



Coordination Chemistry in Protein Cages

This book deals with protein

structures that are cage-like (in a broad sense) and incorporate metal ions or metal compounds. The focus is on non-natural—i.e., chemically modified or fully synthetic—systems. This research area is topical and dynamic, as documented by many recent publications in top journals. During recent years, facets of this field have been covered by review articles, but to my knowledge this book provides the first comprehensive overview. The editors have structured the subject in six sections, which are subdivided into chapters contributed by various authors.

Part I, "Coordination Chemistry in Native Protein Cages", introduces protein cages with metal-oxide cores, and begins with the well-explored topic of ferritin, an important iron-storage protein for many living organisms, including humans. Ferritin can host up to 4500 iron ions in a spherical inner cavity, and is probably the most popular model for the development of biologically inspired protein cages. The following chapter covers less-familiar proteins that accumulate other metal ions such as vanadium, molybdenum, or tungsten as oxides.

Part II, "Design of Metal-Protein Cages", begins with a description of synthetic helix bundles, which bind metal cofactors and serve as simple models for metalloproteins. Another chapter focuses on heme proteins, illustrating how new catalytic functions can be created (e.g., myoglobin as peroxidase), either by mutation of the protein component or by chemical modification of the heme cofactor, including its exchange by synthetic metal complexes. Following that, the engineering of metalloproteins is discussed from a broader perspective. Even though some spectacular examples have been reported, such as the oxygenation of methane to methanol with atmospheric dioxygen by modified P450 enzymes, it is only rarely that desired enzymatic functions, in particular high catalytic activity, have been achieved through targeted design.

Assembled cage-type structures are the focus of Part III, "Coordination Chemistry of Protein Assembly Cages". It is shown how metal ions, in particular Zn²⁺, can serve as templates for the association of proteins to form superstructures. In the following chapter, editor Takafumi Ueno highlights examples of efficient catalytic organometallic reactions inside modified ferritins, such as Pdcatalyzed olefin hydrogenation or the Suzuki-Miyaura coupling. The final chapter of this section presents impressive work by Ward on enantiose-

lective catalysis by organometallic complexes that are anchored via a biotin linker in the asymmetric protein cavity of streptavidin. I would rather have placed this chapter in Part II, since Ward's approach implies the screening of protein mutants.

Part IV, "Applications in Biology", starts with a chapter on fluorescent labeling of proteins with metal compounds. Without any doubt, metal-based labeling reagents are important to the life sciences, but it is not clear to me how this topic fits within the book's context of cage-like protein structures. The tailor-made magnetosomes described later are iron-oxide particles in membrane vesicles of bacteria. Particle morphology and surface modification can be controlled by genetic engineering of membrane associated proteins. Because of favorable material characteristics such as single-domain structure, tailor-made magnetosomes are a potential alternative to classical magnetic nanoparticles.

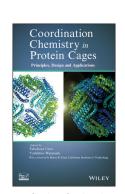
Applications in nanotechnology (Part V) are first discussed in the context of hybrid materials: important topics include the formation of metal-oxide nanoparticles in ferritins and viral capsids, and the assembly of (coordination) polymers in protein cages. Precise positioning of protein-coated nanoparticles on structured surfaces may open new perspectives in the engineering of nanostructured electronic devices. Ferritins, for example, can be functionalized with small peptides that bind selectively to titanium or silver surfaces. This part ends with a discussion of the potential of tailor-made protein cages for the size- and shape-controlled generation of nanoparticles and nanostructured surfaces.

The book concludes with Part VI, "Coordination Chemistry Inspired by Protein Cages", and highlights Makoto Fujita's spectacular synthetic cage structures, many of which are built by spontaneous self-assembly of polytopic pyridyl ligands and palladium(II) ions or complex fragments. Such cages that are large enough to accommodate proteins have recently been constructed. An impressive example is a Pd₁₂ cage hosting the 8500-dalton protein ubiquitin—a protein within a metal complex cage!

Coordination Chemistry in Protein Cages provides an up-to-date and comprehensive overview of a specialized, but very exciting and dynamic, field of research. It takes a little time to get used to the structure and organization of the work. The book is recommended for researchers in the fields of bioorganic and bio-inorganic chemistry and nanosciences.

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