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Controlled transformations of alkylzinc guanidinates to zinc oxide nanocrystals

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Presented PhD thesis concerns the research areas of synthesis of alkylzinc complexes stabilised by bicyclic guanidinate ligands and their controlled transformations into zinc oxide nanocrystals. The first chapter presenting the conducted research involves the synthesis of alkylzinc complexes formed in reaction of dialkylzinc species and various bicyclic guanidines. As a result a series of novel alkylzinc complexes, incorporating 3 to 5 metal centres, has been prepared and fully characterized. Moreover, the influence of the substrate type and reaction conditions on the structure of the resulting complexes was analysed.

Alkylzinc complexes developed within the first stage of research were then used as substrates in further study concerning their reactivity towards water and dioxygen, which allowed for preparation and characterization of a wide range of products differing in chemical constitution and coordination structure. One of the most prominent groups of products included the $\{[RZn(L)]_n \bullet [ZnO]\}$ and $\{[RZn(L)]_n \bullet [RZnOH]\}$ complexes representing a tendency of unreacted [RZn(L)] species to stabilize the initial products of the alkylzinc hydrolysis and oxygenation. Moreover, the zinc clusters: $[Zn_4O(L)_6]$ and $[Zn_8O_2(OH)_3(L)_9]$, incorporating oxozinc moieties stabilized by guanidinate and hydroxyl ligands, were synthesised by extensive hydrolysis of the examined alkylzinc complexes. A structural investigation of the intermediate and fully hydrolysed products allowed for detailed analysis of the initial evolution of the reaction system involving transformation of the alkylzinc complexes on the way to zinc oxide nanoparticles.

Further study was focused on application of the selected zinc complexes, developed in the previous stage, as direct molecular precursors to ZnO nanocrystals. The transformations were conducted using various substrates and reaction conditions, which allowed for development of procedures of controlled growth of ZnO nanocrystals. One of the key results

was related to the presence of dioxygen during the transformation of alkylzinc substrates to ZnO nanoparticles. Obtained results clearly indicate that alkoxylates, resulting from reaction between alkylzinc species and dioxygen, could direct the ZnO growth process by strong interactions with the surface of forming ZnO nanocrystals. Furthermore, a detailed study involving a series of molecular precursors used in various transformation conditions was conducted in order to determine additional factors responsible for directing the growth of the ZnO nanocrystals. Resulting data can be further applied for development of novel synthetic procedures aimed at ZnO nanostructures of highly controlled properties.

The scientific results included in the thesis represent a significant development in the field of coordination chemistry of alkylzinc complexes and synthesis of zinc oxide nanocrystals. Moreover, demonstrated preparation and structural characterisation of a series of hydrolysis and oxygenation products of alkylzinc complexes provides substantial insight into the chemical mechanisms of transformation of alkylzinc precursors towards ZnO nanostructures. Therefore, presented results might allow for further development of even more controlled procedures of preparation of ZnO nanostructures.