

Closure of a doctorate

„*p*-Tolylimido rhenium(V) complexes – synthesis, structural and spectroscopic characterization and catalytic activity”

Coordination compounds of rhenium for many years has captured the attention of research centers around the world. In the center of scientific interest are rhenium compounds on the low oxidation states, from -1 to +1, interesting mainly because of their luminescent properties, rhenium compounds on +4 oxidation state, in the form of heterobimetallic compounds showing an interesting magnetic properties, and compounds on high oxidation states. In this group, studies are focused on rhenium compounds on +7 and +5 oxidation state, due to their high catalytic activity as well as potential use as radiopharmaceuticals.

This doctoral thesis concerns rhenium (V) compounds of containing an *p*-tolylimido ligand as well as N,O-donor ligands with alcoholic, phenolic and carboxylic hydroxyl group. The donor nitrogen atoms derived from a variety of N-heterocyclic rings: benzimidazole, benzoxazole, benzothiazole, benzotriazole, indazole, pyridine, pyrazine, quinoline and isoquinoline. The rhenium(V) imidocomplexes are relatively poorly examined group of this element compounds.

Under this thesis I've developed methods for the synthesis and obtained in crystalline form 36 of coordination compounds of the type $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}_2(\text{N-O})(\text{PPh}_3)]$, 4 compounds of the type $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}(\text{N-O})(\text{PPh}_3)_2]\text{ReO}_4$, 8 compounds of the type $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)\text{X}(\text{N-O})(\text{PPh}_3)_2]\text{PF}_6$ and the $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)(\text{hmbzim})_2(\text{PPh}_3)]\text{ReO}_4$ and $[\text{Re}(p\text{-NC}_6\text{H}_4\text{CH}_3)(\text{hpbzim})_2(\text{PPh}_3)]\text{X}$ (X = Cl, Br; hmbzim = 2-(hydroxymethyl)-1H-benzimidazole, hpbzim = 2-(2'-hydroxyphenyl)-1H-benzimidazole) complexes. The crystal and molecular structures of the complexes were confirmed unequivocally by X-ray structural analysis. In addition for all the resulting compounds I have performed spectroscopic studies (UV-Vis, IR and ^1H , ^{13}C , ^{31}P NMR), and the energy levels of molecular orbitals and participation of the atomic orbitals in the occupied (HOMO) and unoccupied (LUMO) molecular orbitals have been determined with use of a quantum mechanical DFT method. This enabled determination of the influence of chelate N,O-donor ligand type on the electronic structure of the rhenium(V) compounds. In addition, to describe the nature of Re-N_{imid} binding, I've performed the natural bond orbital analysis using the NBO 5.0 program.

Furthermore, I've conducted preliminary tests of the catalytic activity of 14 of the obtained compounds in the reaction of synthesis of N-substituted glycine ethyl esters and oxidation of alkanes and alcohols.