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Abstract of the dissertation

Stereochemistry and properties of 4+1 coordination derivatives of zinc phthalocyanine

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The subject of this PhD project was synthesis and crystallization of new coordination derivatives of zinc phthalocyanine (ZnPc) with organic and inorganic ligands as well as complete structural characteristic based on diffraction measurements. The aim of this research was determination of axial coordination influence for π - π interaction between molecules in solid state in relation to non-coordinated ZnPc. It is very important due to the fact that ZnPc and other metallophthalocyanines exhibit very poor solubility in many organic solvents which seriously limit their applications. An introduction of the additional ligand to the coordination sphere of the central ion is one of possible methods to increasing solubility of ZnPc. The ligand plays role of a steric hindrance for π - π interaction from one side of molecule and displacement of the central ion from the plane of the molecule towards the ligand causes deformation of the macrocycle which weakens these interaction from the other side.

In this thesis synthesis and crystallization of 9 complexes of ZnPc with following ligands: *n*-butylamine, *n*-pentylamine, *n*-hexylamine, 3,4-dimethylpyridine, 4-ethylpyridine, imidazole, *N*-methylimidazole, *N*-(2-pyrimidinyl)imidazole and bromide anion were described. Overall, 10 crystal structures were characterised (two polymorphic forms of complex with 3,4-dimethylpyridine were found).

For complexes of ZnPc with aromatic ligands significantly increased solubility in common organic solvents, in relation to the parent ZnPc, were stated. Considering the potential application of these complexes, measurements of UV-Vis-NIR absorption spectra of these complexes in solutions were performed. Moreover, their thermal stability was determined using thermogravimetric analysis of crystalline samples.

Additionally, DFT calculation was accomplished in order to geometry optimization, using atomic coordinates obtained by diffraction measurements as input data. DFT data allowed also for determination of HOMO and LUMO orbitals contours of the complexes. It let to state that ligation of ZnPc does not change its electronic structure, which was also confirmed by UV-Vis-NIR measurements – the spectra of ZnPcs complexes and free ZnPc were quite similar.