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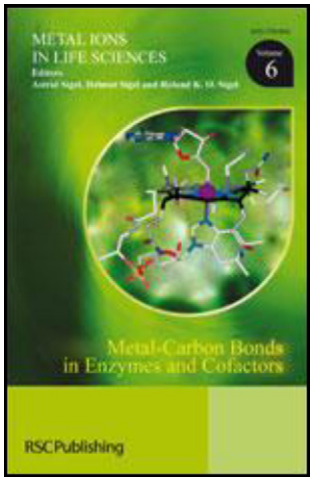
Book review

Metal–carbon bonds in enzymes and cofactors

Metal Ions in Life Sciences, A. Sigel, H. Sigel, R.K.O. Sigel (Eds.). RSC Publishing (2009). Hardback, Price: £150.00, ISBN: 978-1-84755-915-9



The sixth volume in the Metal Ions in Life Sciences series, "Metal–Carbon Bonds in Enzymes and Cofactors", is a comprehensive and authoritative reference covering the current understanding of naturally occurring metal–carbon bonds. The book includes 12 chapters, all authored by experts in their particular area. The volume describes ways that nature uses the organometallic bond to house a latent radical, to stabilize the catalytically active electronic state of a metal ion, and to activate a substrate in an enzymatic reaction. It also describes systems in which the metal–carbon bond represents an inhibited state of an enzyme and ways that chemists use the organometallic bond to probe the active site of an enzyme. The book is recommended for researchers studying any subject relating to transition metal and organometallic chemistry and to the roles of metals in biology.

Coenzyme B_{12} was the first metal–carbon bond described in an enzyme; thus, it is fitting that the volume open with two chapters on vitamin B_{12} chemistry and biochemistry. The first one, by Kräutler, focuses on the chemical structure and reactivity of methyl- and adenosylcobalamin and on the thermodynamics and kinetics of the redox chemistry that control formation and lysis of the carbon–cobalt bond. This chapter will serve as a valuable resource for scientists to relate the properties of B12 enzymes to those of model systems. Chapter 2 by Matthews, which authoritatively covers the biochemistry of enzymes that utilize or form methyl- or adenosylcobalamin, features exciting recent structural and mechanistic insights into the properties of these two important classes of bioorganometallic systems and how they promote nucleophilic versus radical cleavage/formation of the carbon–cobalt bond.

The next two chapters cover the other major enzymatic systems that appear to generate organometallic intermediates during their catalytic mechanisms: the nickel-dependent methyl-coenzyme M reductase and acetyl-CoA synthase/carbon monoxide dehydrogenase. Chapter 3 by Jaun and Thauer covers the model chemistry and enzymology related to the formation of a methylnickel intermediate in methyl-coenzyme M reductase and the subsequent generation of methane from this organometallic intermediate. This chapter includes the evidence for and against the intermediacy of methylnickel in catalysis by this enzyme. Chapter 4 by Lindahl describes the remarkable mechanisms of acetyl-CoA synthase, which appears to generate acetyl-CoA through a series of organometallic methyl-Ni, Ni–CO, and acetyl-Ni intermediates, and of carbon monoxide dehydrogenase, which forms a Ni–CO intermediate during CO oxidation. However, of these, the paramagnetic Ni–CO complex on acetyl-CoA synthase is the only species that has been trapped and demonstrated to be a catalytically competent intermediate.

The next three chapters on the [Ni–Fe], [Fe–Fe], and [Fe] hydrogenases, respectively, continue the theme of metal complexes with diatomic metals. Remarkably, these three classes of convergently evolved enzymes form Fe–CO (and Fe–CN in the [Ni–Fe] and [Fe–Fe] enzymes) bonds to stabilize a low-spin low-valent iron center, thus, promoting the catalytic cleavage and formation of hydrogen gas. Another common striking feature of these three classes of enzymes is that they undergo competitive inhibition by CO and CN. The NiFe hydrogenase review by Fontecilla–Camps also covers the surprising biosynthesis of the intrinsic CN ligand from carbamoyl phosphate; future studies will be required to elucidate the origin of CO in these proteins.

CO again takes center stage in chapter 8, which describes the synthesis of CO during heme breakdown catalyzed by heme oxygenase. Rivera and Rodriguez begin by pointing out the Janus nature of CO both as a toxin (at high levels) and as a cytoprotective molecule. Then, they describe the incisive mechanistic studies that have led to our understanding of how heme oxygenase catalyzes the amazing degradation of heme to biliverdin, CO and Fe(II) in a reaction that requires seven electrons and three oxygenation cycles. The review covers important issues related to how the electronic structure and dynamics tune the properties of the enzyme to establish a rigid H-bonding network near the heme to promote oxygen activation, hydroperoxide formation and heme cleavage as well as to allow mobility in the protein periphery to facilitate substrate binding and interactions with electron transfer partners.

In chapter 9, Lucas and Karlin describe the use of CO and cyanide as mechanistic and structural probes of the active site of copper proteins, with CO often used as a surrogate for dioxygen. Then, in chapter 10, Sosa-Torres and Kroneck focus on the interaction of cyanide with metals as a structural and mechanistic probe

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and also as an inhibitor for vanadium, manganese, iron, and zinc enzymes.

While the other 11 chapters of this volume focus on the importance of bioorganometallic species in enzyme mechanisms, chapter 11 by Hille describes evidence against the formation of metal carbon bonds in the mechanism of xanthine oxidoreductase. Some spectroscopic evidence has indicated that the "very rapid" Mo(V) catalytic intermediate on xanthine oxidoreductase involves a Mo–C bond. This review describes conclusive evidence, based on spectroscopic and crystallographic studies, that instead of a metal–carbon bond, a metal–oxo bond is formed with the "carbon" too distant from the metal to be considered as a ligand.

The final chapter describes computational studies of many of the enzymes described in the volume, including the methyl- and adenosylcobalamin dependent enzymes, the three Ni enzymes (methyl-coenzyme M reductase, CO dehydrogenase and acetyl-CoA synthase), and the [Fe–Fe] hydrogenases. This valuable chapter by Brunold, Liptak, and Van Heuvelen describes theoretical approaches and focuses on the insights that computational methods have provided into the electronic structures and the catalytic cycles of the active sites of these proteins.

In summary, this is a valuable book that covers the state-of-the-art in bioorganometallic chemistry. Only a few metal–carbon bonds have been found to naturally occur in enzymes, compared to the numerous examples of complexes between metals and sulfur, nitrogen, and oxygen. This text describes the special properties of the metal–carbon bond and the many chemical, biochemical, and biophysical methods that have been brought to bear on the subject.

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