
The importance of metal ions in life processes in living systems, and their health and well-being has become increasingly known during the last 50 years leading to a fast development in Bioinorganic Chemistry. The objective of the editors is to highlight this important aspect of the subject. In the present volume having 15 Chapters the following are broadly covered with illustrations and pertinent references: peptide bond characteristics, lanthanide ion-mediated peptide hydrolysis, Co(III)-promoted hydrolysis of amides and small peptides, synthetic Cu(II) and Ni(II) peptidases, Pd(II) and Pt(II) complexes as synthetic peptidases, protease activity of 1,10-phenanthroline-Cu systems, specific protein degradation by Cu(II) ions, artificial iron-dependent proteases, hydroxyl radical footprinting of proteins using metal ion complexes, nickel and cobalt dependent oxidation and cross-linking of proteins, effects of metal ions on the oxidation and nitrosation of cysteine residues in proteins and enzymes, protein cross-linking mediated by metal ion complexes, ferrocenoyl amino acids and peptides:probing peptide structure, synthetic analogs of zinc enzymes, and mimicking biological electron transfer and oxygen activation involving iron and copper proteins: a bioinorganic supramolecular approach; all these topics authored by persons with knowledge and expertise in these fields.

Chapter 1 summarizes the basic characteristics of the peptide or amide bond, emphasizing its interaction with H+ and metal ions. Also included is a discussion on free energy of formation and hydrolysis of peptide bond. Effects of metal ions on peptide bond formation equilibria and rates of hydrolysis of peptide bonds are also discussed in this chapter. There are a total of 56 literature citations pertinent to the discussions.

Chapter 2 presents a review of the features of amide hydrolysis by lanthanide ions; the catalytic mechanism responsible for the remarkable activities of the lanthanide ions are discussed at length, with 30 literature citations.

Chapter 3 is on detailed accounts, particularly of the last 25 years, on the role of Co(III) complexes in promoting hydrolysis of peptide bond and its mechanism, with 86 literature citations.

Chapter 4 is devoted to studies on cleavage of amides, peptides and proteins by Cu(II) and Ni(II) which provide insight into the mechanism of metal ion-promoted amide hydrolysis; reports of investigations with the aqua ions and the complexes are included. A binuclear complex of Ni(II) which functions as urease model has been discussed. The knowledge gained on synthetic complexes so far provides a clue as to why no naturally occurring hydrolases employ Cu(II) as the activator, and nature’s preference for Ni(II). There are 38 literature citations.

Chapter 5 is on studies on complexes of Pd(II) and Pt(II) as reagents for cleaving of peptides and proteins, the mechanisms of such processes, i.e., their role as peptidases, and a rationale for their practical applications which has emerged. The fact that in all the cases studied Pd(II) is a better promoter than Pt(II) in peptide cleavage is due to greater lability of the Pd-ligand bond that facilitates its comparatively much more ready attachment to the peptide. There are 40 literature citations.

Chapter 6 is devoted to 1,10-phenanthroline-micelle-Cu(II) complex showing protease-like activity in protein degradation. It functions through formation of a Cu(I) complex which acts as a redox catalyst in generating OH (hydroxyl) radical in presence of O2. This OH radical attacks and degrades the protein. High concentration of 1,10-phenanthroline needed to form micelles is required, for the activity, and ordinary Cu(phen)2+ is devoid of such activity. The 1,10-phenanthroline-micelle-Cu(II) complex is able to attach to the protein and displays the catalytic activity. Much of the work has been done during the last ca. 15 years and there are 15 literature citations.

Chapter 7 is on degradation of specific proteins by Cu(II) ions and covers aspects such as conditions affecting rate of cleavage of peptides by Cu(II) ions, their possible mechanisms, and physiological relevance of the process. There are 26 literature citations, mostly the recent ones of the 1980s and 1990s.

Chapter 8 deals with artificial iron-dependent proteases in cleavage of proteins which is an
important approach to characterization of the structural features of proteins and protein-nucleic acid complexes. The synthesis of Fe(III) complexes of two bifunctional ligands, which are C-substituted EDTA, and their functions are discussed with the mechanism of action. There are 89 literature citations.

Chapter 9 deals with experimental methodology of protein footprinting, applications of the methodology, and future possibilities, based on metal ion complexes which catalyse generation of CH (hydroxyl) radical. The limitations of the methodology are also discussed. There are 37 literature citations, mostly very recent ones.

Chapter 10 is devoted to nickel- and cobalt-dependent oxidation and cross-linking of proteins. Much of our interest on Ni and Co in biological systems (where they are present in trace concentrations) is because of some fascinating enzymes that utilize Ni and Co ions and their associated coenzymes, F430 (Ni) and B12 (Co). Model studies with nickel peptides has led to an understanding of the general basis for redox activation. There are 92 literature citations.

Chapter 11 deals with the effects of metal ions on oxidation and nitrosoation of cysteine residues in proteins and enzymes. Chemical modification of cysteine residues in proteins can have profound effects on cell biochemistry. The oxidation or S-nitrosoation of these residues may be associated with important signaling or regulatory pathways. In this chapter the reviewers have focused on examples in which metal ions modulate the products, equilibria, and rates of cysteine oxidation and S-nitrosoation in proteins. There are 132 literature citations.

Chapter 12 is on protein cross-linking mediated by metal ion complexes. Metal-based cross-linking reagents have greatly expanded the utility of cross-linking as a method for probing the architecture of protein complexes. They have been shown to be highly efficient and specific reagents. There are 83 literature citations.

Chapter 13 deals with ferrocenoyl amino acids and peptides in probing peptide structure. Inorganic and organometallic moieties can now be readily incorporated in a variety of biomolecules, allowing the study of interactions of the labeled biomolecules with other biomolecules under physiological conditions using spectroscopic and electrochemical techniques. There are 51 literature citations, mostly of investigations reported during the 1990s.

In the last two chapters, Chapters 14 and 15, a different approach for probing metalloproteins is outlined. Synthetic analogs of metalloenzymes are considered with the aim to mimic both structure and function of active sites of enzymes. The synthetic analogs of zinc enzymes are discussed in Chapter 14, with 103 reference citations, while electron transfer and oxygen activation by iron and copper proteins are discussed in Chapter 15 with 827 literature citations.

This volume is a store-house of up-to-date information in one of the most promising field of research in bioinorganic chemistry, viz., probing enzymes and proteins by metal ions and low molecular weight complexes thereof, being reviewed by 26 renowned authorities covering 15 chapters. Like all the previous volumes of the series it would be a treasure worthy of a science library that can afford its rather high cost. The reviewer feels inclined to suggest that the Publisher ought to seriously consider bringing out much cheaper paper-back versions of this series for the benefit of those who are less privileged as in the developing countries like India.

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