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BOOK REVIEWS

Modern Terpyridine Chemistry. By Ulrich S. Schubert (Eindhoven University of Technology, Eindhoven, the Netherlands), Harald Hofmeier (Eindhoven University of Technology), and George R. Newkome (University of Akron, USA). Wiley-VCH Verlag GmbH & Co. KgaA: Weinheim. 2006. VIII + 230 pp. $110.00. ISBN 3-527-31475-X.

The careful design of ligands to control the structure and properties of their corresponding metal complexes has become an area of considerable interest and importance. In this regard, a great deal of recent attention has been directed toward the polypyridines, especially bipyridine and terpyridine (tpy). As the title suggests, this monograph explores the more “modern” aspects of tpy. Although the chemistry of bipyridine is far more extensive than that of tpy, the latter species offers a distinct advantage in that 4′-substitution maintains the symmetry of the ligand and allows the facile incorporation of this species into larger assemblies without the isomer problems that result with a monosubstituted bipyridine.

Chapter 1 is a brief introduction to the topic and includes an interesting histogram showing the dramatic increase in publications relating to tpy since 1950. Much of this chemistry is a direct consequence of improved and simplified methods for the preparation of the parent molecule as well as substituted analogues, a subject that is overviewed in Chapter 2. Synthetic approaches are divided into those that use the methodologies of Kröhnke or Potts/Jameson to assemble the central ring and those that use a variety of increasingly popular cross-coupling methods. Various fused ring and bridged derivatives of tpy, available through Friedländer chemistry, are not considered.

The authors address the chemistry and properties of mononuclear tpy complexes in Chapter 3. The material presented here provides the basis for the following four chapters involving systems having higher nuclearity. This chapter gives a well-organized, clearly illustrated introduction to the basic physical methods used to analyze tpy complexes: NMR, electronic absorption and emission, and mass spectrometry. The emphasis is on complexes of Ru(II) that have been most widely studied. Unfortunately, the stepwise process in which two tpy’s coordinate to form $[Ru(tpy)_2]^{2+}$ is not addressed. The involvement of the tpy motif in bridging ligands is covered in Chapter 4, with an impressive array of polynuclear complexes being built up from the judicious arrangement of tpy subunits. In this context, the concept of using these arrays as molecular wires for the transmission of energy or electrons is set forth. The principle of self-assembly is illustrated in a most effective manner through the use of ligands having multiple linearly arranged tpy binding sites that form grid- and rack-type structures through the information that is programmed into their preorganized structure. The next two chapters relate more closely to the research interests of the authors, who discuss functional polymers that incorporate tpy, dendrimers, and other bulk assemblies involving tpy. In both chapters the emphasis is on design features that take intriguing advantage of the structural consequences inherent in the tridentate coordination of tpy. The last chapter is more materials related and covers the modification of surfaces with tpy complexes bound either through covalent sulfur linkages or through coordinative bonds.

Overall the book is well composed with excellent graphics and a multitude of clearly drawn chemical formulas. The approach is structure-based and detailed photophysical properties of the complexes are not included, making the text quite friendly to the casual reader. The references are up-to-date although, of necessity, some work is not included. With the advent of SciFinder, there is little need for encyclopedic reviews. The book is recommended for those involved in ligand design and supramolecular chemistry involving metal complexes. It should serve as an inspiration for new ideas in this quickly growing field. A similar overview of bipyridine chemistry would be a welcome complement to this timely monograph.

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Name Reactions: A Collection of Detailed Reaction Mechanisms, 3rd ed. By Jack Li (Pfizer Global Research and Development, Ann Arbor, MI). Springer: Berlin, Heidelberg, New York. 2006. xx + 652 pp. $89.95. ISBN 3-540-30030-9.

Like its predecessors, this edition of *Name Reactions* covers over 300 classical and contemporary name reactions, with each entry including the name of the reaction, a short description of it, the step-by-step mechanism, and a list of references. Improvements to this edition include updated references, two to three examples of applications of the featured reaction to highlight its “synthetic utility”, brief biographical sketches of the discoverers and developers of the reaction in question, and an expanded subject index.

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The Chemistry of Peroxides, Volume 2, Parts 1−2. From the Patai Series: The Chemistry of Functional Groups. Edited by Zvi Rappoport (The Hebrew University, Jerusalem). John Wiley & Sons, Ltd.: Chichester. 2006. xx + xx + 1498 pp. $990. ISBN 0-470-86274-2.

Parts 1 and 2 of this volume contain 17 chapters dealing with a wide range of structural, mechanistic, and theoretical features of the chemistry of peroxides. Coverage of the literature is generally through 2003−2004 and focuses on many of the significant advances in the field since the publication of Volume

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1 (1983) with Supplement E2 (1993) of this series and the Wiley book *Organic Peroxides*, edited by Ando (1992).

Part 1 opens with an exciting chapter by Bach on the theoretical aspects of the peroxide group. Comprehensive, timely coverage of the computational approaches to studying the oxygen-atom transfer processes of small flavinoid peroxides is provided. A chapter on the structural chemistry of organic acyclic peroxides by Hartung and Svoboda is nicely organized by type of compound to demonstrate the set of five effects that is thought to control most of the important structural features, which ultimately affect/relate to reactivity. Chapter 3 by Slayden and Liebman covers the thermochemistry of peroxides. The available data on organic peroxides are nicely organized in this review, despite, as pointed out by the authors, the lack of activity in this area in the past decade. Cerioni and Mocci provide an extensive overview of the ^{17}O NMR spectroscopy of organic peroxides. The focus is on organic peroxides, ozonides, and trioxides with a brief section on biological applications. An exhaustive review of the synthesis of cyclic peroxides, excluding dioxetane, dioxirane, ozonide, and other related systems, is presented by Korshin and Bachi. The emphasis is on the synthesis of cyclic peroxides with ring sizes of five to seven members and that of 1,2,4-trioxanes. Berkessel and Vogl provide a careful review of the synthetic methodologies for the synthesis of organic peroxides as well as synthetic applications of organic peroxides, including hydroperoxides. A large portion of the review is devoted to asymmetric oxidations of organic hydroperoxides and peroxides. Part 1 concludes with an illustrative but extensive review by Zabicky of the analytical methods of identifying, determining, and characterizing peroxides by type. The section on safety is quite general and directs the reader to other sources.

Part 2 begins with an excellent contribution by Ando on silicon and germanium peroxides. The synthesis and applications of these relatively stable compounds are clearly presented. The singlet oxygen "ene" reaction of alkenes to form allylic hydroperoxides is the object of a lengthy review by Orfanopoulos, Vougioukalakis, and Stratakis. The focus is on the mechanistic features that lead to selectivity. Chapter 10 by Kim presents a classic physical–organic analysis of polar effects in thermolytical decomposition and related reactions of organic peroxides. An extensive review of peroxides in biological systems is provided by Cadet and Di Mascio. The organization of the chapter is based on the oxidation of nucleic acids, lipids, and proteins (and components) to yield, in general, the corresponding hydroperoxides. Sulfur and phosphorus peroxides are reviewed by Jadhav, Park, and Kim. Sulfur peroxide chemistry constitutes the bulk of the coverage with a large section on "oxone" (peroxymonosulfate) oxidations. The synthesis and oxidation of transition metal peroxides are reviewed by Conte and Bortolini, wherein the synthetic and mechanistic advances in peroxy, peroxo, and μ-peroxo complexes, with the exclusion of bio-related aspects, are presented. Dioxirane and dioxetane chemistry are covered in two chapters by Adam with Zhao and Trofimov, respectively. The review of reactions of dioxiranes covers recent advances in epoxidation (including catalysts for asymmetric preparation), heteroatom oxidation, and CH insertions. Mechanistic and applied features of dioxetane and dioxetanone (α-peroxy lactone) chemiluminescent reactions are highlighted in the second review. The subsequent contribution by Baader, Stevani, and Bastos covers the chemiluminescent chemistry of organic peroxides in general. In addition to coverage of the basic principles of chemiluminescence, the classic systems from dioxetane/dioxetanones to luminol and currently accepted mechanisms are presented. The final chapter is a detailed review of biomimetic Fe(II) chemistry and work on antimalarial (artemisinin-related) and antitumor endoperoxides by O'Neill, Chadwick, and Rawe. Progress in the understanding of the processes of antimalarial activity of endoperoxides is the main focus of the chapter with a concluding section on the assessment of antitumor activity. Extensive author and subject indices complete the entire work.

In summary, this volume is an extremely useful background/overview resource that should be part of the collection of any comprehensive chemistry library. In addition, the timely coverage of the major research areas should inspire many researchers to explore exciting, new applications of peroxide chemistry.

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Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. IUCr Texts on Crystallography, 8. By Peter Müller (Massachusetts Institute of Technology, Cambridge, USA), Regine Herbst-Irmer (University of Göttingen, Germany), Anthony L. Spek (Utrecht University, The Netherlands), Thomas R. Schneider (The FIRC Institute of Molecular Oncology, Biocrystallography, and Structural Bioinformatics, Italy), and Michael R. Sawaya (University of California, Los Angeles, USA). Oxford University Press: Oxford, New York. 2006. XVIII + 214 pp. $98.50. ISBN 0-19-857076-7.

This book covers the "more advanced aspects of crystal structure refinement" and "focuses on practical problems in the everyday life of the crystallographer". The first two chapters are an introduction to SHELXL and a survey of the refinement of crystal structures, respectively, whereas most of the remaining chapters concern different aspects of structure refinement and include a range of topics from the treatment of hydrogen atoms to twinning. There are also chapters on protein refinement, artifacts, and validating structures, and a final chapter entitled "General Remarks" that resembles an FAQ document and includes helpful information that could not be fit into the context of any of the preceding chapters. Examples of refinement based on SHELXL are included in most of the chapters, and the book comes with a CD-ROM that contains the necessary data for reproducing the refinements.

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Structure and Chemistry of Crystalline Solids. By Bodie E. Douglas and Shih-Ming Ho (University of Pittsburgh). Springer Science + Business Media, Inc.: New York. 2006. x + 346 pp. $129.00. ISBN 0-387-26147-8.

The authors' objective in writing this book was to present a system of notation and classification for systematically describing the structures of crystalline solids. The so-called “PTOT” notation (P = packing atom, T = tetrahedral site, O = octahedral site) is used to describe hundreds of known crystal structures exhaustively, with a nice emphasis on highlighting the similarities among seemingly disparate structures.

The PTOT formalism is introduced in the first chapter, and the notation of the formalism must be mastered before proceeding to any of the subsequent chapters. A very concise review of basic crystal chemistry is presented in the second chapter before the authors move to in-depth PTOT descriptions of common close-packed structures, which is the focus of Chapter 3. Chapters 4−11 are organized by types of structures, including elements, molecular crystals, structures with a variety of different layer sequences, and a small sampling of intermetallic, silicate, and organic structures. In all cases, the focus is on applying the PTOT formalism to the crystal structures that are presented. The book concludes with a short summary that focuses on the prediction of structures and general guidelines for assigning PTOT notation to other structures.

In addition to presenting a systematic formalism for describing crystal structures, this book could also serve as a reference that includes a significant amount of tabulated data, such as structures and densities of elemental metals, space groups and unit cell dimensions for many crystal structures, and pictures of structures in various orientations. Many tables throughout the book provide classification of structures by type, which is a convenient complement to information given in Pearson’s *Handbook of Crystallographic Data for Intermetallic Phases*, for example, although the basis for the structural assignments is unclear.

The focus of this book is clearly on crystal structures and delineating their PTOT descriptors. Despite the title’s implication that synthesis and bonding may be part of this book, there are only a few cursory statements about the conditions for preparation and very little about bonding. There are, however, some nice but sporadic diversions in which historical accounts and interesting physical properties are described. This book would not be appropriate as a stand-alone text, because it leaves out several important concepts in solid-state chemistry. Also, while useful as a unifying and information-rich notation scheme for describing crystal structures and as a tool for recognizing similarities and differences among structures, the PTOT notation will probably not be widely used in the language of mainstream crystal chemistry.

High-quality graphics are critical for a book that focuses on structural solid-state chemistry, since complex three-dimensional structures must be clearly represented within the physical confines of a two-dimensional sheet of paper. Unfortunately, the graphics in this book are generally substandard. They are all black-and-white, with many hand-drawn crystal structures that are reminiscent of, or borrowed directly from, decades-old books. For the structures that are reproduced from books such as Pearson’s *The Crystal Chemistry and Physics of Metals and Alloys* (1972) and Wyckoff’s *Crystal Structures* (1963), the labels and text are generally too small to read, rendering the graphics much less useful than in their original published forms. These dated graphics are interspersed with more contemporary images produced by CrystalMaker. However, the orientations in which the structures are presented are not always those that are the most clear. Also, the lack of contrast and color differences among the atoms, coupled with sporadic labeling, makes it difficult to tell the identities of atoms in many of the crystal structures. Fortunately, a supplementary CD-ROM with interactive CrystalMaker files is included, and this provides better representations of some of the structures discussed in the book.

Overall, this book is very interesting and useful for its ability to describe systematically the often-overlooked similarities among crystal structures that appear, at first glance, to be very different. As such, it will appeal to specialists in crystal chemistry who are interested in probing deeper into structural similarities and differences in solid-state compounds and also to educators and students who desire supplementary information about crystal structures.

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