BOOK REVIEWS

Iron Porphyrins, Parts I and II
(Volumes 1 and 2 of Physical Bioinorganic Chemistry Series). A. B. P. Lever and H. B. Gray, (eds.)
Addison-Wesley, 1983, Vol. 1, 281 p., Tables, Figures, Indexes; Vol. 2, 254 p., Tables, Figures, Indexes

These two volumes inaugurate an open-ended series which is aimed to cover, at an advanced but still pedagogical level, the physico-chemical theories and techniques used for the investigation of the structure and role of metal ions in living systems. The volumes are appropriately dedicated to iron porphyrins, which are probably the most familiar examples of bioinorganic chemistry to non specialists in the field. Some of the most outstanding personalities in this field have contributed chapters covering the various physico-chemical aspects of iron porphyrin chemistry.

Part I.

Chapter 1 by Gilda H. Loew (87 pages, 157 refs.) reflects the long-standing experience of the author, who assembles the theoretical methods for the investigation of iron porphyrins, from the relatively old all-valence extended Hückel to its iterative, exchange-energy-corrected version, to INDO, Xα, and *ab initio* approaches. Chapter 2 by Robert W. Scheidt and Martin Gouterman (50 pages, 120 refs.) gives in a clear and well organized way the theoretical basis for establishing relationships among nature of the ligands, spin state, and geometry in iron porphyrins and other metalloporphyrins. These two chapters together are an excellent updating of reviews which appeared in 'The Porphyrins' series five years before. Chapter 3 by Marvin W. Makinen and Antonie K. Churg (94 pages, 187 refs.) dealing with the electronic spectra of hemeproteins gives a sound theoretical basis for the assignment of the charge transfer transitions in several oxidation and spin states of the iron, among which the high oxidation numbers are now of particular interest, and establishes an interesting relationship between redox potentials and transition energies. The first volume ends with a Chapter by Harold M. Goff (44 pages, 198 refs.) on the NMR or iron porphyrins containing selected topics among the vast literature on the subject. While not as deep as other review articles on the matter, it is still a useful guideline for experimentalists.

Part II.

Chapter 1 by Samaresh Mitra (42 pages, 80 refs.) is the first detailed review article on magnetic susceptibility as applied to heme-containing systems and, as such, constitutes a precious tool for anyone approaching the field. In Chapter 2 (45 pages, 89 refs.) Graham Palmer gives a plain introduction to EPR spectroscopy as applied to hemeproteins where one can find both the theoretical background for the interpretation of the spectra and a substantial updating of the literature since the appearance of a review article by the same author in 'The Porphyrins' series (1979). Chapter 3 by Thomas J. Spiro (70 pages, 236 refs.) gives a deep and updated account of the Resonance Raman technique as applied to metalloporphyrins and hemeproteins. Finally, Chapter 4 by Karl M. Kadish (88 pages, 176 refs.) covers extensively the various electrochemical techniques applied to the study of iron porphyrins in non aqueous media, and their implications for the understanding of the electron transfer process.

All together, these two volumes are an excellent contribution to the area of bioinorganic-biophysical chemistry; the Editors' personalities and the outstanding standard of these volumes are the best guarantee for the success of the series.

Claudio Luchinat

Advances in Inorganic and Bioinorganic Mechanisms.
Edited by A. G. Sykes, Academic Press Volume 1 (1982)

This first volume of a new series deals with seven separate subjects, five of which relate to inorganic chemistry and two to structure and function of iron and copper-containing proteins. The volume is consistent in one respect in that it contains a comprehensive kinetic treatment in support of most of the proposed mechanisms.

The first chapter by James Espenson deals with the synthesis and reactivity of the Cr^{III}–C σ bond. There are many similarities between this chemistry and that of the well established field of Co^{III}–C organometallic chemistry. Espenson's strength is in his treatment of the kinetics of these reactions which show that S_E^2 and S_H^2 reactions predominate. The S_H^2 reactions are particularly interesting since they provide further experimental support for Jay Kochi's ideas on electron-transfer.

The second chapter by Fraser Armstrong is largely a literature survey on the iron–sulfur proteins and is rather non-critical but it does supply some useful data on the kinetics of electron-transfer. The weakest part is the discussion of the newly discovered Fe_3S_3 systems, and their equilibria with Fe_4S_4 complexes. Both Fe_3S_3 and Fe_4S_4 complexes on the same pro-

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tein have been shown to function at different parts of the electron-transfer chain for sulfate reduction by Xavier's group in Lisbon. Armstrong tends to take the conservative view suggested by Münck, that the Fe_3S_3 complex is likely to be an artifact of the isolation procedures for nature Fe_4S_4 precursors. It is rare to observe reversible equilibria of this kind without an inherent biological function. Such a regulatory function for free Fe^{2+} has been reviewed by R. J. P. Williams recently.

The chapter by Sykes on biological oxygen carriers is excellent in its treatment of both structure and function of these molecules. The chapter which follows by Daito and Dasaki is strictly a treatment of the inorganic chemistry of oxo-metal complexes without extrapolation to analogous systems in biology. Similarly, Lockhart's chapter on the kinetics and mechanisms for reactions of elements in groups I to III fails to deal adequately with biologically derived macrocycles which provides one of the most exciting aspects of this field.

A monumental chapter appears in the middle of the volume on the chemistry of sulfur coordination to transition metals. This chapter by Deutsch and coworkers is 130 pages long with 296 references. Almost a monograph of the subject, it is extremely well written and covers an area which was badly needed. It represents a systematic examination of the chemistry of S–metal complexes and forms a very important source of information for those biochemists who are struggling to understand the reactions of coordinated thiols.

The final chapter by Yeselwitz and Taube takes a new look at the old problem of self-exchange in cobalt ammines, and serves to show that much work remains to be done before such mechanisms are fully understood.

John Wood

Biological and Environmental Aspects of Chromium. Vol. 5, Topics in Environmental Health, ed. by S. Langard, Elsevier Biomedical Press, Amsterdam, 1982, v + 277 pages; US $ 85.00.

This volume introduces chromium as one of the few chemical elements for which all three fundamental aspects of its perspectives in life subsist: technological, nutritional and toxicological. For the two last aspects the uncertainty derived from the analytical and interpretative difficulties is pointed out, especially with regard to the rôle of chromium in the maintenance of normal glucose tolerance and insulin power.

For the metallurgy of chromites and the property of relative products a problem arises: occupational exposure to chromium at the various stages of production and utilization (plating, tanning, welding, painting).

Two chapters are dedicated to the chemical and physical properties of chromium and its compounds in water, soil and air and to a pathway of bioassimilation, the detection limits of which are discussed together with sampling and analytical instrumentation and the relative strategy and sensibility levels.

Numerous and more recent investigations are reviewed on the behaviour of chromium in the human organism with regard to both uptake and cellular retention.

The fractionation studies on the molecular size of chromium compounds in lysates of cells are of great interest. These studies supply hypotheses of chemical behaviour in relation to various bonds including the polymeric one through OH bridges.

Recent in vivo studies are also mentioned.

Chromium also has a nutritional rôle, reviewed in the book from uptake to excretion, but its mutagenic activity is the main problem for mankind. Cr^{+6} reduction in the cell nucleus of the binding of Cr^{+3} to DNA would cause genetic and carinogenic effects (see biochemical hypothesis on glycidal synthesis).

Other morphological and biochemical investigations are in the last chapter, the content of which is mainly medical.

This volume is particularly notable for the inclusion of many articles by distinguished authors and for its technical and scientific detail.

Carlo Alberto Cecconi

Reactive Intermediates, Vol. 3, Edited by R. A. Abramovitch, Plenum Press, New York and London, 1983, xiv + 630 pages, $59.50.

These enterprising volumes on reactive intermediates contain material of interest to a very wide range of chemists, although the emphasis is usually in organic chemistry. In this latest volume by far the longest chapter is that by Z. Rappoport on Vinyl Cations (189 pages, 354 refs.), and this detailed and very authoritative account could appropriately have appeared as a separate monograph. Its interest to inorganic or organometallic chemists will necessarily mainly be indirect (somewhat puzzlingly no mention is made of the acid cleavage of alkynyl-metal derivatives, such as $RC{\equiv}CMR_3$ (M = Si, Ge, or Sn), and the implied marked stabilization of vinyl cations by β-metal substituents); this is also true of the chapter on Bridgehead Olefins by G. Szeimies (68 pages, 224 refs.) (which does not deal with any aspects of com-