CHEMICAL REVIEWS

Volume 96, Number 7 November 1996

Preface: Bioinorganic Enzymology

The subject of biological inorganic chemistry is one of the most intellectually attractive and experimentally demanding frontiers in modern chemical science. Its scope is enormous, ranging from chemical synthesis and molecular characterization to enzymology and molecular biology, and to clinical medicine. Metallobiomolecules are natural products that in their essence are highly elaborated metal complexes equipped with the necessary protein structure for complementarity and all other aspects of function. The active sites of a significant fraction of all proteins and enzymes contain one or more metal ions, superbly—and perhaps optimally—conditioned by protein structure and environment toward accomplishment of evolutionarily directed function. Their structural and electronic properties are often modulated from those of small molecules containing the same metal ion. Understanding these differences is essential to understanding function, and the optimal starting point for this endeavor is the crystal structure of the metallobiomolecule. In this regard, we have recently entered a remarkable phase in bioinorganic chemistry where an accelerating number of the basic types of metal coordination units, together with overall protein structure, have become defined by crystallographic methods at atomic resolution. In these cases, research can now focus more intensely on learning how function relates to structure. As evoked by the cover scheme, the many disciplines embodied in the subject make major contributions to this goal. The spectroscopist defines electronic structure (often unique to the biological site), the enzymologist determines equilibrium and rate parameters and endeavors to relate function to structure, the molecular biologist perturbs structure and observes the effect on reactivity and structure at all levels, and the synthetic chemist assembles minimal site representations and determines intrinsic geometric, electronic, and reactivity properties. All this is directed toward what is to many the ultimate goal of bioinorganic research: definition of function in terms of structure.

In this thematic volume, the present state of understanding of many important topics in bioinorganic chemistry is presented. The theme emphasized is reactivity, and for that reason we have chosen the name "Bioinorganic Enzymology" for this special issue. In the initial article, we provide a transitional account, perhaps particularly useful to the nonexpert, of some of the basic concepts of bioinorganic chemistry by examining the properties and roles of metal ions against the background of a database of metallobiomolecular X-ray structures. Correlations that can be drawn between function and structure are provided. Authoritative treatments follow on zinc and related nonredox enzymes, kinetics and thermodynamics of long-range electron transfer, metal sites involved in O_2-activation, multielectron reduction, O—O bond formation and peroxide dismutation, structural and functional aspects of nitrogenase and NO_x-reducing enzymes, carbon and hydrogen metabolism, and biological oxygen atom transfer. Lastly, our intent has been to produce a unique resource in the literature of bioinorganic chemistry that should find wide application in both research and teaching. Toward this end, we greatly appreciate the cooperation of all contributing authors and the outstanding quality of their presentations.

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CR9604144

S0009-2665(96)00414-1 CCC: $25.00 © 1996 American Chemical Society