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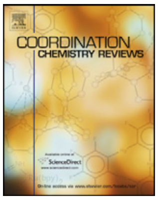

Review

An evolution of bioinorganic chemistry from molecular to geological level—Daryle H. Busch's contribution

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ABSTRACT

The evolution of the discipline Bioinorganic Chemistry and how Daryle H. Busch contributed to it are reviewed from a personal perspective of this author. The initial motivation was intimated in a review article published in the third volume (1968) of this journal. Bioinorganic chemistry has been expanded from the molecular level to include the environmental and geological aspects.

1. Beginnings of bioinorganic chemistry

This article is not intended to review the entire development of "Bioinorganic Chemistry", but is to view it from this writer's personal perspective, particularly with regard to his association with Daryle H. Busch.

In the third volume of *Coordination Chemistry Review* this writer published a review article titled "Catalytic Functions of Metal Ions and Their Complexes" [1]. It was an English translation of a review article written in Japanese [2], which was written as a preparation for his PhD work that focused on the catalytic reactions of various types by transition metal complexes [3,4]. He intimated in the original review [1] that a lot about the catalytic functions of metal complexes can be learned from the studies of metal-containing enzymes, and also suggested that metal coordination chemistry can make a significant contribution to understanding of the metallo-enzymes. This implies "bioinorganic chemistry".

It should be pointed out, though, that discovery and research on metal-containing enzymes and pharmaceuticals had already begun. Research on metal-containing enzymes had been in progress long before this writer's coming into the field. Indeed, this writer took a course on metallo-enzymes in his graduate studies (in Tokyo) in early 1960s. Perhaps, R.J.P. Williams was one of the earliest to recognize the importance of metals in biological systems; the first article on the subject by him was published as early as 1953 [5]. He also wrote review articles on metallo-enzymes and metalloporphyrins in 1956 [6].

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As a postdoctoral fellow (1966–1968) in the Lab of Daryle H. Busch at the Ohio State University, Ochiai investigated the coordination chemistry of macrocyclic ligands [7,8] and then extended the investigation to include a macrocyclic organometallic compound containing cobalt under the encouragement by Daryle H. Busch. It was meant to be a model for vitamin B_{12} coenzyme or cobalamin, the only then-known organometallic compound naturally occurring [9,10]. Thus, "Bioinorganic Chemistry" did become an intentional target of his pursuit while working in Daryle H. Busch's lab.

The people in the lab began to talk about a possibility to have a small gathering on "Bioinorganic Chemistry". It materialized as a mini-symposium as a part of the 25th ACS Northwest Regional Meeting in June 1970, where Daryle H. Busch gave a talk titled "Metals and Enzymes-Multiple Juxtapositional Fixedness (MJF)" [11]. This idea MJF anticipates the special structural features of the enzymes' active sites. Though the title of the mini-symposium was "Inorganic Biochemistry", it might have been the first official meeting of an interdisciplinary new field: "Bioinorganic Chemistry". Since these early days, Daryle H. Busch has been eying the field of bioinorganic chemistry from his own "coordination chemistry" perspective.

2. An attempt to overview bioinorganic chemistry

While he was at the University of British Columbia, this writer attempted to gather together the most significant findings and experimental data up to that point with regard to the research areas bordering on inorganic chemistry and biology/physiology. This effort was materialized in the form of a book: "Bioinorganic Chemistry, an Introduction" [12] in 1977. It was published as a book in the Allyn and Bacon Chemistry Series for which Daryle H. Busch was a consulting editor. He read the entire manuscript and made innumerable valuable comments and suggestions, and also provided an English editor (one of his graduate students at the time) for the author.

The book viewed the subject in terms of elements, transition metals, alkali and alkaline elements. An emphasis of this book was placed on the physicochemical data and their interpretations regarding metals in, particularly metallo-enzymes and metal-activated enzymes. It also discussed the methodology of experimental investigation, again emphasizing physicochemical methods. Biochemical and other methods, e.g., to manipulate the protein sequences had not been well developed at the time. Also included in the book was a chapter titled "environmental bioinorganic chemistry", as many of environmental issues, toxicity, *etc.*, are indeed caused by inorganic elements such as heavy metals [13]. Environmental bioinorganic chemistry is now indeed thriving as a sub-discipline of bioinorganic chemistry. Meetings of this title are now regularly held as a Gordon Research Conference; e.g., see [14].

While writing the book, he focused his research on oxygenation/oxidation [15]. Daryle H. Busch, after moving to Kansas University, has also intensified the work on the oxygenation/oxidation by transition metals with tight-binding ligands [16]. This is an area bordering on both bioinorganic chemistry and "green" chemistry [16], as well. Indeed, bioinorganic chemistry could suggest much for "green" chemistry.

3. Birth of ICBIC and thereafter

1983 saw an international conference on bioinorganic chemistry (ICBIC) being held for the first time in Florence, Italy. ICBIC is now being held every second year, and the 14th conference was held in Nagoya, Japan in July 2009. In other words, the discipline "bioinorganic chemistry" is now officially just over quarter a century old. This writer attended many of the ICBIC meetings including the first one. The research in bioinorganic chemistry has intensified and expanded rapidly since the establishment of it as an internationally recognized official discipline.

A second book on bioinorganic chemistry [17] was conceived and published while the writer was at Juniata College, Pennsylvania. This time it was written from a different perspective from the previous one. The main focus was a question: Why has a certain element been chosen for a certain biological function (acid–base catalysis, oxidation–reduction catalysis, *etc.*). It might be pointed out that this question is rarely asked, let alone being answered. It also discussed the biological metabolism of elements, and the toxicity of and the biological defenses against elements.

Ochiai's research focus in this period was on ribonucleotide reductase [18,19], and cobalamin. Several different forms of ribonucleotide reductase are known: cobalamin-, iron- and manganese-dependent ones, and all are based on a free radical mechanism, and the transition metals are involved in the formation of free radical entities. The enzymes (including a ribonucleotide reductase) dependent on cobalamin were also shown to involve a free radical entity. It turned out that free radicals are involved in far more enzymatic systems involving metals than expected [20,21].

4. Geobiology–geological aspects of bioinorganic chemistry

A new idea arose in 1978 [22,23]. Specific elements (inorganic) are required by specific organisms, though some of the elements such as iron and calcium are almost universally required. The atmospheric oxygen content in the atmosphere has evolved over the history of the earth from almost none in the Archean period to the present level (see a more recent review on this issue [24]). Some of the important bio-elements are subject to oxidation–reduction, and the earth's oxidation–reduction level varied as the atmospheric oxygen content changed. An element's availability (to organisms), i.e., solubility (in aqueous medium) depends on its oxidation state, and the counter anions. If one combines all these factors, then one may be able to look into the biological evolution (and origins) of life on the earth in terms of the availability of various elements. For example, an organism that requires specifically copper would not have evolved before the copper became available to it. If the time can be identified when copper became available likely in the form of Cu(II), it may be inferred that this particular organism emerged only after that time. With this simplistic idea, an attempt was made to deduce the time and the time sequence of the biological evolution [22,23].

The notion expressed in the paper [22] that geology and biology (and its origin and evolution) are and were intimately intertwined has led to the publication in 2005 of a new journal "*Geobiology*" dedicated to the pursuit of this issue (see an example of relevant articles [25]). One of the crucial issues in this regard is availability (and accessibility to organisms) of elements, and a single most important factor in this regard is "sulfide" anion that combines with metallic elements forming metal sulfide ores. The idea of autotrophic origin of life [26] is based upon availability of metal sulfides, iron sulfide in particular, which is supposed to be responsible for the origin of modern proteins, ferredoxins [23]. For example, Saito et al. published a detailed analysis of metal sulfides and their levels in the environment and its relationship with the evolution of cyanobacteria [27]. R.J.P. Williams tried to generalize the ideas and proposed a chemical systems approach to evolution [28], in contrast to the molecular evolution idea based on the DNA and the protein sequences.

This idea then led to another extension of bioinorganic chemistry; the area had been known as biogeochemical cycling of elements, and pursued by geochemists. The "bio" portion of this process is indeed a bioinorganic chemistry, and hence bioinorganic chemistry may make some contribution to understanding of the biogeochemical cycling of elements. The process was relabeled as "global metabolism of elements" [29]. An attempt was made to evaluate the quantities and the flow rates of an element among the atmosphere, the hydrosphere, the lithosphere and the biosphere for many of the major elements including C, N, P, S, Ca, Fe, Zn, As and Hg. This was published in "Encyclopedia of Life Support Systems" (UNESCO) [30,31].

5. The scope of bioinorganic chemistry

Bioinorganic chemistry or rather the scope it represents is perceived by this writer to be an overall picture of the movements of elements on the Earth. The biosphere is a pivotal factor in this large picture. The biosphere is a sum of the ecological system representing interrelationships among organisms and the individual organisms in it. The biosphere is surrounded by and intimately associated with the "inorganic portion" (atmosphere, hydrosphere and lithosphere) of the Earth, and this fact implies that "bioinorganic chemistry" is universal, and that the systems approach [28] makes sense.

A single organism may consist of cells, tissues and organs, though most microorganisms are mono-cellular. The elements are involved in functioning of the biological system, whether a single cell organism, a multi-cellular organism or an ecological system. We need to look at functioning of elements at molecular level, cellular level, physiological, ecological and geological level. Chemistry, bioinorganic chemistry included, tends to be "analytical", looking into the details of molecular interactions, and, of course, should necessarily be so. However, a large picture, somewhat "holistic", needs also be painted in order to gain a better understanding of the whole business of how elements are working together. With this perspective in mind, Ochiai wrote yet another book 30 years after the first book; that is "Bioinorganic Chemistry, a Survey" [32].

This writer is very much indebted to all the researchers who have made important contributions and brought an excitement to this growing field. He would not have been able to develop and keep his interest in the field without their contributions.

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