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Dissertation topic: **Transition metal complexes with carboxylate and carboxamidate ligands as precursors for functional materials**

## Abstract

The topics of the presented dissertation included the design and synthesis of molecular homo- and hetero metal complexes and their use as precursors for the production of hybrid inorganic-organic MOF-type materials, including the development of a method for producing MOF material with simultaneous encapsulation of bioactive molecules. An integral part of this work was to determine the structure and study the physicochemical properties of the obtained complexes and materials.

In the first part of the dissertation, research was carried out on the extension of the **SMART** (SBU-based Mechanochemical Approach for pRecursors Transformation) method for the preparation of MOF materials based on the  $Zn_4O(-COO)_6$  building unit, using the  $Zn_4O(HNO_2Ph)_6$  oxozinc complex as a precursor. As a result, a number of MOF materials based on dicarboxylate (IRMOF-3, IRMOF-9/10) and tricarboxylate (MOF-177) ligands were obtained and characterized. The described versatility of the SMART method also leads us to assume that this method will find wide application in the construction of MOF materials for many other reaction systems composed of appropriately designed molecular metallic precursors and organic linkers.

The second part of the dissertation was devoted to the development of a solvent-free mechanochemical synthesis of HKUST-1 material with ibuprofen encapsulated in the pores (IBU@HKUST-1). In this case, the precursor  $[Cu_2(ibu)_4] \cdot 2DMF$  acted as both the pre-designed metal node of the MOF material and the donor of the drug molecule (ibuprofen) released during the reaction. An important observation is that DMF molecules coordinated to the metal centres of the precursor made it possible to carry out the reaction in a solid state with a supporting liquid, so to speak, combining the neat grinding method with the LAG method.

The research has opened new paths in the synthesis of MOF porous materials with active substances having carboxyl groups encapsulated in the pores.

The last part describes the use of controlled hydrolysis of ethylzinc carboxylates in the presence of transition metal benzoates in the preparation of new heterometallic complexes with complex cores. Two new highly nuclear clusters built from  $\{M_4(\mu_4-O)\}$  type subunits were obtained:  $Zn_{5,6}Co_{7,4}(\mu_4-O)_4(O_2CPh)_{18}$  and  $Zn_{5,8}Fe_{4,2}(\mu_4-O)_4(\mu_2-Cl)_2(O_2CPh)_{12}(THF)_2$ . In addition, the hydroxyl cluster  $Zn_{3,6}Co_{2,4}(\mu_3-OH)_2(O_2CPh)_{10}(THF)_4$  and two simple homometallic benzoates  $Ni_3(O_2CPh)_6(THF)_4$  and  $Cr_2(O_2CPh)_2(THF)_2$  were obtained. Based on recent literature reports, it can be speculated that the heterometallic complexes obtained in this part of the work can be useful precursors in the synthesis of MOF-type materials with non-classical cores, which have not been obtained so far using standard synthetic methods.