

Abstract

Porphyrins and heteroporphyrins typically bind transition metal ions in the central macrocyclic cavity to form metalloporphyrins. Alternatively, metal ions may be attached outside the cavity, in a side-on fashion, or at the macrocyclic periphery. An entirely different and new mode of metal binding within the porphyrin macrocycle involves the replacement of a core heteroatom by a metal atom. Products of such a replacement, metallaporphyrins, constitute a novel class of organometallic compounds, incorporating metallacyclopentadiene rings within an aromatic macrocyclic frame. This class of macrocycles was limited to 21-metalla-23-telluraporphyrins, containing one transition metal ion, palladium(II), platinum(II), or platinum(IV). Therefore, the goal of the research presented in the Thesis was to introduce another metallic element, rhodium, in place of the heteroatom in the porphyrin skeleton; it means a replacement of a pyrrole unit with a rhodacyclopentadiene ring. In particular, the project objective was to obtain a series of rhodaporphyrins, including homo- and heterobimetallic systems in which the metal–metal interaction would be sterically forced.

The project involved developing and optimizing rhodaporphyrins synthesis starting from telluraporphyrins, based on the previously known method of tellurium→metal exchange. The obtained compounds were thoroughly characterized, and an insight into the mechanism of the tellurium→rhodium exchange has been obtained. In addition, the effect of meso substituents with electron withdrawing and electron donating groups on the substitution of the tellurium atom with the rhodium atom was investigated. Several tellurium-containing precursors were employed, that is telluraporphyrinoids with a different number of tellurium atoms, different sizes of the skeleton, and different degrees of aromaticity. As a result of the tellurium→rhodium exchange, various products were obtained, differing in geometry around the central rhodium ion, depending on the availability of donors within the porphyrinoid. The homo- and heterobimetallic porphyrins were obtained by replacing two tellurium atoms with metal atoms in 21,23-ditelluraporphyrin; the oxidation state of the metal ion was an additional degree of freedom.

The compounds were characterized by NMR, UV-Vis, IR spectroscopy, mass spectrometry, X-ray structure, and DFT calculation methods. The analogue of the previously known metallaporphyrins is 21-rhoda-23-telluraporphyrin, showing such features as an unusual geometry of the macrocyclic skeleton, asymmetry, dynamic behavior in solution, and an atypical geometry of the tellurophene binding to the central ion. On the other hand, a new structural motive has been introduced to the metallaporphyrin chemistry with 21-oxa-23-rhodaporphyrin, 21-rhoda-23-thiaporphyrin, and non-stable 21-rhodaporphyrin, which all possess two-fold symmetry. The 21-oxa-23-rhodaporphyrin may be obtained from 21,23-ditelluraporphyrin as a result of a double exchange: one tellurium atom is replaced by a rhodium atom, and the other by an oxygen atom. A double tellurium-to-rhodium exchange yielded 21,23-dirhodaporphyrin, the first dimetallaporphyrin. Similar reactivity was also employed to obtain 21-platina-23-rhodaporphyrin, using two different transition metals.

21,23-Dirhodaporphyrin and two 21-platina-23-rhodaporphyrins were analyzed for the possible metal–metal interaction.

The chemistry of 21-metallaporphyrins has been extended to non-aromatic analogues. 21,23-Ditelluraporphodimethene underwent tellurium to rhodium exchange, selectively in the π -conjugated moiety, yielding 21-rhoda-23-telluraporphodimethene, with a protonated pyrrole ring. Derivatives containing such a unit were also obtained for 21-rhoda-23-telluraporphyrin, impeding its dynamic behavior, and for 21-oxa-23-rhodaporphyrin, and 21-rhoda-23-thiaporphyrin.