Book Review

# Humic Substances: Molecular Details and Applications in Land and Water Conservation Edited by Elham A Ghabbour (Northeastern University, Boston and Soil, Water and Environmental Research Institute, Alexandria, Egypt) and Geoffrey Davies (Northeastern University). Taylor and Francis, Inc.: New York. 2005. xviii + 268 pp. $119.95. ISBN 1-59169-031-5.

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BOOK REVIEWS

**Encyclopedia of Chromatography, 2nd ed., Volumes 1 and 2**. Edited by Jack Cazes (Florida Atlantic University). Taylor and Francis Group, LLC: Boca Raton, FL. 2005. 1928 pp. $506.00. ISBN 0-8247-2786-X.

This second edition of this valuable resource of chromatographic techniques, principles, and references has been completely updated and expanded, containing more than 400 articles and including more than 80 new additions—growth such that this edition is now published in two volumes. This edition, like the previous one, is also published online, where new developments in the field of chromatography will be added.

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**Progress in Inorganic Chemistry, Volume 35**. Edited by Kenneth D. Karlin (Johns Hopkins University). John Wiley & Sons, Inc.: Hoboken, NJ. 2005. viii + 604 pp. $150.00. ISBN 0-471-46370-1.

This volume of the series *Progress in Inorganic Chemistry* covers the chemistry of main group and transition metal dithiocarbamate complexes. As an undergraduate and graduate student, I remember this series as priceless for seeking background information and understanding of a range of topics. It was always a resource for information and ideas for research. Many of the chapters simply provided a single source for all the references on a particular subject. However, a simple list of compounds and structures has less and less value in today's age of electronic libraries except when the review expands our understanding of the subject and adds to our knowledge by bringing together various sources. Unfortunately, there is a clear disparity in this regard between the two chapters in this volume, which is not limited to their difference in length (69 versus 491 pages) or number of citations (375 versus 2070).

Chapter 1, "Main Group Dithiocarbamate Complexes" by Peter Heard, is a simple list of compounds, reactions, and structures, with no real global view of the subject and very little insight provided by the author. After all, the author has probably gained some knowledge not available to the average reader simply because he has read every reference. This type of perspective is totally absent from Chapter 1, although thankfully it is demonstrated in Chapter 2. There are also no sections containing a conclusion or an overview of the field, and there is also only one paragraph on applications. This is not to say that the collection is not useful. The tabulation of $^{119}$Sn and $^{125}$Te NMR spectral shifts and $^{119}$Sn Mossbauer should be very useful to workers in these areas. However, I was annoyed with Heard's use of ORTEP-style figures. First, they are all shown with isotropic thermal parameters, thus obviating the whole point of a "thermal ellipsoid plot". Second, the structures are simple enough that a ChemDraw-style diagram would have sufficed. The author thanks the referees in the acknowledgments. My only comment to the editor is "do not use these referees again". They clearly failed to grasp the difference between "data" and "information".

The second chapter, "Transition Metal Dithiocarbamates: 1978−2003" by Graeme Hogarth, is much better organized. It contains a section on the synthesis and properties of the dithiocarbamate ligands themselves, which should be very useful to anyone attempting to make a new compound (I do wonder, though, why this section, or a section like it, was not included in Heard's chapter, where it would have been appropriate). Despite this quibble, Chapter 2 is organized so that the same data may be found in different sections, a redundancy that makes using the chapter much easier. Are you interested in a particular metal or are you interested in a binding mode? Either way, you can find the compound and the reference. Sections on synthesis, binding mode, structure, thermodynamic properties, and binding constants are followed by a group-by-group survey of the known compounds, and a complete summary of the "Noninnocent behaviour" of the dithiocarbamate ligands in transition metal compounds is delineated into various reaction mechanisms. The inclusion of a section for applications is very interesting, especially with regard to the Zn, Cd, and Hg compounds. Finally, Hogarth provides a summary of the chemistry to date and a warning to anyone foolhardy enough to update his chapter in 15 to 20 years time that their task may be far beyond his.

In summary, is this volume worth the price of its purchase? The answer must be yes and no. Most of the information in Chapter 1 can be obtained online in short order, and there are other reviews already published that will provide the same information. On the other hand, Chapter 2 is so complete I defy anyone to do a better job. The 2070 references Hogarth cites would make collecting this data a daunting task. He should be congratulated for bring them together in an excellent chapter that should be required on the bookshelves of any chemists with even passing interest in metal dithiocarbamate compounds. I will certainly use my review copy!

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**Humic Substances: Molecular Details and Applications in Land and Water Conservation**. Edited by Elham A Ghabbour (Northeastern University, Boston and Soil, Water and Environmental Research Institute, Alexandria, Egypt) and Geoffrey Davies (Northeastern University). Taylor and Francis, Inc.: New York. 2005. xviii + 268 pp. $119.95. ISBN 1-59169-031-5.

This book features papers presented at the 2004 Humic Substances Seminar VII held at Northeastern University in Boston in March 2004 and is a companion to the earlier volume

Unsigned book reviews are by the Book Review Editor.

*Humic Substances: Nature's Most Versatile Materials*, published in 2003. There are 15 chapters, which are organized under the following headings: Part 1. Sources and Characterization; Part 2. Sorption and Reactivity; Part 3. Metal Binding and Mobility: Data and Theory; and Part 4. Soil Aggregation. A subject index concludes the book.

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**CRC Handbook of Thermodynamic Data of Polymer Solutions at Elevated Pressures**. By Christian Wohlfarth (Martin Luther University, Halle-Wittenberg, Germany). CRC Press LLC (imprint of Taylor & Francis Group): Boca Raton, FL. 2005. x + 642 pp. $269.95. ISBN 0-8493-3246-X.

This book is an up-to-date compilation of available thermodynamic data pertaining to polymer solutions at elevated pressures. There are seven chapters: (1) Introduction; (2) Vapor−Liquid Equilibrium (VLE) Data and Gas Solubilities at Elevated Pressures; (3) Liquid−Liquid Equilibrium (LLE) Data of Polymer Solutions at Elevated Pressures; (4) High-Pressure Fluid Phase Equilibrium (HPPE) Data of Polymer Solutions; (5) Enthalpy Changes in Polymer Solutions at Elevated Pressures; (6) PVT Data of Polymers and Solutions; and (7) Pressure Dependence of the Second Virial Coefficients ($A_2$) of Polymer Solutions. Three appendices providing lists of systems and properties in order of polymers, solvents in alphabetical order, and solvents in order of their molecular formulas, respectively, follow the chapters, and a very short (one-page) index completes the book.

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**Acetylene Chemistry: Chemistry, Biology, and Material Science**. Edited by François Diederich (ETH-Zuerich), Peter J. Stang, (University of Utah, Salt Lake City), and Rik R. Tykwinski, (University of Alberta, Edmonton). Wiley-VCH GmbH & Co. KGaA: Weinheim. xx + 508 pp. $185.00. ISBN 3-527-30781-8.

This book is a very timely and well-written account of modern acetylene chemistry and the importance of this area to a broad cross-section of current interdisciplinary science particularly in chemistry, biology, and materials science. Consequently, it was a surprise to read the second sentence of the Preface: "Only during the past two decades, however, has it [the carbon−carbon triple bond] become a mainstay in the toolbox of synthetic organic chemists, biochemists, and materials scientists". We all stand on the shoulders of those who have preceded us. What about the pioneering work of earlier decades with a much smaller arsenal of tools, for example, the work of Bohlmann, Cadiot, Castro, Chodkiewicz, Eglinton, Hay, Jones, Raphael, Staab, Stephens, etc.? Their research helped lead to the glorious advancements of the past decade, aided in large measure by parallel progress in organometallic methods. Fortunately, their work is cited in the appropriate sections and reflects the thoroughness of the separate chapters, 11 in total. There are 18 authors who describe the most significant aspects of current research in acetylene chemistry in a broad cross-section of interrelated topics. These include theoretical aspects, practical applications, heterocylic ring construction, asymmetric carbonyl additions, polyynes, shape-persistent acetylene macrocycles, acetylenic saccharides, annulenes and related macrocycles, as well as natural and unnatural products with designed features and functionality.

The first chapter, entitled "Theoretical Studies on Acetylenic Scaffolds" by Chauvin and Lepetit, is a discussion, in turn, of linear, cyclic, star-shaped, and cage acetylenic scaffolds. The authors provide information about the electronic properties and diverse architectures of each topic to stimulate both theoreticians and experimentalists alike.

The following two chapters are "Synthesis of Heterocycles and Carbocycles by Electrophilic Cyclization of Alkynes" by Larock and "Addition of Terminal Acetylenes to C═O and C═N Electrophiles" by Aschwanden and Carreira, respectively. Various procedures are outlined in Chapter 2 to prepare a variety of heterocyclic and carbocylic ring systems in a direct manner that complements older methods; some of these procedures have potential for natural product synthesis. In Chapter 3, the authors describe the evolution of organometallic acetylene additions to carbonyl and imine compounds. The choice of ligands from initial stoichiometric methods to asymmetric catalytic procedures facilitate the selection of the appropriate combination for diverse applications. Unfortunately, there are no ketone examples. This suggests an unfilled need for future research. In a related synthetic vein, Chapter 5, entitled "Acetylenosaccharides" by Bernet and Vasella, opens with some examples of acetylene natural product syntheses, followed by an impressive array of acetylenic "sugar" structures and their methods of construction. A brief explanation of interesting mechanisms and examples of radical cyclizations, enyne metathesis, and Pauson−Khand reactions provide a bonus. Chapter 4, "Transition Metal Acetylides" by Rosenthal, is a summary of a broad cross-section of various organometallic complexes in which acetylenes occupy one or more of the ligands.

Carbon-based molecular electronic devices hold great promise for our future. Chapter 6, "Semiconducting Poly(arylene ethynylene)s" by Swager, covers recent progress in this area. Synthetic methods encompass Sonogashira cross-coupling of acetylenes and alkyne metathesis. Further synthetic manipulation provides control of $\pi$-stacking motifs, intermolecular interactions, and fine-tuning of properties to generate polymer sensors capable of detecting trinitrotoluene (TNT) in land mines. Different aspects of polyynes are discussed in Chapter 7 "Polyynes via Alkylidene Carbenes and Carbenoids" by Eisler and Tykwinski and in Chapter 9 "Carbon-Rich Compounds: Acetylene-Based Carbon Allotropes" by Tobe and Wakabayashi. These reviews complement each other. The first covers carbenoid rearrangements, particularly the versatility of the Fritsch−Buttenberg−Wiechell rearrangement for a variety of targets, including "insertion" of triple bonds into macrocycles and polyacetylenes. A discussion of nonlinear optical properties is also included. The second emphasizes linear carbon clusters and polyynes, particularly organometallic examples, plus monocyclic and multicyclic polyyne-based carbon clusters.

Chapter 8, "Macrocycles Based on Phenylacetylene Scaffolding" by Jones, O'Connor, and Haley, presents a very through compilation of the synthetic strategies, synthetic methods, and

family relationships among these various phenylacetylenic structures. These range from smaller strained ring systems to larger macrocyclic molecules. A clear introduction of the definitions and key features of shape-persistent molecules is given in Chapter 10 "Shape-Persistent Acetylenic Macrocycles for Ordered Systems" by Höger, which is followed by a discussion of host−guest complexes, aggregates in solution, thermotropic liquid crystals, and two-dimensional solid-state super structures. In the concluding chapter, "Chiral Acetylenic Polymers", Pu discusses dendrimers and phenylene ethynylenes based on 1,1′-bi-2-naphthol (BINOL), but unfortunately the double helical BINOL-derived cyclic acetylenic cyclophanes of Otera and co-workers (*Angew. Chem., Int. Ed.* **2002**, *41*, 171) are not mentioned.

There is minimal overlap of structures and references between and within chapters except where these are required for a comprehensive review. However, in one chapter our own work is cited twice with two different reference numbers! An additional bonus is the experimental procedures appended to each chapter.

It is strongly recommended that this excellent review of complementary topics in modern acetylene chemistry be added to personal and institutional libraries. Unfortunately, the cost of $185 is excessive for graduate students who reside outside the United States in countries with nonequivalent currencies.

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**Metal Carbenes in Organic Synthesis. Topics in Organometallic Chemistry, 13**. Edited by K. H. Dötz (Rheinische Friedrich-Wilhelms-Universität). Springer-Verlag: Berlin, Heidelberg. 2004. x + 378 pp. $359.00. ISBN 3-540-21833-5.

As stated by the editor, "the aim of this book is to convince the reader that metal carbene complexes have made their way from organometallic curiosities to valuable, and in part unique, reagents for application in synthesis and catalysis." By this measure, this book has succeeded. Three different aspects of the chemistry of metal carbene complexes are featured: the remarkably diverse chemistry of Fischer carbene complexes, those reactions that involve in situ generated carbene complexes, and carbene complexes that are active in olefin metathesis reactions. These three areas have evolved to a great degree in an independent fashion over the last three to five decades. Given the diversity of chemistry associated with these areas, the editor solicited several experts to contribute to this effort.

The only chapter that contrasts and compares the different types of carbene complexes is the first chapter by Strassner, "Electronic Structure and Reactivity of Metal Carbenes". This is a very excellent overview that provides a physical understanding of the electrophilicity of Fischer complexes, the nucleophilicity of Schrock type complexes, and the unreactivity of NHC complexes. The latter function as nonparticipating ligands in modern metathesis catalysts, of course.

Four chapters in the book are devoted to the chemistry of Fischer carbene complexes. Despite the fact that they have been known for over 40 years, new reactions of these complexes are still being discovered at a rapid pace, and the diversity of the chemistry and the reaction pathways and structural types of the literally dozens and dozens of different products from these reactions is a source of constant amazement to anyone who sets out to learn about or follow this chemistry.

The chapter on the photochemical reactions of Fischer carbene complexes, written by Hegedus, who first developed the synthetic chemistry of the photoinduced reactions of Fischer carbene complexes, is the only chapter that comprehensively covers its topic. Dötz and Minatti contributed the chapter on the formation of phenols and quinone from the reactions of Fischer carbene complexes with alkynes. Dötz was the first to describe the reaction of Fischer carbene complexes with alkynes, which is the most synthetically important reaction of Fischer carbene complexes. Dötz's review is not comprehensive but rather focuses on the literature from approximately the last 10 years.

The chapters by Wu and de Meijere and by Barluenga et al., respectively, were greatly anticipated since both de Meijere and Barluenga have been responsible for the many of the exciting new developments in the chemistry of Fischer carbene complexes in recent years. The chapter by de Meijere et al. is mainly focused on the reactions of alkynes with $\beta$-heteroatom-*a*,*b*-unsaturated Fischer carbene complexes. The chapter by Barluenga et al. is broader and covers basically all cycloaddition reactions not covered by the other three chapters on Fischer carbene complexes. The material is organized by the number of reacting components and then by the size of the ring being formed. Some previous, now out-of-date reviews have used this type of organization before, but upon reading this chapter and reviewing all that has happened in the last 10−15 years (a number of references in 2003 are cited), one is struck by the truly amazing diversity of the chemistry of Fischer carbene complexes. In addition, although this chapter is 62 pages, it is not long enough to make a comprehensive review even remotely possible. The outcome of many reactions of Fischer carbene complexes is at first glance often puzzling, and the author has done a good job at providing possible explanations. One drawback of this type of organization is that dramatic changes in a reaction's course due to subtle changes in substrate structure are not brought to light. For example, a slight change in the substituents in a 1,3-diene may result in a six-membered instead of a five-membered ring, but this effect would not be obvious to the reader because the two reactions would be in different parts of the chapter. Nonetheless, this organization is of value since it provides a construct for the mental organization of the often-complicated reactions of Fischer carbene complexes.

The applications of in situ generated carbene complexes to organic synthesis have a long history, and a number of different reactions could have been covered in the chapter treating this topic. Perhaps due to timeliness and the wealth of reviews on the topic, this chapter is limited to the reactions of dirhodium catalysts with diazo compounds, with an emphasis on the control of stereochemistry. Authored by Doyle, a major player in this very active field, the review is terse, and many of the schemes consist of structures of products with the % ee for their formation adjacent to them. This is useful in terms of being able to visually access a lot of information correlating structure of product with % ee in its formation. The drawback is that sometimes it takes a little while to figure out which reaction a particular structure may have come from.

Clearly, one of the most important contributions of carbene complexes to organic synthesis has been in the area of olefin

metathesis. Two excellent chapters, one by Schmidt and Hermanns and the other by Mulzer and Öhler, cover this area. The focus of the former is on the development and comparison of various ruthenium-based catalysts and on metathesis of "nonstandard" double bonds, which include olefins that bear oxygen, nitrogen, halogen, silicon, phosphorus, sulfur, and boron substituents. This chapter is well written and very informative, a good primer for ruthenium-based metathesis catalysts. The final chapter by Mulzer and Öhler is on the applications of diene, enyne, and diyne metathesis in natural product synthesis. The fact that it is the longest chapter in the book and yet is rather limited to recent examples is a clear testament to the power of the olefin metathesis reaction in synthesis. The chapter is very easy to read and gives the reader a great sense of the types and sizes of ring systems that can be accessed with various catalysts, the nature of peripheral functional groups that are compatible with the major types of catalysts, and an overview of the different types of strategies that can be brought to bear.

Overall, this is a valuable book for those who are interested in research in the area of carbene complexes or who would just like to use carbene complexes in organic synthesis. The contributions are up-to-date, and they have references to 2003 and some to 2004. Each chapter was written with previous reviews in mind and, thus, will contain information that either is not present in other reviews or is organized in a manner not found there. The book is highly recommended, although most readers will be forced to depend on their local libraries for access, given its price.

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**Contrast Agents III: Radiopharmaceuticals—From Diagnostics to Therapeutics: Topics in Current Chemistry, 252**. Edited by Werner Krause (Berlex, Monteville, NJ). Springer: Berlin, Heidelberg, New York. 2005. xii + 222 pp. $189.00. ISBN 3-540-22577-3.

Growing interest in the development of novel radiopharmaceutical agents for studies in biomedical imaging and for radiotherapeutic interventions has spawned major efforts to expand the chemistry of radionuclides. While the chemical methods needed to introduce radioisotopes of main group elements and halogens are, in most cases, well developed, the increasing popularity of radiometals for diagnostic imaging and radiotherapy is driving a resurgence of interest in metal chelates and organometallic systems that can be used for these purposes. Accounts of such chemistry are evident in the abstracts of a recent meeting (16th International Symposium of Radiopharmaceutical Chemistry, *Journal of Labeled Compounds and Radiopharmaceuticals*, 48, Supplement 1, June 2005). The fact that this research activity is both varied and diverse makes the seven topical reviews presented in this book all the more valuable, because they are timely, up-to-date, well organized, and, to a large extent, comprehensive. All are written by leaders in their fields.

Four of the chapters have a structural and mechanistic focus on the chemistry of technetium and rhenium, two of the most popular radioisotopes for imaging and therapy. The lead chapter provides a comprehensive and up-to-date review of the new chemistry of the low-valency tricarbonylmetal chelate and cyclopentadienyl systems. The coverage of this broad and rapidly developing area, in which contributions have been made by many laboratories, is excellent. Systems for tethering these metals via phosphine ligands or through nitrido or hydrazino donors are also covered thoroughly in subsequent chapters. Each of the remaining three chapters is focused on radiopharmaceutical targets of relevance to cancer, multidrug resistance transport systems, somatostatin receptors, and integrin receptors. These chapters, though shorter, provide useful coverage of these more narrow areas and are likewise comprehensive and up-to-date.

As one would expect from the title, most of the coverage deals with synthesis and structure of these radiometallic complexes, although elements of practical radioanalytical methodologies and imaging applications are also introduced in some of the chapters. In this respect, the book is a little uneven. Also missing from this volume and earlier ones in this series on radiopharmaceuticals is a comprehensive coverage of radiohalogens and other nonmetallic radioisotopes that are used for diagnostic imaging and radiotherapy.

This volume in the *Topics in Current Chemistry* series is a very valuable resource on the modern radiopharmaceutical chemistry of imaging agents, and together with the companion volumes, *Contrast Agents I: Magnetic Resonance Imaging* (Volume 221) and *Contrast Agents II: "Optical, Ultrasound, X-ray and Radiopharmaceutical Imaging* (Volume 222), it provides a solid chemical foundation of the imaging sciences.

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