, brought special attention of Dr. Hosmane's work in utilizing magnetic nanomaterials for effective drug delivery in cancer research. He has published over 270 papers in leading scientific journals.

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