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BOOK REVIEWS

Magnetism: Molecules to Materials V. Edited by Joel S. Miller (University of Utah) and Marc Drillon (Institut de Physique et Chimie des Matériaux de Strasbourg). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2005. xiv + 381 pp. $190.00. ISBN 3-527-30665-X.

The field of molecular magnetism has been growing rapidly for nearly two decades and is beginning to make significant contributions to a wide variety of fields. These include applications in materials science related to conductivity, optical properties, and nanoporous materials. As such, more and more scientists are entering the field and require a convenient and thorough means to acquaint themselves with the background, both experimental and theoretical, of molecular magnetism and its recent applications. This volume, like its predecessors, continues to provide this background in a clear and well-organized manner. A variety of topics are presented, providing the necessary review of the literature to set the scene and finishing with the latest developments in the field.

Drillon and Miller have collected recognized experts, who are currently in the forefront of their field, to write each chapter so that the reader is treated to the point of view of someone active in the field. The breadth of applications and the recent emphasis on cooperative properties make this all the more critical and useful. I personally found the chapters on the uses of scaling theory (Souletie, Rabu, and Drillon) and Monte Carlo simulations (Cano and Journaux) to be especially helpful in showing potential applications. The chapter on exchange in lanthanide systems (Sutter and Kahn) should spawn additional interest in an area that needs additional study, due to the large moments available in some lanthanide ions. An excellent review of the state of analogues of Prussian blue (Verdaguer and Girolami) is also included. These compounds were among the first in recent times to demonstrate the possibility of "magnets by design" with spontaneous moments near or above room temperature and therefore provide a good basis for thinking about the design of new systems.

Overall, the book is a good general primer for applications of molecular magnetism and is useful as general reading for scientists entering the field, especially students. The clear designation of topics also makes it a useful reference work, although I personally would have liked to see more emphasis on recent work and a bit less review material in some of the sections. However, as the editors point out in the preface, the series is intended to provide critical reviews of the literature and this is accomplished clearly and completely.

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Chemistry and Physics of Carbon, Volume 29. Edited by Ljubisa R. Radovic (Pennsylvania State University). Marcel Dekker: New York. 2004. xvi + 430 pp. $189.95. ISBN 0-8247-4088-2.

This book should be of interest to scientists and engineers engaged in basic and applied research in a number of disciplines, including physics, chemistry, materials science, geology, and environmental and biological sciences, to name a few. As eloquently stated by the editor in the preface, this book is a compilation of "three authoritative reviews on old but new topics, on old but new carbon materials...Another demonstration that carbon is indeed the supreme cameleon and that its chemistry and physics offer endless opportunities for doing imaginative and innovative research and developing exciting new technologies!"

The first chapter by Inagaki et al. provides a detailed description of the phenomenon of exfoliation of graphite. Beginning with a brief historical account, the authors describe methods used in industry for producing exfoliated graphite, discuss the effects of different exfoliation conditions, parameters, and intercalations on the resulting material, and present an overview of some of the techniques and applications for characterizing exfoliated materials. The authors do well in presenting a detailed, albeit qualitative, description of the subject matter. Inclusion of some of the theoretical ideas that have been employed for understanding the physical properties of heterogeneous disordered materials, for example, the theories of percolation and effective medium, would have benefited a wider readership.

Diamond synthesis at low pressure, the topic of the second chapter by Marinković, was being investigated vigorously worldwide during the 1980s and early 1990s. Remarkable research activity during this period resulted in the development of several techniques for the growth and characterization of the material and an understanding of the fundamental mechanisms underlying the synthesis of diamond at low pressure. The author presents a good qualitative review of the experimental techniques, nucleation and growth, thin-film properties, doping, and applications of chemical vapor deposited (CVD) diamond. The inclusion of several tables provides a useful and quick reference for the reader. There is also a discussion of the numerous applications of CVD diamond, from cutting tools to electronic and optical devices, which should stimulate interest in diamond synthesis at low pressure among potential newcomers to the field. The chapter includes only limited accounts of the rich phase diagram of carbon, the surface science of the negative electron affinity of diamond thin films, the nature and characterization of lattice defects in diamond thin films, and theoretical models of nucleation and growth. With only 118 references, the chapter is considerably under-referenced.

The third chapter by Bottani and Tascón is a detailed discussion of the energetics of the physical adsorption of gases and vapors on carbon. It is a comprehensive chapter that covers classical thermodynamics and statistical mechanics of gas physisorption, analysis methods and techniques, theoretical methods, and numeric simulations. It also includes an extensive list of 969 references, plus a section on, primarily, simulations of adsorption on fullerenes and carbon nanotubes. The latter is

a subject of significant current interest, but the chapter includes only a brief account of selected results from this area of research. Nonetheless, as the editor writes in the preface of the volume, this chapter should be "a lasting tribute to Eduardo's memory" (Eduardo Bottani died during the writing of this chapter).

In summary, this volume presents detailed reviews on the exfoliation of graphite via intercalation compounds, diamond synthesis at low pressure, and energetics of physical adsorption of gases and vapors. Each of these topics could have easily been the sole subject of its own volume, and with continually emerging important results, it must have been a challenge to present a balanced and *up-to-date* discussion of these topics in a treatise only 430 pages in length. It should serve as a useful reference for scientists and engineers engaged in research on carbon-based materials, as well as stimulate interest among the potential newcomers to this rich area of research.

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Templates in Chemistry I. Topics in Current Chemistry, 248. Edited by Christoph A. Schalley, Fritz Vögtle, and Karl H. Dötz (Kekule Institute für Organische Chemie and Biochemie, Bonn). Springer-Verlag: Berlin, Heidelberg. 2004. x + 280 pp. $229.00. ISBN 3-540-22547-1.

As expected for a monograph in the *Topics in Current Chemistry* series, *Templates in Chemistry I* provides a logical and abundantly illustrated description of the topics at hand. Even though templating is described as an old concept in the preface, the currency of the reference list after each chapter, with about 40% of all the listed references published since 1999, indicates a continuing interest in the topic.

Some representative examples of templating provided in this monograph are chromium carbene-mediated covalent bond formations and gel-mediated supramolecular assemblies, although the purpose for including them is unclear to this reviewer. For instance, while the reactions of chromium carbenes are examples of chromium-based templating, they do not provide the conceptual novelty expected from a chapter in this monograph. Perhaps these topics were included to provide the groundwork for understanding the principles of templating. Moreover, in my opinion, a chapter on template-directed asymmetric synthesis would have been an appropriate addition to the coverage in the book.

A chapter by Jung et al. includes single molecular entity-based gel-like supramolecular assemblies as examples of templating, which unfortunately irrationally extends the concept of templating beyond its traditional definition, begging the question whether all crystallizations can similarly be termed as template-mediated. Within this chapter, however, are interesting examples of templating, such as double helical and donor−acceptor triggered gels. A greater focus on templating instead of describing small molecule organic gelators in general would have been preferable.

One of the aims of the monograph, to paraphrase from the preface, is "to make templates an issue of design and careful planning" so that they can be "implemented into novel synthetic strategies of the future". The chapters on covalent templating involving fullerenes and chromium−carbenes, metal-chelated templating involving helicates, and even weak intermolecular force-mediated templating involving rotaxanes, etc., do provide a rational account of templating that can be extrapolated to newer syntheses and multicomponent assemblies. However, such an extrapolation of principles involving templated solid-state assemblies or gels can be less predictable, which is important to know for a designer and planner employing them. Unfortunately, this unpredictability is not clearly explained in the chapters.

Overall, while the inclusion of certain chapters can be questioned, this book will provide both a historical account and an up-to-date view for future researchers in the field of chemical templates.

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Handbook of Prompt Gamma Activation Analysis with Neutron Beams. Edited by Gábor L. Molnár (Chemical Research Centre, Budapest). Kluwer Academic Publishers: Dordrecht, Boston, London. 2004. xvi + 424 pp. $180.00. ISBN 1-4020-1304-3.

Prompt gamma neutron analysis (PGAA) has been in existence since the mid 1960s, and many high quality research papers and review articles have since been published. This new handbook is the second one published on PGAA. While the first one by Chung and Alfassi (1995) was more of an overview of prompt gamma neutron activation analysis encompassing other similar techniques as well, the current effort is much more directed toward neutron beams from research reactors. The book has some very good attributes and should be useful to anyone in the field or thinking about using the numerous applications of PGAA.

Molnár, who was a world leader in PGAA, assembled several outstanding contributors to write the eight chapters of this book. Unfortunately, he never saw his work come to fruition due to his sudden and untimely death two years ago. The book begins with four well-written chapters on the fundamental theory of PGAA, neutron beams and facilities, sample and standards, and γ-ray spectrometry. The next two chapters on quantitative analysis and applications of PGAA are also very informative and concise, with excellent referenced examples of its use. A tremendous contribution has been made to the world-wide PGAA community by providing an exhaustive database of spectra and γ-ray energies. This has taken many years to accumulate with many painstaking hours of experimental time. There are detailed descriptions of the laboratory requirements from shielding materials, neutron guides, sample holders, spectroscopy, electronics, calibration, and peak fitting procedures. There is a subset of the data in chapter seven, but the complete version is given in the CD ROM available with the book. The appendix of reference data of fundamental constants, properties of chemical elements as they pertain to PGAA, isotopic data, radioactive nuclides, energy and intensity standards, and thermal neutron cross section data is also very informative, useful, and well-presented.

The reading of the individual chapters flows very well, the figures are well illustrated, and the references are both historical in nature and very much up-to-date. This is an excellent addition to the PGAA community and will set the standard for similar books to be written in nuclear analytical methods in chemical analysis.

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Progress in Inorganic Chemistry, Volume 54. Edited by Kenneth Karlin (Johns Hopkins University). John Wiley & Sons, Inc.: Hoboken, NJ. 2005. viii + 536 pp. $150.00. ISBN 0-471-72348-7.

This volume makes one realize that the discipline of inorganic chemistry is remarkably broad and new fields are continually being created. It begins with two chapters on contemporary solid-state chemistry, with thorough and well-cited reviews of hexanuclear transition metal chalcohalide clusters and doped semiconductor nanocrystals. In the first chapter, the synthesis and structural analysis of an array of new complexes of 2nd and 3rd row transition elements with reduced oxidation states, e.g., $Re_6Se_8Cl_6^{4-}$ or $Nb_6SBr_{18}^{4-}$, are described. Several synthetic approaches and the distinct coordination geometries of the M_6 units are covered. Useful electrochemical, paramagnetic, photochemical, and other properties are also discussed. The next chapter is a review of doped semiconductor nanocrystals and their functions as luminescent labels, components in solar cells, optical gain devices, and more. Especially valuable is the coverage of dopants, e.g., Mn^{2+}/ZnS, to affect magnetism, conductivity, and luminescence. Numerous systems, such as TiO_2, SnO_2, CdSe, and ZnSe and their doped analogues, and their characterization are discussed. The two chapters are well-written and valuable contributions to these rather new areas of solid-state chemistry.

The next two chapters are on coordination chemistry, the first on stereochemical aspects of metal xanthate complexes, e.g., $Cr(S_2COEt)_3$, and the other on trivalent uranium. In the former, a thorough review of xanthates of essentially all of the metals from Mn to Pb and the main group elements P, As, Sb, and Bi is given. The coordination geometries and stoichiometries are quite variable, and the versatile nature of these alkyl esters of dithiocarbonic acids (xanthates (RO)C(═S)SH) as ligands is clearly shown. The latter chapter is a description of the rather unusual nature, structure, and reactivity of U(III) complexes. Uranium in this rather low oxidation state can affect four-electron reduction of nitrogen moieties, and $(Cp^*)_2UCl(═NR)$ intermediates are proposed. Overall, U(III) behaves somewhat like Sm(II) in its chemistry. These two chapters on unusual coordination chemistries are up-to-date and well-organized.

The book then leaps into the field of bioinorganic chemistry. The chapter on NO and HNO chemical biology is especially timely and fascinating. The versatility of nitrogen in nature as NH_3, NO_3, NO, HNO, and NH_2OH is described, and how molecular nitrogen is converted into these species is examined. Surprisingly, NO can be regulatory, protective, or deleterious in the human body, depending on its concentration and other reagents. The lifetime of NO in the presence of oxygenated hemoglobin is very short, and yet—luckily—the oxidation of NO by O_2 is slow due to the reaction being second-order in NO.

The last two chapters deal with nucleobases and their pK_a values—especially in the presence of coordinating metal ions—and cover functionalization of myoglobin, active sites for enantioselective oxidation of sulfides, metal substitution, artificial ligand frameworks, and related biochemical aspects.

The editor has ensured that these chapters are well-organized and well-written, and their references are up-to-date (to 2004). He also has shown how inorganic chemistry cuts across materials science, chemistry, biochemistry, and biology, a remarkable aspect of this field. Furthermore, this volume has an excellent subject index as well as a cumulative index of Volumes 1−54. Volume 54 is an important and valuable addition to the series.

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Principles and Applications of Density Functional Theory in Inorganic Chemistry, Vols. I and II. Structure and Bonding, Vols. 112 and 113. Edited by N. Kaltoyannis (University College London) and J. E. McGrady (University of York). Series edited by D. M. P. Mingos. Springer-Verlag: Berlin, Heidelberg, New York. 2004. x + 194 pp. $149.00. ISBN 3-540-21860-2 (Vol. 1) and x + 244 pp. $199.00. ISBN 3-540-21861-0 (Vol. 2).

These two volumes comprise a timely set of nine chapters that cover the important and growing field of density functional theory (DFT) and its applications to problems in inorganic chemistry, especially transition-metal complexes, reactions, and materials. All appear to be fairly up-to-date with many 2003 and some 2004 references.

The series begins with two comprehensive reviews of techniques and applications of DFT calculations to NMR parameters and excitation energies of transition-metal complexes. The first chapter includes an introduction to the computational methodology and examples of both nuclear shielding and spin−spin coupling calculations. The second chapter on excitation energies also gives a useful introduction to the theory before focusing on the tremendous success of time-dependent DFT (TDDFT). This latter chapter also includes numerous helpful comparisons between the results of TDDFT and those of traditional wave function-based methods.

These are followed by three more chemically oriented reviews on homogeneous catalysis, agostic interactions, and bioinorganic chemistry. The chapter on homogeneous catalysis focuses on results of quantum-mechanical/molecular-mechanical methods, especially those using hybrid DFT as the quantum mechanical component. The chapter on agostic interactions emphasizes intramolecular cases, i.e., the nature of the apparently weak interaction between a metal and a σ-bond in a more remote part of the ligand, rather than intermolecular ones that are now referred to as σ-complexes. The chapter on bioinorganic chemistry addresses modeling of metalloenzymes.

The complications from the large number of spin states available to transition-metal systems are covered in two

complementary chapters on spin-state energetics in mononuclear metal systems and exchange coupling in polynuclear metal systems. The first of these chapters covers how well different functionals perform on the relative ordering of spin states. Generally, hybrid functionals containing true Hartree−Fock exchange tend to favor high-spin states, whereas most pure functionals favor low-spin states. The second provides a nice introduction to the extremely complex problem of ferromagnetic versus antiferromagnetic coupling of clusters of ligated metal atoms.

The volumes close with two chapters on solid-state computational chemistry: the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code and the British-Italian collaboration on the CRYSTAL code. Since both codes are based on atomic orbitals (AO) rather than plane waves (PW), they have the advantage of being able to use hybrid functionals. Together, these reviews form a fairly comprehensive view of the AO approach, but neglect the contributions of the PW approach to this area of computational materials science.

Overall, these two volumes are a useful addition to the literature. Many chapters will be helpful to beginning graduate students and others coming into a particular aspect of the field for the first time. As with most reviews, these chapters are somewhat more focused on the authors' own approaches and interests rather than a totally comprehensive account of the field.

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