

Book Review

Making Crystals By Design: Methods, Techniques and Applications Edited by Dario Braga and Fabrizia Grepioni (University Bologna). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2007. xiv + 348 pp. \$190. ISBN 978-3-527-31506-2.

K. Travis Holman

J. Am. Chem. Soc., **2008**, 130 (9), 2878-2878 • DOI: 10.1021/ja0769090

Downloaded from <http://pubs.acs.org> on February 8, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Making Crystals By Design: Methods, Techniques and Applications. Edited by Dario Braga and Fabrizia Grepioni (University Bologna). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2007. xiv + 348 pp. \$190. ISBN 978-3-527-31506-2.

The concept of designing crystalline solid-state structures has been topical as of late, and with good reason. Never has the relationship between bulk structure and properties been so broadly appreciated by the scientific community, and never have scientists been more capable of manipulating structure on the molecular level. Thus, the drive to make crystals by design has been a strong influence across the disciplines of chemistry, from synthetic to computational, organic to inorganic, characterization to application. This book nicely complements others in this field of crystal engineering by providing small glimpses into various “goings on” in the context of molecule-based designer crystal chemistry. As such, it is by no means historically exhaustive, nor does it pretend to be. Rather, the 12 chapters, written by an interdisciplinary group of leaders-in-the-field, constitute vignettes and perspectives into designer molecule-based crystal chemistry.

The book is formally divided into three sections: Geometry and Energetics (three chapters), Design and Reactivity (four chapters), and Characterizations and Applications (four chapters). The chapters are generally written from a welcoming and educational perspective, with a sprinkling of current references to recent advances and findings. The first two chapters nicely deliver the theoretical underpinnings of the supramolecular interactions in crystals, but the absence of a chapter concerning the state-of-the-art in predicting crystal structures is somewhat conspicuous. A good treatment of networks and topology completes the first section.

The second section begins with a three-chapter emphasis on predicting and designing reactivity in molecular crystals, thoroughly addressing the work on controlling nearest neighbor orientations in crystals and solid–solid reactions. It is concluded by two chapters that most directly relate to the title of the book, one concerning strategies for making coordination frameworks and another for assembling molecular crystals by noncovalent interactions.

Finally, the third section has less to do with making crystals by design but rather addresses some of the more important techniques—diffraction, solid-state NMR spectroscopy, thermal analysis, and gas sorption—and phenomena of interest, such as polymorphism and porosity, to the crystal engineering community at large. Overall, there is little doubt that this text accomplishes its principal goals. It nicely provides, as the editors had hoped, an “Arianna’s

thread to beginners” navigating their way through the labyrinth of this exciting and burgeoning field of making crystals by design.

K. Travis Holman, *Georgetown University*

JA0769090

10.1021/ja0769090

Endoglycosidases: Biochemistry, Biotechnology, Application. Edited by Masahiko Endo (Hirosaki University, Aomori, Japan), Sumihiro Hase (Osaka University, Osaka, Japan), Kenji Yamamoto (Kyoto University, Kyoto, Japan), and Keiichi Takagaki (Hirosaki University School of Medicine, Aomori, Japan). Kodansha Ltd: Tokyo and Springer: Berlin, Heidelberg, New York. 2006. xvi + 255 pp. \$169.00. ISBN 4-06-212192-2 (Kodansha) and 3-540-34494-2 (Springer).

Endoglycosidases play important physiological roles in development by catabolizing glyconjugates. These exquisitely selective enzymes have been referred to as the carbohydrate equivalents to the restriction enzymes, which are so important to the manipulation of nucleic acids. In addition to cleaving sugar chains “in the middle”—in contrast to exoglycosidases that cleave a single carbohydrate unit from the nonreducing end of a carbohydrate chain—endoglycosidases will also catalyze the transfer of oligosaccharides from one substrate to another. This latter property makes these enzymes extremely useful for the reconstruction of complex glycopeptides and glycoproteins, as well as polysaccharides and glycolipids. This concise and useful book is the product of 19 contributors with expertise in a number of chemical and biological areas and reviews the diverse possibilities for the application of glycobiological techniques toward the understanding of physiological processes. As such, it provides important introductory material for the nonspecialist (or cross-specialist) that might not normally be included in a more focused monograph, as well as specific examples of applications with the provision of precise details. This is really a “how to” book.

There are seven chapters, the first being a review of the carbohydrate structures and enzymes encountered in biological systems, the highly specialized techniques involved in the purification and cloning of endoglycosidases, and the measurement of enzyme activity. The first chapter includes a brief review of basic carbohydrate structures as well. The second chapter provides an introduction to representative endoglycosidases and an overview of their use in the synthesis of *N*- and *O*-linked glycopeptides and glycoproteins, as well as a discussion of the synthesis of proteoglycan fragments and glycosphingolipids. These first two chapters comprise half of the book. The next four provide specific and detailed examples of the use of endoglycosidases in the enzymatic synthesis of these biological molecules and analogues, e.g., libraries, fluorescent derivatives,

Unsigned book reviews are by the Book Review Editor.

non-naturally occurring homologues. The explanations are clear and concise and are accompanied by useful figures and detailed illustrations, such as pictures of gels, TLC plates, spectra, HPLC traces, etc. The final chapter is focused on classical glycobiology, including examples of enzymatic release, purification, and analysis of carbohydrate structures using endoglycosidases. Also included is an appendix of specificities for more than 40 endoglycosidases as well as information on commercial availability. A brief but useful index is included.

The book is better written and more comprehensive in terms of the required techniques than the *CRC Handbook of Endoglycosidases and Glycoamidases* by Takahashi and Muramatsu (1992) and should be part of the library of any serious glycobiochemist.

Robin Polt, Ph.D., *The University of Arizona*

JA076925X

10.1021/ja076925x

Heterocycles from Carbohydrate Precursors. Topics in Heterocyclic Chemistry, 07. Edited by El Sayed H. El Ashry (Alexandria University, Egypt). Series Edited by R. R. Gupta. Springer: Berlin, Heidelberg, New York. 2007. xii + 354 pp. \$349.00. ISBN 3-540-72956-3.

This book is a compilation of recent information on a diverse array of topics related to the use of carbohydrates either as backbones or as templates for the synthesis of heterocycles. The medicinal and industrial importance of pursuing molecules of these types drives the discussion of why they are constructed, and the value of using this inexpensive chiral pool in synthesis is another focus of this volume. Some of the material presented is very general in nature, whereas other topics are written for a highly specialized audience.

There are nine chapters written by individuals who have published extensively in this area of synthetic chemistry. The content includes a general overview of methods to prepare heterocycles from sugar carbon atoms in the first chapter, as well as chapters on more specific carbohydrate starting materials, such as amino and azido sugars (Chapter 2), carbohydrate isothiocyanates (Chapter 3), and anhydro sugars (Chapter 9). The use of alkyne-azide and nitron-alkene cycloaddition reactions (Chapters 5 and 8, respectively) to prepare heterocycles from sugars is also discussed. Recent literature syntheses of carbohydrate-derived β -lactams are summarized in Chapter 4, and methods for synthesizing the antibiotic (-)anisomycin and its derivatives are discussed in Chapter 7. Approaches for the synthesis of glycoporphyrins (Chapter 6) are also detailed in this volume. Embedded in several of the chapters are discussions on the construction of cyclodextrin analogues and derivatives and methods for the preparation of glycoclusters, glycodendrimers, and glycopolymers. The preparation of nucleosides is briefly discussed in Chapters 1, 2, and 8 and is covered more extensively in Chapter 3.

The authors of the various chapters do a good job of describing the different methods used to synthesize these important molecules. Overall, the book reads well and contains only a few minor typographical errors. It is essential reading

for individuals doing research in this area of chemistry and will be of particular interest to chemists working in the pharmaceutical industry and to those with an interest in medicinal chemistry. However, the cost of this volume will preclude personal ownership for most readers.

Cecilia H. Marzabadi, *Seton Hall University*

JA077015I

10.1021/ja077015i

Advances in Chemical Physics, Volume 136. Edited by Stuart A. Rice (The University of Chicago). John Wiley & Sons, Inc.: Hoboken, NJ. 2007. x + 318 pp. \$175. ISBN 978-0-471-68232-5.

This issue of *Advances in Chemical Physics* comprises five contributions covering a range of theoretical and experimental topics, from those within the broader areas of small gas systems and bulk amorphous materials to the experimental properties of diamondoid molecules.

The first chapter by Goldfield and Gray is a comprehensive discussion of the method of real wave packet propagation developed by the authors for quantum dynamics in small, three- to four-atom chemical systems. They present efficient numerical representations of the wave packet in a methodical manner and discuss the needed development of parallel computing algorithms—of which they present three versions—to tackle the more formidable four-atom problems, such as the dynamics of dissociation of H_2O_2 and CH_2O . In their opinion, full quantum treatment of larger systems appears to be unlikely, and approximation methods, such as reduced-dimensionality models, are discussed.

The second chapter is on quantum monodromy and molecular spectroscopy, in which Child discusses the abstract mathematical concepts of moving around singularities, which can be related to a number of quantum level structures, in a language usable by and comprehensible to the community of chemical physicists. Quantum states form lattice points in the space of their quantum numbers—here, a two-dimensional space of bending and angular momentum. When the lattice is regular, the quantum numbers can be globally defined and hence are good for all values. If the lattice has a defect, then the quantum numbers can only be defined locally; i.e., the system has monodromy, a singularity in the lattice space around which the “good” quantum numbers can change. These basic ideas are presented first in the context of quasi-linear molecules, followed by applications to HCP, LiCN, and a series of systems with Fermi resonances.

Topics shift completely in the third chapter to the condensed phase, as Lubchenko and Wolynes discuss the microscopic quantum theory of amorphous solids at low temperatures. The random first-order transition theory of glasses, developed to explain the glass transition quantitatively, has been extended to cover a broader range of issues in amorphous materials. Using a semiclassical approach, the authors give a detailed account of the low-temperature anomalies in the heat capacities of glassy materials. They then present a purely quantum phenomenon of level mixing, its effect on the density of states of tunneling centers, and how the interactions among these centers mediated

by phonons can contribute to the negative thermal expansivity observed in amorphous materials.

In the next chapter, Mansoori describes the experimental properties of a specific class of materials, diamondoid molecules. These molecules possess the same carbon-carbon framework present in the diamond lattice structure, which consists of repeating units of 10 carbon atoms forming a tetracyclic cage system. The simplest and smallest member of this group is adamantane, C₁₀H₁₆. Here, Mansoori presents the chemical and physical properties of diamondoid molecules, along with methods of their synthesis. The structural complexity and variety of these compounds and their unique properties have led to a wide range of uses. Examples are given in which these molecules serve as templates and building blocks for polymers, nanostructures, drug targeting and delivery, DNA-directed assembly, and host-guest chemistry.

The final chapter in the book is a brief summary of recent advances in time-resolved X-ray diffraction of liquids by Bratos and Wulff. Laser technology and the development of ultrafast (nanosecond to femtosecond) X-ray sources now allow researchers to monitor atomic motions of chemical processes in real time. The basics of both experimental methods and supporting theory are briefly covered. The remainder of the chapter is devoted to recent studies in diffraction/absorption, visualization of atomic motion, chemical structure of reaction intermediates, and dynamics of laser-heated liquids and closes with a somewhat distantly related discussion of gold nanoparticles in water.

It is clear from the wide range of topics presented that readers will likely be attracted to specific chapters of interest as opposed to the book as a whole, as there is no single unifying theme to this particular volume. They will be rewarded for their efforts by the careful and lucid presentations of the contributing authors to these areas of current and active interest.

James M. Lisy, *University of Illinois at Urbana-Champaign*

JA077010L

10.1021/ja077010I

Analytical Instrumentation: A Guide to Laboratory, Portable and Miniaturized Instruments. By Gillian McMahon (Dublin City University, Ireland). John Wiley & Sons, Ltd: Chichester. 2007. xxii + 296 pp. \$100. ISBN 978-0-470-02795-0.

In this book, the author discusses analytical instruments that are currently available, from established benchtop equipment to the latest trends in miniature devices, all from a practical rather than a theoretical point of view. She takes the reader from large and more traditional instruments in the beginning of the book to small, more modern instruments at the end of it. The first chapter is an introduction to analytical instrumentation and the analytical process. The remaining chapters are organized into the following sections: (I) Laboratory Analytical Instrumentation; (II) Portable Analytical Instrumentation; (III) Process

Analytical Instrumentation; and (IV) Miniaturized Analytical Instrumentation. A subject index completes the book.

JA800425V

10.1021/ja800425v

Progress in Inorganic Chemistry, Volume 55. Edited by Kenneth D. Karlin (Johns Hopkins University, Baltimore, MD). John Wiley & Sons, Inc.: Hoboken, NJ. 2007. vi + 760 pp. \$175.00. ISBN 978-0-471-68242-4.

Volume 55 of *Progress in Inorganic Chemistry* is capacious—a total of 760 pages—with nine excellent, timely articles on bioinorganic and organometallic topics of current interest. It begins with a contribution from Farver and Pecht entitled “Elucidation of Electron Transfer Pathways in Copper and Iron Proteins by Pulse Radiolysis Experiments”. Determination of three-dimensional structures of numerous proteins has fostered attempts to elucidate the electron transfer (ET) pathways in proteins and the mechanism(s) of ET processes. Time-resolved absorption spectroscopy, coupled with pulse radiolysis, has been particularly helpful in the case of various copper- and iron-containing redox proteins, such as azurin and cytochrome c oxidase, and Chapter 1 is a concise account of progress made in this area. The authors have carefully discussed the results of various measurements, including EPR and EXAFS, on selected mononuclear and multinuclear copper-, iron-, and copper-iron-containing proteins for the readers to readily identify the critical parameters that dictate the rate of ET in these macromolecules with special architectures and appreciate the role of intervening peptide matrices. Proteins from various sources performing a similar function, such as bacterial copper- and iron-containing nitrite reductases, are compared to highlight the intricate controls operating in multicenter redox enzymes.

In Chapter 2, Chei and Suh review “Peptide- or Protein-Cleaving Agents Based on Metal Complexes”. Recently synthesized metal complexes that mimic hydrolytic metalloenzymes have held promise as tools in applications such as proteomics and artificial enzymes (chemozymes). This chapter begins with a nice discussion on the roles of metal ions, such as Zn(II) and Co(III), in promoting hydrolysis of coordinated ligand frames and the mechanistic aspects of metalloproteases. The authors then systematically cover (a) redox-active copper and iron complexes derived from organic moieties readily recognized by proteins—species that have been employed as agents for oxidative cleavage of proteins, (b) various soluble metal complexes that nonselectively cleave proteins, and (c) materials with embedded copper complexes that act as artificial proteases applicable to protein industries. The final section on metal complexes selective for target peptides or proteins is an excellent introduction to the emerging paradigm in drug design. Discussions of PNA-tethered Cu-cyclen derivatives and Co-cyclen derivatives convince the reader of the prospect of synthesizing target-specific artificial proteases.

During the past two decades, rapid progress has been made in porous coordination polymers (CPs) and metal-organic frameworks (MOFs) based on assemblies of metal centers polymerized through multifunctional organic linker molecules. Such high-dimensional solids are desirable because of their range of applications. Although several reviews on CP and MOF

have already been published, lanthanide (Ln)-based materials have been the subject of very few articles. Chapter 3 by de Lill and Cahill, "Coordination Polymers of the Lanthanide Elements: A Structural Survey", effectively fills this void. The authors provide extensive tables and figures that highlight the structural variations and extended topologies observed with Ln-based materials with various N,O-linkers. They also give excellent discussions on different modes of binding of the linkers, various design principles, methods of synthesis, and the properties and use of the resulting materials. Inclusion of recent reports on heterobimetallic systems, structures with multiple linkers, and extended structures of various lanthanide oxalates, phosphonates, and sulfonates makes this account quite up-to-date.

"Supramolecular Chemistry of Gases" by Rudkevich focuses on factors that dictate selective binding of small gaseous molecules to supramolecular structures. Although substantial progress has been made in the area of host-guest complexation and sensing of ionic and organic species with the aid of supramolecular chemistry, molecular recognition of gases by supramolecular hosts or networks has not been studied to a great extent so far. Such studies are important in relation to gas storage and purification as well as in medicine. In this opportune review, the author discusses the roles of forces like hydrogen bonding, Lewis acid-base interactions, and dipole-dipole interactions that are responsible for encapsulation of gases in a variety of supramolecular entities. The excellent discussion of heme-model systems, designed on the basis of principles that govern binding of O₂, NO, and CO to hemoglobin, demonstrates how lessons from nature can be exploited in designing macromolecular assemblies that can bind gases (even reversibly). Pertinent topics, such as gas entrapment by porous MOFs, covalent organic frameworks and clathrates, reversible chemical fixation of gases, and calixarene-based xerogels crosslinked by CO₂, highlight this emerging area of research on interactions of gaseous guests with designed supramolecular assemblies.

The concept of "ligand innocence" has drawn special attention recently following identification of numerous stable ligand radicals housed in metal complexes. In addition, many highly reactive and paramagnetic ligand- or metal-based radical species have been shown to participate in various homogeneous and heterogeneous catalytic processes involving organometallic complexes of second- and third-row group 9 and 10 metals. The definition of formal oxidation state becomes less meaningful when there is a great deal of covalency in the metal-ligand bond: an unpaired electron could reside on the metal or the ligand (or somewhere in between) in complexes of second- and third-row metals. In Chapter 5, de Bruin et al. provide a concise review of "The Organometallic Chemistry of Rh-, Ir-, Pd-, and Pt-based Radicals: Higher Valent Species" with emphasis on the non-innocence of ligands. Syntheses of a variety of mono- and polynuclear paramagnetic complexes of these metals in +3 and +4 formal oxidation states are discussed, and analyses of EPR spectra of the various species illustrate how the location of the unpaired electron can be determined. Discussion of the reactivity of paramagnetic species in typical organometallic reactions highlights how the unpaired electron exerts its effect(s) depending on its location on the species involved in carrying out the catalytic transformation. This becomes clearer in the section on reactions of paramagnetic porphyrinato radicals where

bond activation of C-X (X = H, N, O) by such species is discussed in detail. Overall, the authors have done an excellent job in demonstrating the importance of unpaired electron(s) in organometallic reactions involving group 9 and 10 platinum metals in high oxidation states.

Since the early 1980s, metal-alkyne, -enyne, and -enediyne complexes (both σ - and π -bonded) have been studied extensively. Such species with metals in low oxidation states are involved in a myriad of group-transfer metathesis reactions, asymmetric synthesis, and catalysis as well as in the synthesis of dendrimers, molecular photochemical devices, and metal-based macrocycles. Chapter 6, "Unique Metal-Diyne, -Enyne, and -Enediyne Complexes: Part of the Remarkably Diverse World of Metal-Alkyne Chemistry" by Bhattacharya et al. summarizes the thermal reactions, structures, physical properties, and electronic descriptions of metal-acetylides and molecular aggregates having similar types of bonding. The chemistry of these entities is discussed to establish the scope of metal-alkyne interactions in building molecular architecture having desired properties. Specific examples include Pt(II)-Pd(II)-polyyne metallomesogens, cyclometalated luminescent Au(III)-alkyne species, and materials exhibiting nonlinear optical properties. The section on the reactivity of the metal-alkyne π complexes is especially noteworthy as an insightful discussion on various ring-closing enyne cross-metathesis reactions using various catalysts in solution and solid phases. Well-chosen examples of Bergman cyclizations are reviewed, and a discussion on the porphyrin-enediyne conjugates underscores the impact of the Bergman photoreaction on the photochemistry of porphyrin-related materials.

In Chapter 7, Rosenthal and Nocera have compiled the recent advances made in the area of "Oxygen Activation Chemistry of Pacman and Hangman Porphyrin Architectures Based on Xanthene and Dibenzofuran Spacers". These designed cofacial porphyrin metal complexes facilitate multielectron activation of small molecules with minimal structural reorganization. To date, use of specific spacers such as anthracene and selected metal ions has allowed reduction of dioxygen and dinitrogen by such species. This review provides additional information on similar architectures with further modifications. The syntheses, structures, and physical properties of the Pacman porphyrin complexes are thoroughly covered, and coverage of their photophysical properties, emission characteristics, and triplet-state parameters is excellent. Insight into the "Pacman effect" in the catalytic reduction of dioxygen, structures of the various oxygenated intermediates, and the utility of these species as oxidation catalysts are notable highlights. Convincing evidence is presented that proper design of the cleft size and preorganization of redox cofactors around the metal centers in Pacman platforms could lead to specific activation of a variety of small molecules.

Although interaction of metal ions with nucleic acids has been the subject of numerous reviews, research in this burgeoning field continues to afford macromolecules with novel structures and properties. Examples are discussed by He et al. in their article, "Metal-Containing Nucleic Acid Structures Based on Synergetic Hydrogen and Coordination Bonding". Here, the structural features and modes of bonding of intricate mono-nuclear and multinuclear metal-containing duplexes and extended inorganic-nucleic acid hybrid nanostructures derived

from various metal ions and DNA and PNA are reviewed. Synergetic formation of base pairs and coordination of metal ions to built-in ligand moieties on the DNA strands give rise to the extended structures in this supramolecular chemistry. Following a nice overview of changes in the nucleic acid structures upon coordination of metal ions to unmodified DNA duplexes, the authors draw the reader's attention to the more exciting possibility of changes upon the binding of metal ions to ligand-modified DNA duplexes. Structural parameters of a variety of metal–DNA complexes with one or more built-in ligands, such as bipyridine and various Schiff-base ligands, are conveniently compiled in tables. Binding of metal ions to the built-in ligand moieties along the DNA strand at selected sequence effects structural changes that alter the physical and photochemical properties of the metal–DNA conjugates and have been exploited in making molecular beacons and structural probes. The possibility of extending such metal–DNA interactions in three dimensions and forming extended hybrid nanostructures, as discussed in this chapter, will encourage researchers to carry out further investigations in this area.

The last chapter by Comba et al. is a timely review of “Bispidine Coordination Chemistry”. The authors provide an extensive discussion on the various types of bispidine and extended bispidine ligands, their syntheses and stereochemistry in addition to the bonding, isomerism, and dynamics of metal complexes involving these ligands. The list of complexes provided will be a useful guide for those interested in such chemistry. The final section on the reactivity of the copper– and iron–bispidine complexes demonstrates the utility of this set of ligands in biomimetic chemistry.

In summary, the nine chapters of Volume 55 cover a wide variety of topics, from mechanisms of long-range electron transfer in redox proteins to organometallic chemistry of Rh-, Ir-, Pd-, and Pt-based radicals. As with previous volumes, this one serves its purpose of “cutting edge of scientific reporting” and provides stimulation to various inorganic subdisciplines.

Pradip Mascharak, *University of California, Santa Cruz*

JA077001C

10.1021/ja077001c