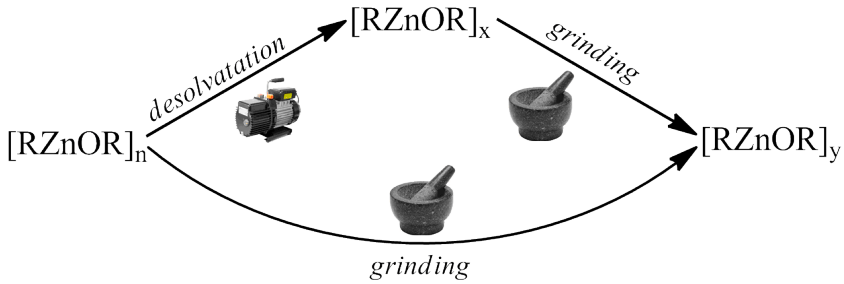
Alkylzinc alkoxide complexes: a new look at the old problem.

Alkylzinc alkoxide complexes have been a subject of investigations for over 150 years. Since the very beginning the problem of their aggregation in solution and solid state has been attracting constant interest both in fundamental studies and when potential applications in various areas were investigated. Thus, the present project is focused on the synthesis of novel complexes with desired and as yet unknown molecular structures. Among others low-coordinated zinc complexes stabilized by Zn…π interactions will be studied. The knowledge about this class of compounds is very limited, which in light of their very promising properties concerning dioxygen activation makes them excellent subject of studies. In the course of the project not only simple compounds will be investigated, but also more complicated, novel systems involving alkoxy and aryloxy ligands with allyl or aromatic termini that extend the variety of possible inter- and intramolecular weak interactions. Obtained compounds will be later used as model systems for further investigations.

The Lewiński Group has been interested in activation of dioxygen for over a decade now. Our recent systematic studies show that intramolecular weak interactions present in the alkylzinc complex strongly influence the course of the oxygenation reaction. This research resulted in characterization of the first, octanuclear aryloxide (hydroxide) zinc complex Zn8(OAr)8(OH)6(O2) with an encapsulated peroxide moiety. Due to the fact that investigations on the exact role of the Zn…π interactions in the activation of dioxygen are in preliminary stage, their continuation is needed in order to study the operating mechanism in detail. Low-coordinated zinc complexes obtained in this project will be used as model systems in test reactions with dry oxygen. These results will be useful in planning of further experiments.

Parallel to research over the activation of dioxygen investigations with bis(allyl)zinc will be conducted. There is very limited number of publications concerning the topic of the structures and reactivity of complexes with the allyl group as the substituent. This project should afford significant development of the knowledge in this area.

Very interesting and particularly innovative part of this project will be investigations on solid state transformations. Systematic studies conducted in the parent group show that such approach can result in obtaining unprecedented and unpredicted even by computer calculations trimeric alkylzinc alkoxide cluster. This compound eluded scientists from determination for decades. To obtain this complex a new synthetic approach was needed (Scheme 1).



Scheme 1.

In the course of the research a dimeric adduct containing two THF molecules was obtained. In the next step it was subjected of desolvation process under mild conditions of lowered pressure and slightly elevated temperature. Recrystallization of the solid residue resulted in crystallization of the long-awaited product. Furthermore, the trimeric complex upon griding with a simple glass rod transformed into tetrameric form (Scheme 1). Within this project I plan to apply both techniques to our synthetic procedures. It is expected that such approach afford novel alkyl(alkoxide) or alkyl(aryloxide) zinc clusters with intriguing structures.

The highlighted investigations will significantly contribute to fundamental understanding of the nature of the solid-state transformations mediated by desolvation and mechanochemical means as well as role of π interactions, for the molecular structures of the complexes and their reactivity towards oxygen.