Abstract. The main focus of our contribution lies on the investigation of molecular ZnO-rich polyoxometallates as model compounds for nanocrystalline ZnO-systems. Following the approach of a chemical building block, well-defined ZnO clusters were synthesized. The formation of insoluble ZnO can be suppressed completely by choosing the appropriate protecting group. In particular, triorganosiloxy groups turned out to be very efficient for this purpose. The facile variation of the organic substituents within a wide range of different sizes and their tendency to act as an electrophilic leaving group increases the selectivity of the consecutive aggregation of the molecular ZnO moieties.

1. INTRODUCTION

Molecular precursors for the synthesis of nanocrystalline metal oxides like metal alkoxides and siloxides have attracted worldwide interest in the fields of material science and catalysis. Many applications of homo- and heterometallic alkoxides and siloxides have been developed,[1,2] but the precursor chemistry of molecular zinc alkoxide[3] and siloxide aggregates[4] has received much less intention. The zinc alkoxide aggregates possess single or edge-fused, four-membered Zn2O2 cores. Furthermore, structurally characterized Zn4O4, edge-shared Zn7O8 double-cubanes, and spirobicyclic Zn3O4 aggregates[3] have been already synthesized. The formation of other types of aggregates or the substitution of the organic ligands at the zinc atom without degradation of the ZnxOy framework seems to be very limited, due to the high polarity of the Zn-O bond. Both the aggregation and the reactivity of those clusters is strongly influenced by the steric and electronic properties at the oxygen atom. Derivatives, which are siloxy-substituted, can be expected to be more versatile building blocks than the alkoxide derivatives. Two types of siloxy-substituted ZnO aggregates have been described by Schmidbaur et al.[5] but no information of the influence of the size of the organic substituents at the silicon or the zinc atom on the aggregation type is yet available. In this report the synthesis of the siloxy-substituted di-,[3a,b] tri-,[3c] and tetranuclear ZnO cluster[3, 4a,b] is described, which represent potentially useful precursors for the synthesis of nanocrystalline ZnO. The organic substituents at the zinc atom in 3a,b can be replaced by iodine, ultimately leading to the respective tetraiodides 4a,b, which may be used for the synthesis of other nonorgano-substituted Zn4O4 heterocubanes.

2. RESULTS AND DISCUSSION

A successful method for synthesizing siloxy-substituted ZnO aggregates represents the simple Brönsted acid/base reaction of triorganosilanols with dialkyl- and diamidozinc compounds. These reaction furnishes, depending on the steric demand of the substituents, di-, tri-, and tetranuclear ZnO aggregates of types1-3. [6] For example, the reaction of iPr3SiOH with