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Review

Artificial metalloenzymes as catalysts in non-natural compounds synthesis

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ABSTRACT

The status of high-accuracy studies of metalloenzymes application as catalysts in non-natural compounds synthesis has been presented. The discussion is organized based on their stereo- and regioselectivities, as well as catalytic activities and the majority of these examples were reported within the last few years. Moreover computational methods, which are helpful for further development of new artificial metalloenzyme catalyst systems and explanation of the reaction mechanism, are discussed.

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Contents

1. Introduction	00
2. Metalloenzymes – basic principle	00
3. Artificial metalloenzymes with immobilized metals complexes	00
4. Recent advances in synthesis with artificial metalloenzymes	00
4.1. Oxidation and hydroxylation of olefins and benzyl moieties	00
4.2. Hydrogenation	00
4.3. Olefin metathesis	00
4.4. Diels–Alder reactions	00
4.5. Friedel–Crafts alkylation	00
4.6. Transfer reactions	00
5. Modelling of artificial metalloenzymes	00
6. Conclusions	00
Acknowledgments	00
References	00

1. Introduction

Coordination compounds with metals play an essential role in the life processes. Metal ions are found in one-third of all proteins [1,2]. Some metals are essentials in the biological systems, the

others are considered toxic [3]. The typical properties of metal caused possibility of them to be present in the life processes [4–6]. As it is seen in Fig. 1 metal has got charge, which can be changed depending on the coordination environment from cationic, by neutral to anionic charge. The metals have ability to interact with both organic and inorganic ligands. Depending on the ligands different properties of formed complexes can be obtained. The replacement of ligand or metal in complex structure changes the behaviour of

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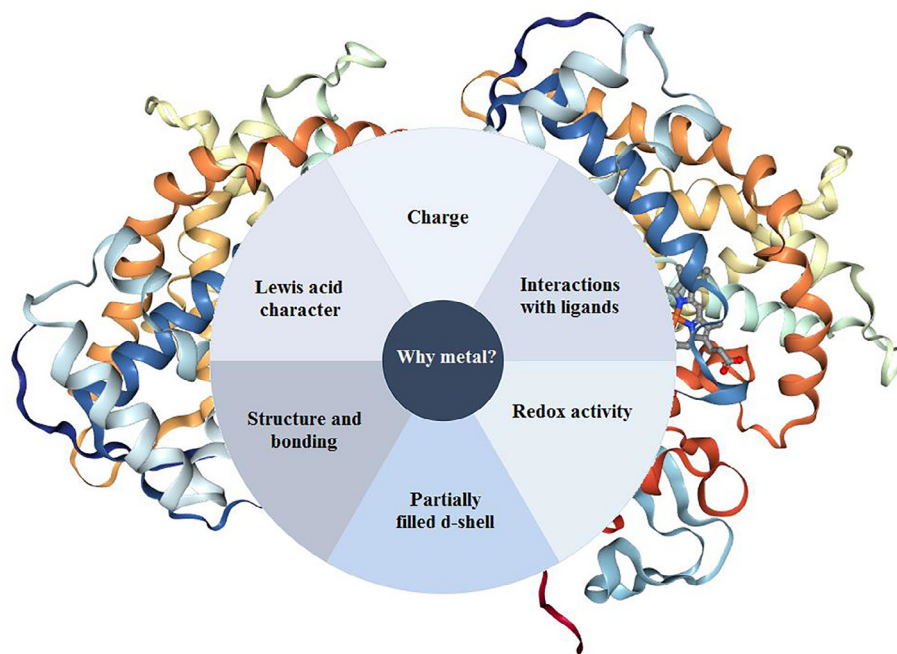


Fig. 1. General chemical properties of metals.

formed compounds. Moreover, the bond lengths, bond angles and number of coordination sites can vary depending on the metal and its oxidation state in the complex compound. Therefore metal–ligand complexes span a range of coordination geometries that give them unique shapes compared to organic molecules. The metal oxidation state has got implications for toxicity. For example chromium(III) ions are necessary to glucose metabolism [7], while chromium ions in the 6^+ are mutagenic and carcinogenic, due to the various forms of DNA damage including DNA interstrand crosslinks, DNA–protein crosslinks, DNA strand breaks, and Cr–DNA adducts [8]. Lewis acid character of metals enables the metal ions with high electron affinity to polarize groups significantly which are coordinated to them (i.e. hydrolysis reactions). Very interesting group of metals are the transition metals with partially filled d-shell or f-shell for lanthanides (sometimes called inner transition elements). The d-block metal ions readily form complexes. The complex formation often is accompanied by a change in colour and sometimes by a change in the intensity of colour. In these orbitals there are a variable number of electrons and these metals have ability to undergo 1-electron oxidation and reduction reactions. The occurrence of variable oxidation states and, often, the interconversion between them, is a characteristic of most d-block metals [9]. Moreover the complexes formed with such metals have got interesting electronic and magnetic properties. It is worth to mention that d-block metals are very often used to produce catalysts applied in chemical industry. It could be used as catalyst in well-known reactions such as iron in the Haber process to obtain ammonium, nickel in the hydrogenation of C=C bonds, vanadium (V) oxide in conversion reaction of sulphur dioxide into sulphur trioxide, as well as new as described in [10–15].

Metals can easily lose electrons from the familiar elemental or metallic state and form positively charged ions. The cationic forms of metals are soluble in biological fluids. Moreover the metal ions, which are electron deficient, can bind and interact with electron rich molecules. Examples of such molecules are biological compounds such as proteins and DNA [16]. The metal ions present in biological systems (mainly metalloproteins) have different functions such as [17]: (i) structural (stabilization of protein chain by Zn^{2+} forms strong bonds to sulphur ligands, mainly from amino

acid cysteine), (ii) transmission of impulses along nerve fibres (associated with the change in K^+ and Na^+ concentration inside the fibre and outside pattern; Na^+/K^+ pump), (iii) messenger in nerve action (Ca^{2+} complexes), (iv) blood clotting (Ca^{2+} complexes). But the most important function of metal ions is their participation in the biological reaction, as respiration, energy transfer, photosynthesis, nitrogen fixation.

The bioinorganic species are often remarkably effective catalysts, known as metalloenzymes [18]. These compounds are enzyme proteins containing the metal ions bonded with the protein or the enzyme-bound nonprotein components. They are characterized by high reactivity and selectivity. Moreover, Sigel and Pyle [19] suggested that also ribozymes, i.e., RNA molecules with enzyme function may be considered as metalloenzymes because of the presence of functionally important metal ions (mostly divalent metal ions such as Mg^{2+}) in their structure.

This review will cover challenges in an application of artificial metalloenzymes as catalysts in non-natural compounds synthesis. Artificial metalloenzymes are the superior alternatives to native metalloenzymes and classical organocatalysts. In most cases, conditions required with enzymes are milder than those required with either homogeneous or heterogeneous catalysts. The discussion is organized based on their enantio- and regioselectivities, as well as catalytic activities and the majority of these examples were reported within the last few years. Moreover computational methods, which are helpful for further development of new artificial metalloenzyme catalyst systems and explanation of the reaction mechanism, are discussed.

2. Metalloenzymes – basic principle

The selection of a metal for use in enzymatic catalysis results from the combination of its physicochemical properties such as redox potential and coordination chemistry, and its accessibility in the environment for biological systems [20].

Researchers have studied the properties, function and mechanism of natural metalloenzymes for many years [21–30]. The studies indicate that the reactivity of them depends on several factors,

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