Abstract

This Ph. D. thesis is concerned with the synthesis and characterization of complex compounds and N-confused porphyrin derivatives. The main topic is the use of complex compounds of N-confused porphyrin derivatives as ligands for transition metal ions. Previously known systems were used for this purpose as well as new metalloligands were obtained. The presented results are divided into two parts - the first part deals with systems in which the metal ion is coordinated to the periphery of the macrocycle in a chelating manner, while the second part describes monodetal coordination.

The first part presents the description of the syntheses and characterization of the obtained new coordination compounds - iridium(III) N-confused porphyrin, as well as iridium(III), ruthenium(II) and rhodium(III) with ligands based on nickel(II) and ruthenium(II) complexes of N-confused porphyrin derivatives. The possibility of the separation of enantiomers of ruthenium(II) complex compounds and the synthesis of pure enantiomers of iridium(III) compounds is presented. Systems containing an externally co-ordinated iridium(III) ion have been verified as catalysts in the N-heterocyclization reaction of a primary amine with a diol.

The dissertation also includes a description of the study of the coordination properties of the previously obtained 3-pyrrole N-confused porphyrin ligand. Three new complex compounds were obtained and characterised: palladium(II), platinum(II) and rhodium(I). Exploration of the structure of the rhodium(I) compound made it possible to demonstrate a chelating mode of coordination of the metal ion via an 'additional' and an 'confused' pyrrole subunit. The possibility of separating the enantiomers of the rhodium(I) compound was also demonstrated and its redox properties were investigated.

Research topics related to 3-thio N-confused carbachlorin are also addressed. A new synthesis method and its optimisation are described. The possibility of selective alkylation on the sulphur atom is demonstrated, leading to new 3S-substituted N-confused porphyrin derivatives. These products were characterised and used in the synthesis of nickel(II) and palladium(II) complex compounds.

The characterization of the compounds in the first part was performed using, among others, ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, UV-Vis spectroscopy, electrochemical methods (for selected systems), as well as single crystals for 11 compounds were obtained and their crystal structures were solved.

Part two covers the subject of the study of the newly obtained imidazolocarbachlorin ligand and its complex compounds. Silver(III) and gold(III) complex compounds have been obtained. A new two-core gold(III) N-confused porphyrin compound was also obtained. Silver(III) imidazolocarbachlorin compounds undergo selective alkylation on the nitrogen atom of the imidazole ring. It has been shown that methylated derivatives of silver(III) complex compounds can serve as precursors of the N-heterocyclic carbene ligand, leading to gold(I) coordination compounds. Methylated derivatives of silver(III) complex compounds have also been used in transmetallation reactions to obtain zwitterionic palladium(II) compounds. Depending on the palladium source used, it is possible to obtain a system with an additional six-membered aromatic ring formed by the formation of a carbon-carbon bond between the imidazole ring and the aryl ring of the *meso* position. The obtained compounds have been characterized by NMR spectroscopy, UV-Vis spectroscopy, X-ray crystallography (10 compounds), and electrochemical methods.