

Abstract

The incorporation of a phenanthrene moiety into a porphyrin framework results in the formation of a hybrid macrocycle – phenanthriporphyrin (C₂P) – merging the structural features of polycyclic aromatic hydrocarbons and dicarbaporphyrinoids. Consequently, the macrocycle can act as a macrocyclic organometallic ligand –with trianionic coordination core (CCNN).

The aim of this dissertation was to explore coordination chemistry of 5,6-dimethoxyphenanthriporphyrin with *d*-block metal ions such as Cu, Rh, Ru, and Fe. Simultaneously, the activation of C–H and M–C bonds has to be emphasized as the important research target. Consequently, organometallic copper(III) and ruthenium(III) phenanthriporphyrins were synthesized and characterized. In addition, it was unambiguously proven that paramagnetic copper(II) phenanthriporphyrin, with a specific „*side on*” geometry is a crucial intermediate, formed in the course of copper(III) insertion.

The square-planar geometry of the central metal ion with a similar coordination motif, as seen for the copper(II) intermediate (MNN), was also detected for dicarbonylrhodium(I) phenanthriporphyrin. Reaction with triruthenium dodecacarbonyl [Ru₃(CO)₁₂] contributed to generation of two original structural motifs (a) the dimer form (C₂P)Ru(III)≡Ru(III)(C₂P) and (b) the complex structure with cluster [Ru₃(CO)₇] coordinating to *meso* bridge carbon atom and the adjacent pyrrole ring in η⁵ mode.

Photooxidation of 5,6-dimethoxyphenanthriporphyrin and their copper(III) complexes, resulted in the regioselective cleavage of the macrocycle. The process afforded open-chain analogues of biliverdin and their copper(III), rhodium(I), and boron(III) complexes.

A straightforward demethylation of 5,6-dimethoxyphenanthriporphyrin afforded a macrocycle that incorporates a phenanthrenequinone unit – 5,6-dioxophenanthriporphyrin. This peripheral modification ring enabled the borylation centered at carbonyl oxygen atoms yielding the BF₂-derivative or the specific carbonyl protonation. The perimeter reactivity resulted in profound modification of nonaromatic electronics structure affording the macrocyclic aromatic character.