

ABSTRACT

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Organozinc complexes stabilized by oxygen-nitrogen ligands: Synthesis, structure, reactivity and self-assembly processes

The presented PhD thesis describes the synthesis and characterization of alkylzinc complexes stabilized by N,O-donating ligands such as pyrrole and indole derivatives as well as phthalimide, and their reactivity towards small molecules: dioxygen, water and elemental sulphur. The first part of the study included the synthesis of alkylzinc complexes stabilized by the selected ligands and investigation of the influence of steric and electronic factors (generated by the alkyl group and the chelating ligand) on their structure. An essential element of the study was to investigate the impact of competition between the classic donor-acceptor bond and the $Zn \cdots \pi$ type interaction on the structure of alkylzinc complexes in the solid-state. As a result, an unprecedented one-dimensional polymeric chain interconnected by $Zn \cdots \pi$ type non-covalent interactions was obtained as a result of self-assembly of monomeric alkylzinc fragments stabilized by pyrrole or indole ligands with formulas $[EtZn(L)]_n$ (where L = pyrrole or indole ligand). Moreover, a new approach to the rational synthesis of heterometallic complexes was presented which allow to obtain and characterize in the solid-state the lithium-zinc compound $[(EtZn)_2(L4)_3Li_4(THF)_7]_2$ (where L4 = 2-pyrrolicarboxylic acid dianion). Using rationally designed, trifunctional pyrrole proligands, several ethylzinc complexes were isolated, e.g.: the octanuclear complex $[(EtZn)_2(L6)(Et_2O)]_4$, the 1D organometallic coordination polymer $\{[(EtZn)_2(L6)]_4 \cdot PhCH_3\}_n$, and the 3D interpenetrated structure of $[(EtZn)_2(L6)]_{4n}$. Additionally, the conducted research involved the development of efficient strategies aiming at prevention of undesired interpenetration in microporous materials. The proposed original approach, involving addition of a catalytic amount of an organozinc compound stabilized by a trifunctional pyrrole ligand, with different electronic and steric properties, led to the isolation and characterization of the

non-interpenetrated 3D system $[(\text{EtZn})_2(\text{L6})]_{4n}$ with the same topology as its interpenetrated analogue. The presented methodology opens a new path in the rational prevention of interpenetration in 3D hybrid organic-inorganic porous materials.

Well defined alkylzinc complexes stabilized by mentioned ligands, obtained in the first stage of research, were used as a substrate in further studies concerning their reactivity towards small molecules like dioxygen, water and elemental sulphur. As a result of controlled oxidation of alkylzinc compounds stabilized with a pyrrole ligand with a terminal ester group, alkoxyate complexes with a unique trimeric $[(\text{L2})\text{Zn}(\mu_2\text{-O}^t\text{Bu})_3]$ and tetrameric $[(\text{L2})\text{Zn}(\mu_3\text{-OEt})_4]$ structures were isolated and characterized. It was also shown that the alcoholysis reactions of the $[(\text{L2})\text{ZnEt}]$ complex using EtOH or $t\text{BuOH}$ did not lead to the corresponding zinc alkoxyates compounds, which shows the advantage of the oxidation process over the alcoholysis reactions in the synthesis of zinc alkoxyate compounds.

Very interesting results were also obtained during the investigation of the reactivity of the ethylzinc complex $[(\text{EtZn})_2(\text{L4})(\text{THF})_2]_2$ stabilized by 2-pyrrolecarboxylic acid dianion towards oxygen and water. As a result of controlled oxidation and hydrolysis of the initial compound, $[(\text{EtZn})_2(\text{L4})(\text{THF})_2]_2$, multinuclear complexes were formed: zinc oxoalkylperoxide $[\text{Zn}_3(\mu_3\text{-OOEt})_3\text{Zn}(\mu_4\text{-O})(\text{L4})_3\text{Zn}_3(\mu_2\text{-OOEt})_3(\text{THF})_3]_2$, and zinc oxohydroxide $\{[(\text{HL4})_3\text{Zn}_4(\mu_4\text{-O})\text{Zn}_3(\mu_3\text{-OH})_3(\text{L4})_3]_2 \cdot 8\text{THF}\}$. The former alkylperoxide complex was highly reactive and decomposed spontaneously upon grinding with a glass rod. On the other hand, the latter oxohydroxide complex were found to self-assembly in solid state forming a non-covalent microporous material. Interestingly, further investigation concerning phthalimide-stabilised ethylzinc complexes revealed that upon their reaction with elemental sulphur a unique $\{[(\text{EtZn})_3\text{Zn}_{13}(\mu_4\text{-S})_7(\text{L1})_{15}] \cdot \text{THF}\}$ complex was isolated, which additionally exhibited microporous molecular structure. In its structure, apart from the reactive Et-Zn groups, the motif $[\text{Zn}_4(\mu_4\text{-S})]^{6+}$ can be distinguished which is analogous to the zinc oxides $[\text{Zn}_4(\mu_4\text{-O})]^{6+}$.

In conclusion, the presented results shed new light on the chemistry of alkyl zinc compounds stabilized with pyrrole and phthalimide ligands. Moreover, the data substantially expands and supplements our contemporary knowledge of the reactivity of organozinc complexes towards small molecules: oxygen, elemental sulfur and water. The results of the presented research show the remarkable possibilities of using multifunctional pyrrole ligands to obtain bimetallic systems as well as one- and three-dimensional interpenetrated and non-interpenetrated coordination organozinc polymers. The obtained results open the path to the rational synthesis of functional materials with unique properties.