Book Review

Advances in Inorganic and Bioinorganic Mechanisms. Vol. 2. Edited by A. G. Sykes, Academic Press, London, 1983, 338 pp., U.S. $75.00/U.K. £54.00.

This editorial series consists of several volumes published each year. This second volume in the series contains six contributions on some basic topics in bioinorganic chemistry, these are as follows:

(1) Base Hydrolysis of Transition Metal Complexes by M. L. Tobe

This is an excellently presented contribution which features clear layout as well as completeness of both scientific information and investigation. This is only to be expected of the author who during recent decades has made many invaluable contributions to the elucidation and understanding of base-catalyzed hydrolysis reactions on d^6 metal complexes with a variety of mono- and polydentate ligands. The section offers a complete and interesting picture of the topic. The author exhibits excellent style in treating an important and rather complex subject field. 269 references are quoted.

(2) Substitution Reactions of Divalent and Trivalent Metal Ions by T. W. Swaddle

This section presents a 'state-of-the-art' account of ligand substitution dynamics in single metal ion complexes. Although, as stated by the author, the article is not meant to be 'comprehensive or exhaustive', the systems considered are chosen following a rigorously scientific approach and are critically examined with great clarity. At first the author deals with structural aspects of metal ions in solution from which some important kinetic conclusions can be drawn. Particularly significant are the mechanisms of interchange processes and long-life intermediates. The final topic is of interest describing the relationships between reactivity and selectivity. The complex subject matter is clarified in an elegant manner supported by a wealth of data. The focus on the analysis of physicochemical data relating to the reactivity of metal ions supports the conclusions drawn by the author, making them less personal than might first appear. 243 references are quoted.

(3) Rapid-reaction Techniques and Bioinorganic Reaction Mechanisms by R. G. Wilkins

The author is a pioneer of these techniques and describes with authority and clarity their underlying principles. These techniques have enabled insight into the understanding of reaction mechanisms in systems of great biochemical interest. The most recent techniques for the study of fast reactions in the field of metalloproteins are examined.

In particular, ample treatment is devoted to rate measurements in small molecule interaction with proteins: redox reactions of both the outer-sphere and inner-sphere type, spin-state changes and protein folding. Techniques for rapid generation of transient species are also examined. All the subject matter is presented in an exhaustive manner, with elegant style and scientific soundness in the conclusions drawn. The article is an invaluable aid to active researchers in this important field. 288 references are quoted.

(4) Do Binucleating Ligands have a Biological Relevance?, by D. E. Fenton

The author reviews the most important scientific contributions to the literature concerning the use of binucleating ligands for the synthesis of homo- or hetero-nuclear bimetallic complexes up to mid-1982. Much attention is given to the possibility of assessing whether synthetic polynuclear complexes can be assimilated into biological systems. Heteronuclear complexes with binucleating ligands acting as models for biosites are examined in order to understand the metal environments in bimetallobiomolecules. The author's conclusions warn of 'real difficulties' and also of the dangers of 'straining' the arguments in drawing biochemical conclusions from the study of synthetic polynuclear systems.

The article correctly emphasizes both the enormous possibilities offered by this research field as well as outlining the scope of what has still to be discovered, with of course the potential challenges.

The author has been involved in this field for a long time and his original research has lent authority to his opinions and justifies his enthusiastic expectations. The contribution is very well written, is complete with essential data which fits well with the title, and is free of redundant detail, all of this makes for pleasant reading. The section is a vital source of critical information for those who intend to carry out inorganic biochemistry research. 264 references are quoted.

(5) Molybdenum Enzymes: a Survey of Structural Information from EXAFS and EPR Spectroscopy by S. P. Cramer

This paper reports on basic advances in the understanding of molybdenum environments in metalloenzymes by using the title techniques. Both techniques, X-ray absorption spectroscopy and electron

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paramagnetic resonance, have been applied extensively to structural studies of molybdenum proteins to gain information on the local molybdenum environment so as to rationalize the catalytic activity and the electrochemical properties of the metal site in the various proteins. The article describes the processes catalyzed by these systems (from sulfite oxidation to nitrogen reduction) and the redox potentials of molybdenum enzymes.

An ample treatment is devoted to cofactors, namely the iron–molybdenum cofactor of nitrogenase, 'Fe–Mo-co', and the molybdenum cofactor, 'Mo-co', apparently common to all other molybdenum enzymes.

Cofactors are small molecules containing molybdenum which can be released by a protein and thus inserted into the structure of another apo-protein to form an active enzyme. The article first examines EXAFS *vs.* EPR as a technique for structural investigation for the various systems: nitrogenase, iron–molybdenum cofactor, sulfite oxidase, xanthine oxidase, D. Gigas Mo (2Fe–2S) protein, nitrate reductase, CO_2 reductase, molybdenum processing proteins, molybdenum cofactor. The conclusion is that the most valuable thing gained from the study of molybdenum enzymes is an awareness of their structural diversity, thus significant changes are required in the catalytic mechanisms proposed for these enzymes. The contribution is clearly and concisely written and well balanced in premises and conclusions, which are rigorously documented. Relationships between catalytic activity and structural properties are critically examined. It is an excellent reference for both researchers and students. 137 references are quoted.

(6) Oxygen-18 Exchange Studies of Aqua- and Oxo-ions by H. Gamsjager and R. K. Murmann

This contribution examines the most significant results relating to kinetics of oxo-anion exchange with water, aqua-cation exchange with water; oxo-cation and oligomer exchange with water; oxygen exchange between neutral substances and water. Experimental techniques for the study of these systems are described. Mechanistic aspects are then critically examined with a focus on activation parameters. The paper is written competently, which reflects the thorough knowledge of these systems which the authors have acquired over a long period of study. The subject matter is elegantly presented and clearly indicates the major contribution to our understanding of mechanistic details which the application of the techniques outlined has enabled. The authors should also be praised for their ability to make evident, even to non-experts of the field, the usefulness of these techniques. 223 references are quoted.

Finally Prof. A. G. Sykes, editor of this volume, should be credited for choosing topics of great interest to bioinorganic chemists and for inviting contributions from scientists of great merit and authority, all of whom are leaders in their specific fields.

The volume will certainly meet a well-deserved success among the bioinorganic scientific community.

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