

Book review

Metal ions in Biological Systems, ed. by Helmut Sigel, Marcel Dekker, New York. *Volume 7. Iron in Model and Natural Compounds*, (1978) xvii + 417 pages. *Volume 8. Nucleotides and Derivatives: their ligating ambivalency*, (1979) xix + 232 pages. *Volume 9. Amino Acids and Derivatives as Ambivalent Ligands*, (1979) xix + 277 pages.

This series was initiated in 1973 with the ambitious aim of helping to “break down barriers” between chemistry, biochemistry, biology, medicine and physics. Notable progress has occurred in this direction. For example, Bioinorganic Chemistry is now widely accepted as a respectable subject. However, in many places the barriers are still remarkably resistant. Thus it is with some sadness that one has to note that one or two chapters of the volumes, particularly in Volume 9, leave the impression of having been written by chemists for chemists with no more than lip service being paid to “biological relevance.”

This is not a general complaint, however. Volume 7, which concentrates on iron, is particularly to be recommended and contains a number of authoritative chapters. Much has been written elsewhere on iron-sulphur proteins. However, Averill and Orme-Johnson have produced a comprehensive yet reasonably concise introduction to the field. The chapter by Debrunner et al. on cytochrome P-450 is interesting and concentrates on detailed interpretation of data from a variety of spectroscopic methods on the various reaction states (intermediates) of the enzyme camphor hydroxylase from *Pseudomonas putida*, on which the authors have themselves worked extensively. Developments in understanding the properties of haemoglobin have been rapid and definitive in the last few years. Synthetic analogs of oxygen-binding haemoproteins have played an important part in this work and the chapter on this topic by Reed is clearly written. Jones and Wilson have produced a very readable chapter on catalases and iron complexes with catalase-like properties. It is surprising how little is known about catalase in the true chemical sense. Considerable emphasis is here placed on the catalytic activities of ferrihaems. The final chapter is by Stanley et al. As these authors point out, detailed application of statistical mechanics to biological systems is “far from commonplace.” Their chapter on haemoglobin oxygenation is welcome and should be of interest not only to haemoglobin specialists. The authors note that there are 512 possible states of the haemoglobin tetramer, in the absence of effector molecules but allowing for each of the four sub-units to be oxygenated or de-oxygenated and to exist in one of two possible conformations, and further allowing for the tetramer itself to have two possible conformations. The theories of Monod, Koshland and Perutz are limiting cases of this theory. Having dealt with equilibrium, the authors go on to kinetics and contrive to get away from the mass action approach. As they point out,

particularly stringent tests for theoretical models arise when kinetic and equilibrium data are both fitted to the same model with the same values of the constants.

Volumes 8 and 9 are on entirely different topics from Volume 7. To deal first with Volume 8, nucleotides might bind metal ions via nitrogen or oxygen on the bases, via hydroxyl on the sugar residues, or via the negatively charged oxygen atoms of the phosphate groups. Thus as considered in this Volume, they are "ambivalent ligands." The structure of a copper-adenine complex was first reported in 1967. Since then the field has moved rapidly, spurred on to some extent by speculations about anti-tumour platinum complexes acting by cross-linking DNA. A particularly valuable chapter is by Martin and Mariam, dealing with interactions in solution between metal ions and nucleic acid bases, nucleosides and nucleotides. The chapter by Gellert and Bau on X-ray studies includes work on complexes of t-RNA. Finally, Sigel (the editor of the series) has contributed an interesting chapter on the properties of base-modified nucleotides, including work on adenine *N*-oxide derivatives etc.

Amino acids are themselves perhaps rather uninteresting compounds to biochemists, since they occur only to a limited extent in the free state. They may therefore be surprised to learn how much work has been done by chemists on complex formation between metal ions and amino acids. This field is covered in Volume 9. There is perhaps an unfortunate tendency in this volume for there to be a minimum of references to relevance of the work to studies on metallo- and metal-activated proteins and enzymes. Nevertheless, in general the chapters seem clearly written and will no doubt be of value to workers in the field. The volume is furthermore not limited to amino acids but contains, for example, a chapter on metal complexes of glutathione. This compound occurs naturally at concentrations as high as 2 to 3 mM and is thus likely to form metal complexes *in vivo*.

*School of Molecular Sciences
University of Sussex
Brighton BN1 9QJ (Great Britain)*

R.C. BRAY

Book review

Stereochemistry of Optically Active Transition Metal Complexes, edited by Bodie E. Douglas and Yoshihiko Saito, ACS Symposium Series 119, American Chemical Society, Washington, D.C., 1980, x + 446 pages, \$ 38.50

The book contains most of the papers delivered at a Symposium at the ACS/CSJ Chemical Congress in Hawaii, 1979. This reviewer is always wary of accepting invitations to ACS and IUPAC meetings for fear that, at the last possible moment, he will be told that a manuscript is required. I am not persuaded that this excessive publication is necessary particularly when the work has been or will be published elsewhere. It seems that publications are required to fill the space allotted.

On the whole, this is not a bad book; it contains a lot of interesting work although nearly all of it has been published before. Appropriately, the volume begins with a chapter by J.C. Bailar who discusses, among other historical reflections, the saga of the Bailar inversion. The other important figure in inorganic stereochemistry, Y. Saito, follows with a review of absolute configurations. Matters become heavy when the two chapters by F.S. Richardson and P.E. Schipper on C.D. theory appear. Many an operator is raised and lowered while bras and kets appear in profusion; this reviewer is not clever enough to understand it all.

An organometallic chemist may find the four chapters on various aspects of chiral induction of particular interest. K. Saito describes the kinetic and thermodynamic chiral discrimination of prochiral olefins with chiral platinum(II) complexes. A splendid article by A.M. Sargeson reveals the remarkable rate enhancements and enantioselectivity of cobalt(III) catalysed hydration and amination of olefins. This all seems to happen by proximity. J.M. Brown has a chapter on "Rational Approaches to Asymmetric Hydrogenation". Regrettably, although the approach is rational, it is also wrong, as he and others have subsequently shown. Perhaps of less general interest is the chapter on stereoselective quadridentate ligand synthesis using metal templates.

Two chapters on C.D. spectra of bioinorganic complexes by K.N. Raymond (microbial transport complexes) and J.I. Legg (C.D. as a probe of metal ion interaction with azoproteins) are interesting to those concerned with these matters.

Apart from a chapter on photoacoustic detection of C.D. in crystals, the rest of the book covers the usual C.D. topics. Douglas and Job discuss the important phenomenon of C.D. additivity, Hawkins deals with solvent effects in C.D. spectra, Kirschner has another article on the Pfeiffer Effect, a number of other chapters deal with C.D. spectra of chiral cobalt(III) complexes and Busch proposes a system of nomenclature.

It is perhaps surprising not to find a chapter on exciton C.D., but, apart from this, the book is well presented, is balanced and all of the articles are of

high quality. The editors have done an excellent job of summarizing the field.

As far as the general reader who has only a glancing interest in absolute configurations, C.D. spectra and stereochemical subtleties is concerned, this book may not be of great interest although he may wish to refer to it. For those that are concerned with these things, they will probably find the book superfluous as most of the work has been published before. This, I fear, is the essential paradox of many of the ACS series and others like it.

*Department of Chemistry,
University of Toronto,
Toronto, Ontario (Canada)*

BRICE BOSNICH

Book review

Progress in Inorganic Chemistry, Vol. 27; edited by S.J. Lippard, John Wiley and Sons, New York, 1980, vi + 259 pages, \$ 45.00

When "Progress in Inorganic Chemistry" and "Advances in Inorganic Chemistry and Radiochemistry" both appeared in 1959, there were those of us (graduate students) who questioned the need for two review series in one small field. Some of us even took bets on which series would fold first. With the passing of over twenty years, each series not only has remained strong, but several additional excellent "book type" review series have been added to the list of materials designed to help keep us up-to-date. The "new forum" conceived by F.A. Cotton for "Progress" now is the standard of the discipline. In Volume 27, editor S.J. Lippard continues to maintain the excellence of the "Progress" series. Like earlier volumes, it brings together a mix of topics written in such a way that each article is "comprehensible, but not necessarily readily comprehensible, to a competent Ph.D. level research worker in some branch of inorganic chemistry."

The first article, "Stoichiometric Reactions of Transition Metal Carbene Complexes" by F.J. Brown, is a comprehensive, lengthy (113 pages) but not wordy review of this very important topic. From the abundance of chemical information that has accumulated in only 16 years of research on carbene complexes, it is readily apparent that carbene chemistry has added another dimension to organometallic chemistry. There are 299 figures and 387 references (over 1/3 from E.O. Fischer's laboratory) in this survey.

Gregory L. Geoffroy competently introduces the reader to the relatively unexplored "Photochemistry of Transition Metal Hydride Complexes." While he draws heavily on results obtained in his own laboratory, he does not slight the work of others. Geoffroy has suggested the existence of some general principles governing the photochemical behavior of these hydrides.

The article of Christa G. Kuehn and Stephan S. Isied is on "Some Aspects of the Reactivity of Metal Ion-Sulfur Bonds." The authors limit their review to "spectral, thermodynamic, and kinetic aspects of metal ion-sulfur chemistry" that appear to relate to biology. Much of the excellent work of H. Taube and co-workers on ruthenium-sulfur complexes also is reviewed.

Unfortunately, industrially important metal-catalyzed reactions such as sulfurization and desulfurization are not considered.

Although dithio- β -diketone complexes have been known since 1966, their chemistry has not been reviewed previously. The chapter on "Dithiolium Salts and Dithio- β -diketone Complexes of the Transition Metals" by Trevor N. Lockyer and Raymond L. Martin thus is most welcome. It is an excellent compilation of the chemistry developed to date for these complexes. The chemistry is in some ways similar to, but in many ways very different from, the chemistry of complexes of the more thoroughly studied 1,1- and 1,2-dithiolate ligands.

There is another chapter on stereochemistry by D.L. Kepert. This one "Aspects of ... Four-Coordination and Five-Coordination" has been co-authored by M.C. Favas. Although the emphasis, without apology, is on electron repulsion controlled stereochemistries, with structural results for d^8 (and d^9) complexes termed "anomalous," the review is useful, even with these ions. Significant structural features are identified and the available literature is organized. Unfortunately, some topics such as adducts of sulfur ligand complexes of bis(bidentate ligand)(unidentate ligand) complexes are largely ignored. Included, however, is "another view" of the *trans* influence for four coordination. (Unfortunately the scientific utility of the concept is limited due to its untestable premise of axial charge distribution.)

Volume 27 concludes with a 47 page chapter on "Characterization of Nitrogen Oxides by Vibrational Spectroscopy" by Jaan Laane and James R. Ohlsen.

No serious inorganic chemist can afford to be unaware of the existence of this "Progress" volume and its contents. The price tag of \$ 45 is small when one realizes that nearly 1744 research articles have been examined. Assuming the judgement of the review author is somewhat objective, 2.58 cents per article is a small price to pay.

Department of Chemistry,
Case Western Reserve University,
Cleveland, Ohio 44106 (U.S.A.)

JOHN P. FACKLER, Jr.

Book review

Organic Reactions, Volume 26; John Wiley and Sons, Inc.; New York, Chichester, Brisbane, and Toronto; 488 + vii pages; \$32.00.

Continuing in the best tradition of the first 25 volumes of Organic Reactions, this book discusses "Heteroatom-Facilitated Lithiations" by Heinz W. Gschwend and Herman R. Rodriguez, and "Intramolecular Reactions of Diazocarbonyl Compounds" by Steven D. Burke and Paul A. Grieco. The first chapter should be of particular interest to readers of the Journal of Organometallic Chemistry since it is concerned with the metalation of hydrogen atoms bound to sp^2 -hybridized carbons in molecules which also contain at least one heteroatom. After a brief discussion about two proposed limiting mechanisms of metalation, "coordination only" and "acid-base", space is devoted to the nature and reactivity of the lithiated species, to the effects of other substituents on rates and regioselectivity, and to the compatibility of functional groups with organolithiums. The chapter is then conveniently divided into alpha and beta (directed) lithiations in which hydrogens alpha and beta to the heteroatom are metalated, respectively. Each of these sections is, in turn, codified according to the activating atoms nitrogen, oxygen, sulfur, selenium, tellurium, halogens, and phosphorus positioned in a variety of functional groups. Detailed sections and extensive tables describe such chemistry for the following:

Alpha lithiations: enamines, vinyl isocyanides, formamides and thioformamides, pyrroles, indoles, pyrazoles, imidazoles, benzimidazoles, imidazo[1,2-a]-pyridines, triazoles, tetrazoles, pyridines and pyridine-N-oxides, pyrimidines, alkyl vinyl ethers and thioethers, allenic ethers, furans, oxazoles, oxazolines, vinyl sulfides, vinyl sulfoxides, and vinyl selenides, thiophenes, thiazoles, selenophenes, tellurophenes, haloalkenes, and certain mesoionic compounds.

Beta lithiations: arylamines, α -lithio-(N-alkylidene)arylamines, arylalkylamines, α -alkoxidoaralkylamines, arylcarboxamides and their thio derivatives, 2-aryloxazolines and -oxazines, arylcarbimines, N-arylpyrazoles, aryl nitriles and α,β -unsaturated nitriles, alkyl vinyl ethers, alkyl aryl ethers, alkoxy-alkyl aryl ethers, diaryl ethers, alkyl aralkyl ethers, aralkyl alcohols, α -silyloxystyrenes, arylcarboxylic acids, esters, and ketones, diarylsulfides, sulfones, arylsulfonamides, aryl halides, trifluoromethylbenzenes, arylphosphine oxides and imides, and selenides.

The chapter extends the literature references from an earlier review on metalations in 1954 through December, 1977; some material from 1978 is also included. The authors have included a large number of previously unpublished results obtained in their own laboratories. In light of the extensive use of such reagents in current organic synthetic methodology, it is strongly recommended that all chemists interested in organic synthesis read this chapter. It will certainly be a highly cited one.

The second chapter is primarily concerned with intramolecular cyclizations of α -carbonyl carbenes and carbenoids derived from diazo derivatives. As in the first chapter, space is devoted to mechanism, scope and limitations, eleven typical experimental procedures, and extensive tabular surveys. The latter include intramolecular additions of diazoketones and -esters to olefins, intramolecular insertion of diazocarbonyl compounds into carbon-hydrogen bonds, acid-catalyzed cyclizations of diazoketones, and a table listing several miscellaneous reactions. Literature references are included through December, 1977.

Both chapters are well organized, easy to read, and free of typographical errors. The book whose price is very reasonable should be a valuable addition to the library of most organic chemists.

Department of Chemistry
University of Missouri-Columbia
Columbia, Missouri 65211 USA

Edwin M. Kaiser