Additions and Corrections

Systematic Investigations of the Nature of the Coupling between a Ln(III) Ion (Ln = Ce(III) to Dy(III)) and Its Aminoxyl Radical Ligands. Structural and Magnetic Characteristics of a Series of {Ln(organic radical)$_2$} Compounds and the Related {Ln(Nitrone)$_2$} Derivatives [*J. Am. Chem. Soc.* **2000**, *122*, 3413−3421].MYRTIL L. KAHN, JEAN-PASCAL SUTTER,* STEPHANE GOLHEN, PHILIPPE GUIONNEAU, LAHCENE OUAHAB, OLIVIER KAHN, AND DANIEL CHASSEAU

We noted in the experimental section that one of the reported crystal structures, {Pr(Nitrone)$_2$(NO$_3$)$_3$}, may be better described in the noncentrosymmetric space group $P\bar{1}$ than in the centrosymmetric space group $P1$; this choice was based on better classical quality criterions in the former. Nevertheless, following discussions with careful readers we acknowledge and from consideration based on atomic displacement parameters we believe that this crystal structure is more likely to be centrosymmetric. However, nothing discussed in the article is modified by such a correction.

Supporting Information Available: Corresponding new crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Computer Software Reviews

CAChe: Computer-Aided Chemistry for Macintosh and Windows. Version 3.2 for Windows; Version 4.1 for Macintosh. Fujitsu Systems Business of America, Inc., 14940 Northwest Greenbrier Parkway, Beaverton, OR 97006-5733. http://www.cache.fujitsu.com. Personal CAChe academic price: $499. Commercial price: $1195. Quantum CAChe academic price: $995. Commercial price: $2495. CAChe WorkSystem academic price: $1995. Commercial price: $15,000.

CAChe is designed as an easy-to-use suite of programs for chemists interested in computational molecular modeling. Because the authors opted for speed over sophistication by incorporating an array of low-effort modeling techniques instead of advanced quantum mechanical approaches, it has proved viable for several years on desktop computers running user-friendly operating systems such as MacOS and Microsoft Windows. The newest versions of CAChe for Macintosh and Windows build on this strength by adding interfaces that expand its capabilities. The software now allows even computer-phobic chemists to examine interesting molecules in considerable theoretical detail.

Since it is a suite of modules, CAChe is available in several levels of complexity and cost, from the basic Personal CAChe to the advanced CAChe WorkSystem. The comments below apply to the latter. Version 3.2 of CAChe for Microsoft Windows (hereafter CACheWin) requires a computer containing a Pentium CPU running Windows 95/98 or NT 4.0, 32 MB of RAM (64 MB recommended), 100 MB of hard disk space, a CD-ROM drive, and an SVGA monitor. We had no difficulty installing the package on a Dell Pentium III-based machine with 128 MB of RAM; full installation required about 42 MB of disk space. CACheWin can import and export files in SYBYL, PDB, MDL, CSD CSSR, and SMILES formats among several others. It can also read and generate CAChe for MacOS files. CACheWin comes with a short manual consisting of tutorials and a larger User Guide. Extensive online help is also provided.

The working environment of CACheWin is called the Workspace, and many users will never need to access any other CACheWin application. Here one draws a molecule of interest using a ChemDraw-like interface, which includes a useful toolbar for general operations, a style bar for modifying atom types and characteristics, and a tool palette for operations such as rotation, translation, and atom/group selection. To make this process easier, one-step routines for adding a variety of organic functional groups or hydrogen atoms to molecular skeletons exist, as do simple routines for generating crystal lattices from single molecules. With little effort, one can create several types of molecular graphics, including space-filling and ORTEP models. However, users should recognize that the drawing routine functions mainly as an interface to the modeling programs; it is not really flexible enough to use for generating publishable molecular graphics. For example, the atomic labels cannot be moved from the body of an atom, and the color choices are limited. Similarly, molecular parameters such as bond lengths and angles can be labeled, but the labels cannot be resized or moved, and thus interfere with graphic legibility. If one wishes to utilize Workspace for publication or presentation-style graphics, this is best done by saving the graphic in MDL format and opening it in Chem3D or the equivalent.

Once a molecule has been created, one chooses an "experiment" to apply to it. An experiment may be a single calculation (say, a molecular mechanics optimization) or a sequential set (a fast optimization using mechanics followed by a more accurate, quantum mechanical one using MOPAC). The experiment window provides a capsule summary of what the selected experiment will do and allows switching to other experiments. (The Users Guide provides a useful table of what experiments exist; this table may also be used to determine a particular property.) Using an external application called Procedure Editor, one can create new experiments and save them for future use. Modules available within CACheWin for experiments include Mechanics (MM2 and MM3 molecular mechanics minimizations), Dynamics (time-dependent mechanics), ExtHückel (extended Hückel molecular energies), ZINDO and MOPAC (semiempirical quantum mechanical optimizations, energies, and properties), DGauss (first-principles quantum mechanical calculations), and CONFLEX (conformational space examination).

Once an experiment is completed, one views its results in dual window form within the Workspace. CACheWin provides several map

styles that allow the user to view an array of molecular properties(atomic charges, electrostatic potential, absorption spectrum, or vibrational spectrum, for example), theoretical constructs (molecular orbitals, bond order), or the conformations examined during a Dynamics run. The user can then graph molecular properties against each other. The views are interactive: for example, when one selects a point along the time frame of a Dynamics run graph, the program will display the corresponding molecular conformation in the other window. This allows one to examine chemical evolutions, such as how orbitals change over the course of a reaction. An animation routine provides an automated display of desired evolutions and allows, with screen capture or movie-creating software, the generation of movies of them. The quantum mechanical routines also give output as text files, which can be opened in any text editor (but not in the CAChe program).

Version 4.1 of CAChe for MacOS (hereafter CACheMac) requires a Power Macintosh computer or an older Mac upgraded with an Apple Power Macintosh card, 100 MB of disk space, and a CD-ROM drive. The authors recommend a minimum of 48 MB of RAM, which can be partly built of virtual memory (with the consequent performance degradation). For large ZINDO or MOPAC calculations, total RAM (real + virtual) up to 167 MB is recommended. Installation was extremely simple and rapid on a Macintosh G3/233 running MacOS 8.1 with 96 MB of real RAM; full installation required about 52 MB of disk space.

CACheMac provides no online help but comes with an excellent set of manuals. That entitled "A Chemists' Guide" serves as a very useful tutorial. Since some of CACheMac's procedures are different from those in other Mac programs (for example, changing the window size does not change the size of the molecule correspondingly), we recommend reading this manual thoroughly before using the programs.

CACheMac's interface and module organization are considerably less polished than those in CAChe Win. Rather than being an integrated suite of modules, CACheMac is a linked suite. By this we mean that each module may be called by a menu command within any other, but they run independently. Therefore, although each module may hold several molecules open simultaneously, switching from module to module requires that all molecule files be saved in the first then reopened in the second. This inhibits mass production calculations.

One creates molecules in the Editor, which can open molecular graphics in CACheMac and CAChe Win, Brookhaven, Chem3D, MDL, Tribble, SHELX, and CCD formats and can save files in all but the last two. While the drawing methodology is similar to that in CAChe Win, Editor sports a poorly designed interface; no toolbars, style bars, or tool palettes exist. Procedures such as rotation or expansion require keyboard + mouse routines, some of which are difficult to remember and use. Most of the drawing kudos and caveats noted for CAChe Win apply here. One advantage Editor has over Workspace is a one-step routine for generating a polymer from a monomer.

Once a molecule is created, the user switches to the desired computation module through a menu command. CACheMac contains single-window interfaces to all the modules available in CAChe Win, but since DGauss has not been ported to the Macintosh, it must be run on an external UNIX- or Windows-NT-based server. Since the modules run independently of the Editor, they do not provide the helpful capsules of the CAChe Win experiment mode. Reading the manuals for the modules is critical for their proper use and interpretation of the data.

Output from the computational routines is analyzed in the Tabulator (which also converts data into 3D graphics format) and then inspected in the Visualizer+ module. The latter provides the dual window mode and animation routine described above for CAChe Win.

For property studies across sets of molecules, both versions of CAChe provide the ProjectLeader, which combines the ability to run computational experiments with a spreadsheet format for the input and output data. One adds molecules generated from the Workspace/Editor or MDL files to the sheet and then chooses a property of interest as a column header. Properties available range from the trivial (atom and bond count) to the extremely complex (polymer cohesive energy, polymer T_g, λ_{max}). The program uses an appropriate model to predict property values for each molecule selected in the sheet and adds the data to the appropriate cells. The data can then be subjected to regression or other mathematical analyses and plotted. Users of programs such as Microsoft Excel will find the ProjectLeader procedures easy to understand and impressively automated and implemented.

A demonstration version of CAChe (60-day temporary license) may be ordered from the World Wide Web site http://www.cache.fujitsu.com/demo.shtml. CAChe 4.1 for Macintosh was recently rated 4.5 out of 5 mice by Charles Seiter, Scientific Software Reviewer for *MacWorld* magazine. The review can be found at http://macworld.zdnet.com/2000/04/07/chemsoft.html, or by searching for CAChe at http://www.macbuy.com.

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Origin 6.0: Scientific Data Analysis and Graphing Software Origin. Lab Corporation (formerly Microcal Software, Inc.). Web site: www.originlab.com. Commercial price: $595. Academic price: $446

Origin 6.0 is a software package designed to carry out a vast array of scientific and technical data analysis and graphics applications. The software requires a PC with a 486/DX or higher processor running Microsoft Windows 95 or later, or Windows NT version 4.0 or later, at least 16 MB of RAM, 20 MB of hard disk space, a CD-ROM drive, and an SVGA display or better.

Origin accepts data in either spreadsheet (for two-dimensional plots) or matrix (for three-dimensional plots) formats; both are easily manipulated through clear, intuitive pull-down menus or shortcut buttons. Data are readily imported in ASCII format, and Microsoft Excel worksheets can be opened directly in the Origin workspace. The workspace itself contains some nice features, including a project explorer, which details and organizes all the worksheets, graphs, and matrixes open in the current project, and a results log, which displays all the results from fitting and analysis routines.

Pull-down menus offer a dizzying array of graphing options, ranging from simple scatter plots to statistics to complex stacked plots. Histograms and polar charts, traditional stumbling blocks for basic graphing programs, are executed with speed and style. Formatting charts is extremely easy, with axes, scales, colors, and legends all accessed by simple double-click functions. A particular strength of Origin is the ability to combine and stack plots with independent axes, invaluable for comparing trends on different scales.

Both before and after plotting, Origin offers an impressive variety of analysis options, including statistics, calculus, and FFT functions. Curve fitting is one of its particular strengths. This option allows one able to identify and fit up to 12 peaks or apply one of a vast array of built-in functions from the nonlinear curve-fit library. Although the functions themselves may have cryptic names (yldfert, for example), they are divided into helpful categories such as chromatography, pharmacology, and spectroscopy, and most are described in graph, equation, and parametric forms. Although the built-in function list is extensive, Origin also permits new functions with up to 200 parameters to be defined by the user. This process required assistance from the user manual but yielded excellent results. The one caveat here is that fitting with a simple three-parameter user-defined equation was an order of magnitude slower than fitting with a similar built-in function. However, OriginLab offers to compile user-defined fitting functions for a small fee; once compiled, user-defined functions are just as fast as built-in ones. Data manipulation in matrix form has a bit less scope and utility, but Origin's ability to generate breathtaking 3D surface and contour plots cannot be faulted.

In conclusion, Origin is by far the most flexible and user-friendly technical graphics package available. The few nonintuitive operations are well documented in the user manual, which also provides detailed information on the functions and algorithms used in the data analysis and curve-fitting applications. Perhaps the most refreshing aspect of Origin's documentation is the ability to use the help menu without having to negotiate an animated paperclip. Origin evinces broad utility for a wide range of chemical applications for both academic and industrial settings, handling large data sets and complex fitting functions with ease, producing highly customizable, journal-quality graphics, and requiring little specialized knowledge for effective use.

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Book Reviews *

Advances in Medicinal Chemistry. Volume 5. Edited by Allen B. Reitz and Scott L. Dax (The R.W. Johnson Pharmaceutical Research Institute). JAI Press: Stamford, CT. 2000. x + 201 pp. $115.00. ISBN 0-7623-0593-2.

This volume is the fifth in a series designed to provide first-hand accounts of industrial and academic research projects in medicinal chemistry. In this volume, four contemporary industrial projects are presented. Chapter 1, by G. S. Hamilton and C. Thomas, reviews the fascinating history of the immunophilins and the current state of knowledge about this field, while Chapter 2, by M. W. Holladay and M. W. Decker, describes the serendipitous twists and turns that led to the development and characterization of ABT-594, the first potent analgesic to act at nicotinic acetylcholine receptors. In Chapter 3, D. J. Wustrow discusses the numerous structure−activity relationships of dopamine agonists and partial agonists resulting from efforts to identify a useful drug for the treatment of schizophrenia. In the last chapter, S. Hagen, J. V. N. Vara Prasad, and B. D. Tait focus on their successful program to design non-peptide inhibitors of the human immunodeficiency virus (HIV) protease.

Immunophilins, the authors of Chapter 1 tell us, is the name given to a group of peptidyl prolyl isomerases (PPIases) that serve as targets for the immunosuppressant drugs cyclosporin A, FK506, and rapamycin. The term was coined by Stuart Schreiber, who directed many of the key experiments in this field, including one showing that the PPIase activity and immunosuppression were not linked. This result set off an intensive search for the cellular targets of the drug−immunophilin complexes and, as the authors note, led to the field of chemical biology, "in which fundamental research in cell biology occurs at the interface of the disciplines of chemistry and biology". Subsequently, the chapter covers the many experiments that elucidated the roles played by immunophilins in cellular processes, such as protein trafficking and modulation of signal transduction pathways. The authors also detail the insights gleaned from crystal and NMR structures of immunophilins and their ligands, and how these observations provide a structural framework for understanding the roles of immunophilins in cellular processes. The chapter concludes with a discussion of the neuroimmunophilins, which are immunophilins found in the central nervous system, and the exciting discovery that some small-molecule ligands of this group of immunophilins promote the regrowth of damaged nerves. The immunophilin story is a fascinating one, and the authors have done an outstanding job of recounting it.

The development and characterization of ABT-594 is also an intriguing story and the subject of the next chapter. The story begins when a group at Abbott Laboratories decided to focus on agonists of nicotinic acetylcholine receptors (nAChR) as potential drugs for the treatment of Alzheimer's disease. The group pursued a classic medicinal chemistry approach in which a number of analogues are synthesized and their structure−activity relationships established. In the course of these studies, it was reported that the potent analgesic properties of epibatidine, a substance from the skin of an Ecuadoran frog which shares structural similarities with nicotine, involved the activation of the neuronal nAChRs. The remainder of the chapter then discusses the efforts at Abbott to identify and develop a compound from their existing pool of nAChR ligands that retained the potent analgesic properties of epibatidine, but not its toxicity. The result was ABT-594, which is now on the verge of being tested in human clinical trials as an analgesic agent.

In Chapter 3, the author describes a program to identify dopamine agonists and partial agonists of the so-called dopamine D2 autoreceptors, which control the synthesis and release of dopamine from the neurons. This approach is a novel one in the search for more effective antipsychotic agents. The drugs currently in use are antagonists and block the dopamine D2 receptors. While these drugs can be effective, they cause debilitating side effects. Much of the chapter reviews the structure−activity relationships of several dopamine agonists and partial agonists. The author concludes by indicating that this program has not yet led to a successful drug candidate and the underlying premise remains to be proven.

The last chapter continues along the same lines as the previous two and discusses the program at Parke-Davis to identify and develop non-peptide inhibitors of HIV protease. Two initial lead compounds were discovered by high-throughput screening of approximately 150 000 compounds. One of the lead compounds, a pyrone derivative, was optimized into a preclinical candidate, using a combination of molecular modeling and X-ray crystal analysis. The chapter also discusses the structure−activity relationships that led to the final compound.

Prior to my review of this volume, I was unaware of this series. However, I enjoyed reading the four accounts presented in this volume, and found each one to be comprehensive and very informative. This volume would be especially useful to graduate students, faculty, and research scientists in chemistry as well as medicinal chemistry with an interest in one of these areas. In addition, it might be of interest to a broader audience, as each chapter gives a realistic portrayal of the various approaches that can be used to develop a drug. If the previous four volumes are comparable to this one, then the entire series would be a valuable addition to a chemistry library.

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10.1021/ja004728r

Automated Synthetic Methods for Speciality Chemicals. Edited by W. Hoyle (Consultant). Royal Society of Chemistry: Cambridge. 2000. viii + 114 pp. £49.50. ISBN 0-85404-825-1.

The eight chapters in this book evolved from the papers presented at a symposium organized by the Royal Society of Chemistry in September 1999. The contributions include overviews of and current practices in the application of automated techniques, including microreactors and robots, to the synthesis of specialty chemicals.

JA004771E

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Progress in the Chemistry of Organic Natural Products. Edited by W. Herz (Florida State University), H. Falk (Johannes-Kepler-University), G. W. Kirby (University of Glasgow), and R. E. Moore (University of Hawaii at Manoa). Springer-Verlag: New York. 2000. viii + 256 pp. $169.00. ISBN 3-211-83361-7.

This book contains two review articles: "Synthetic Aspects of Iridoid Chemistry", by H. Franzyk, and "The Defensive Chemistry of Ants", by S. Leclercq, J. C. Braekman, D. Daloze, and J. M. Pasteels. Both articles cover developments in the field over the decade ending in 1998. The chapter on the defensive chemicals produced by ants focuses on non-proteinous poisons delivered in venom or through the Dufour glands and covers both their chemical synthesis and biosynthesis. Author and subject indices complete the book.

JA0047673

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Catalysis by Metal Complexes. Vol. 21. Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes. By Alexander E. Shilov and Georgiy B. Shul'pin (Semenov Institute, Russia). Kluwer: Dordrecht, Boston, and London. 2000. xiv + 534 pp. $228.00. ISBN 0-7923-6101-6.

Alkane functionalization with homogeneous catalysts dates back to Fenton's reagent ($Fe(III)/H_2O_2$) of 1898. From the 1930s, metal-mediated radical autoxidation and, later, superacid catalysis via carbonium ion intermediates both led to important commercial processes. The discovery of the oxidative addition reaction in the late 1960s made this new pathway available for alkane conversion by low-valent transition metal complexes. Alex Shilov has the distinction of having reported the first example of the latter type as early as 1969.

Despite this long history, selective, general alkane functionalization by chemical means with adequate control of selectivity is still an unsolved problem. The "Barton challenge", the conversion of *n*-hexane to 1,6-hexanediol, is still unmet, for example. The area of alkane functionalization therefore remains one of the most significant contemporary challenges in organometallic chemistry.

This new book on the problem by Shilov and Shul'pin builds on

*Unsigned book reviews are by the Book Review Editor.

Shilov's 1984 related book, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*. Not only is the earlier work completely reworked and brought up-to-date, but the scope is extended to include a number of new aspects, most notably bioinorganic applications and reaction pathways not involving metals. Oxidation processes are also given greater attention. The present book is nearly three times the size of the earlier one.

One strong point of this work is the broad coverage and very extensive and up-to-date bibliography. The majority of the references date from the 1990s and coverage goes right up to early 1999. The extensive Russian work is unfortunately still less well known in the West than it deserves, and the authors give this material appropriate emphasis. The discussions have a strong mechanistic flavor and draw on a very broad body of literature.

Apart from rare omissions, such as the Catalytica catalysts for methane conversion to methanol esters, the book gives a very valuable picture of the current state of the field and will be an essential item for academic and industrial libraries.

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Concerted Organic and Bio-organic Mechanisms. By Andrew Williams (University Chemical Laboratory, Canterbury, UK). CRC Press LLC: Boca Raton, FL. 2000. x + 286 pp. $79.95. ISBN 0-8493-9143-1.

This is an excellent and authoritative book that covers not only concerted reactions but also stepwise reactions originally proposed to be concerted. The book is very densely written, with much information, and with a careful reasoning style that demands concentration from the reader.

The classes of reactions considered are proton transfers, nucleophilic displacements at unsaturated carbon, nucleophilic displacements at saturated carbon, displacements at heteroatoms, cyclic reactions, and enzyme reactions. Addition reactions are omitted, and eliminations and electrophilic substitutions are discussed very briefly. Many readers may be interested in only one class of reaction, and it is possible to ascertain what Williams concludes about their mechanisms. In my view, the triumph of this book is the presentation of the epistemological principles. Following a brief introductory chapter of definitions, there is a very instructive chapter presenting the techniques used to draw inferences about the concertedness of reactions.

How is it ever possible to obtain evidence for a concerted reaction? How can the presence of an intermediate be rigorously excluded? Even if experimental results fail to support an intermediate, it might be too unstable to detect or trap. Yet there are convincing observations to exclude intermediates and support concertedness. Three of the most powerful are (1) a strictly linear free-energy correlation without the deviation associated with a change of rate-limiting step, (2) an estimated or extrapolated lifetime that is too short for a putative intermediate's existence, and (3) the absence of double isotope fractionation (isotope effect on an isotope effect) that arises from a change of the partitioning ratio in a stepwise reaction.

Williams's own major research contribution is the observation that many acyl transfers, such as the reaction of substituted pyridines with *N*-methoxycarbonyl isoquinolinium ions, are concerted. This is an example of a type of reaction that might automatically be assumed to proceed via a tetrahedral intermediate, like so many other carbonyl reactions (according to classic studies of ^{18}O incorporation into esters). Indeed, throughout the book there are frequent surprises for those who have not kept current with the vast range of mechanistic results. Unfortunately, there are no general principles to permit a priori judgment of whether a reaction is concerted or stepwise.

The book maintains a good balance between detailed reasoning and a summary of conclusions. The key logic behind the free-energy nonlinearity arising from a change of rate-limiting step is repeated several times, but the experimental results expected from such proposed mechanisms are sketched only briefly. There are many clarifying schemes and chemical structures that are essential for understanding; mechanisms are designated according to the IUPAC-recommended nomenclature of Guthrie and Jencks, rather than the older Ingold system ($D_N + A_N$ and A_ND_N, rather than S_N1 and S_N2).

There are few misprints or misstatements, but some criticisms should be noted. These include the failure to provide an explicit definition of β_{nuc} and β_{lg}, and the discrepancy between Scheme 6.26, which claims to illustrate intermediates in a $D_N + A_N$ mechanism, and Scheme 6.24, where it is indicated that these arise via $A_{xh}D_H + A_N$. Moreover, skepticism over the role of lone pairs antiperiplanar to a leaving group would have been appropriate, in view of results from amidine hydrolyses, which unfortunately were ignored. On another matter, it makes no sense to claim that front-side nucleophilic displacement at a saturated carbon would lead to racemization if the Nu−C−Lg angle were tetrahedral, and it is unclear why cyclization of squalene epoxide is considered to be a cyclic reaction, since it is not pericyclic like the other reactions in Scheme 7.1. Finally, a neglected clarification is that the femtosecond kinetics of the reverse Diels−Alder reaction of norbornene are of an electronically excited state. These deficiencies detract only modestly from the overall value of the book.

Each study that is discussed includes citations to the original literature, so that the reader can readily obtain additional details. There is a valuable list of general references for each topic and a useful subject index, including symbols, but no author index. References are included up to 1998.

In summary, this book offers a concise guide to a wide range of mechanistic studies. It will reward the careful student or researcher.

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Inorganic Electronic Structure and Spectroscopy. Volume I. Methodology. Edited by Edward I. Solomon (Stanford University) and A. B. P. (Barry) Lever (York University). Wiley-Interscience: New York. 1999. xiv + 732 pp. $150.00. ISBN 0-471-15406-7. Set (with Volume II): $260.00. ISBN 0-471-32683-6.

This two-volume set (a separate review of Volume II follows) is an excellent compilation of very readable and up-to-date chapters by experts on a wide variety of spectroscopic and computational techniques of importance to a detailed understanding of transition metal species. The title, however, is misleading because, with only a few exceptions, the main-group, lanthanide, and actinide elements are virtually ignored. Thus, the volumes would be better entitled "Transition Metal Electronic Structure and Spectroscopy".

There are many excellent chapters in both volumes, most of which stand on their own. This reviewer found the first chapter of the second volume, "Bioinorganic Spectroscopy", by E. Solomon and M. Hanson, to be the most interesting and recommends it as a good place to start reading. Confining their discussion to bioinorganic iron and copper, they provide a vast array of methodology that has been used in bioinorganic chemistry. The chapter even brings in missing elements from the methodology chapters of Volume I. For example, the Q, S, L, and C bands of EPR spectroscopy and the methodology of magnetic circular dichroism are first discussed in this chapter.

Volume I, Methodology, begins with a chapter by the editors on ligand field theory and properties of transition metal complexes. This chapter provides the expected background on crystal field, ligand field, angular overlap, and molecular orbital descriptions as well as multielectron complications to spectroscopy and relations of ligand field theory to physical properties. Overall, the chapter is very well done. Chapter 2 (A. Bencini and D. Gatteschi) on electron paramagnetic resonance spectroscopy has very readable theoretical discussions and a valuable table of g values for d^n ions in pseudo-octahedral coordination. The following chapter, by P. Gütlich and J. Ensling, provides a very well written and well illustrated introduction to Mössbauer spectroscopy. Its weakest points are a lack of references beyond 1985 other than three from the authors' laboratory and only one non-iron example. Chapter 4 (M. A. Hitchman and M. J. Riley) is a welcome description of the polarized absorption spectroscopy of oriented single crystals. Where else would you learn that tetracyanoplatinate(II) salts, although colorless in solution, absorb visible light in the solid state with a strong counterion color dependence?

T. C. Brunold and H. U. Güdel provide a good discussion of theory and instrumentation for luminescence spectroscopy in Chapter 5, and in addition to the standard continuous wave method, they present four other experimental techniques in the field. Examples of determining geometry from emission spectra, d−d and charge-transfer luminescence spectra, and the problems of nonradiation competition, multiphoton

relaxation, and pressure are capped with a discussion of laser materials. In the next chapter, E. Krausz and H. Reisen describe laser spectroscopy by discussing topics such as tunable and single frequency lasers, laser pulse time and intensity dependence, time versus spectral resolution, light mixing (harmonic and sum−difference mixing), Raman shift lasers, and line width and line shapes. Although the reader is referred to Chapter 5 for MCD spectra and the rigid shift approximation early in this chapter, terms for them or for magnetic circular dichroism do not appear in the index to this volume.

Chapter 7 (R. S. Czernuszewicz and T. G. Spiro) on infrared, Raman, and resonance Raman spectroscopies is an excellent chapter. The illustrations in this chapter on vibrational spectroscopies are particularly helpful in providing a thorough understanding of the material. G. M. Bancroft and Y. F. Hu then focus on the photoelectron spectra of inorganic and organometallic molecules in the gas phase using synchrotron radiation and provide a detailed background on the application of the principles of photoelectron spectroscopy to all of inorganic chemistry. Chapter 9 (H. H. Zhang, B. Hedman, and K. O. Hodgson) covers X-ray absorption spectroscopy and EXAFS (X-ray absorption fine structure) analysis with emphasis on the multiple-scattering method and applications in inorganic and bioinorganic chemistry. This chapter provides an excellent analysis of the methodology behind the interpretation of EXAFS spectra, including both the strengths and pitfalls inherent in the explication of such spectra.

The following two chapters, by C. H. Martin and M. C. Zerner and J. Li, L. Noodleman, and D. A. Case, respectively, are detailed discussions of theory as applied to metal complexes. Martin and Zerner provide sufficient details on ab initio and approximate models for transition metals for the nonexpert to comprehend the topic, whereas Li et al. discuss the application of density functional methods to transition metals. Their contribution would have benefited both from more detailed captions with their first two figures, because density functional methods provide energy level diagrams that are somewhat different from other molecular orbital diagrams, and from a more logical sequence of discussion of the various components of the six pages of Figure 2. However, the results are very interesting and suggest that all chemists should become more familiar with density functional methods.

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Inorganic Electronic Structure and Spectroscopy. Volume II. Applications and Case Studies. Edited by Edward I. Solomon (Stanford University) and A. B. P. (Barry) Lever (York University). Wiley-Interscience: New York. 1999. xiv + 658 pp. $150.00. ISBN 0-471-32682-8. Set (with Volume I): $260.00. ISBN 0-471-32683-6.

Volume II, The Applications and Case Studies, opens with an insightful discussion of the boundless spectroscopic methodologies available to the chemist. D. E. Richardson's following chapter on electron-transfer reaction rate theory is an understandable and up-to-date discussion of the Marcus−Hush theories. Gas-phase and solution aspects are presented in some detail, and these are followed by a short discussion of intramolecular and biological electron transfer. A description of Piepho, Krausz, and Schatz theory begins Chapter 3 (P. N. Schatz) and is followed by a discussion of the Piepho molecular orbital (MO) approach to mixed valence species. Because the conclusion is that the MO approach is better for unsymmetrical cases, this reviewer wonders why not just use the MO approach? The next chapter, by A. B. P. Lever and E. S. Dodsworth, addresses electrochemistry, charge-transfer spectroscopy, and electronic structure, centering on the Lever electrochemical ligand and metal parameters and the extension of this concept to charge-transfer spectral correlations. A theoretical treatment of charge-transfer spectra and of the relationship between charge-transfer spectra and Hammett substituent constants is included.

The photophysics and photochemistry of coordination compounds are the subjects of Chapter 5, by J. F. Endicott. Vibrationally equilibrated excited-state concepts are developed in considerable detail as the essential basis for determining the photochemistry that can take place via ligand field or charge-transfer excitation. Discussion of photochemical reactions (including ligand field excitation, charge-transfer photochemistry, energy transfer, and multiphotonic processes) completes this informative chapter. Chapter 6 (V. M. Miskowski, M. D. Hopkins, J. R. Winkler, and H. B. Gray) is a thorough compilation and discussion of the electronic structures and spectra of binuclear transition metal species containing multiple metal−metal bonds−tabulated and discussed with a simple crystal-field type model. Chapter 7 (B. L. Westcott and J. H. Enemark) provides structural and spectroscopic details on transition metal nitrosyls and emphasizes the relationships between the electronic structures of such nitrosyls and their geometry and reactivity. G. Loew discusses the electronic structure of the heme sites of globins, peroxidases, and cytochrome P450 in the next chapter, providing extensive information on spectral and magnetic properties common to all hemes and specific details on the three classes of hemes. The roles of the axial ligands and the proteins are also explored.

In Chapter 9, N. E. Gruhn and D. L. Lichtenberger characterize the electronic structures of transition metal carbonyls and metallocenes. After an introduction to metal carbonyl and metallocene bonding, the authors discuss spectroscopic methods for carbonyls and metallocenes, including Auger and Penning ionization electron spectroscopy, techniques that are complementary to photoelectron spectroscopy because they provide more definitive assignments of ionization levels. P. Gütlich, H. Spiering, and A. Hauser follow with a chapter detailing the spin transition that occurs in certain iron(II) compounds. Ligand-field theory, physical characterization, mechanism of spin-change in solids, light-induced spin-state trapping and light-induced bistability, relaxation dynamics, and nuclear-decay induced spin crossover are all covered in this chapter. P. Day's contribution on neutron and optical spectra of magnetically ordered crystals completes Volume II. He describes the excitation of spins in chains, sheets, and infinite lattices that produces long-range magnetic order. The chapter introduces inelastic neutron scattering spectroscopy and provides insight into the information it can provide in measuring spin excitations.

Overall, the reviewer found both volumes to be very informative and interesting (a separate review of Volume I precedes this one) and feels that all chemists who deal with the spectroscopic evaluation of transition metal species will want to have the two-volume set at their fingertips. However, a few annoyances include the incomplete index, a change in the abbreviations for 2,2′-bipyridine and 1,10-phenanthroline between Chapters 1 and 2, scattered lists of abbreviations, and the Tanabe−Sugano diagrams of Chapter 1 that looked like copies of copies—not the usual Wiley quality.

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