

## Facile synthesis and structural variation of novel heterobimetallic alkali metal–zinc-alkoxide and -siloxide clusters †

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The novel alkali metal zinc-alkoxide and the first -siloxide aggregates  $[(\text{thf})\text{M}(\text{MeZn}(\text{O}'\text{Bu}))_2]_2$  **1a** ( $\text{M} = \text{Li}$ ), **1b** ( $\text{M} = \text{Na}$ ),  $[(\text{thf})_2\text{K}(\text{MeZn}(\text{OSiMe}_3)_2)_2]$  **2** and  $[(\text{tmeda})\text{KZn}(\text{OSiMe}_3)_3]_2$  **3** are easily accessible from the reaction of  $\text{Me}_2\text{Zn}$  with MOR (molar ratio 1 : 1;  $\text{M} = \text{Li}, \text{Na}, \text{K}$ ;  $\text{R} = \text{'Bu}, \text{SiMe}_3$ ) in boiling thf and tmeda, respectively. While **1a**, **1b** and **2** possess distorted  $\text{M}_2\text{Zn}_2\text{O}_4$  heterocubane frameworks, compound **3** consists of a  $\text{K}_2\text{Zn}_2\text{O}_6$  core of a strongly distorted, face-fused double-heterocubane with two missing corners. In contrast, heating a mixture of  $\text{Me}_2\text{Zn}$  and  $\text{KO}'\text{Bu}$  in the molar ratio of 1 : 1 in toluene affords the donor solvent-free  $\text{K-Zn-O}$  cluster  $[\text{K}(\text{MeZn})_3(\text{O}'\text{Bu})_4]$  **4** which crystallizes as a polymer of strongly distorted  $[\text{KZn}_3\text{O}_4]$  heterocubanes *via* intermolecular agostic  $\text{K} \cdots \text{MeZn}$  interactions. The formation of the clusters may be rationalized in terms of alkali metal ion- and donor solvent-dependent ligand exchange reactions of methyl(alkoxide)- and methyl(siloxide)-zincates as initial products. Some of the initial products have been detected by means of electro spray ionisation (ESI) mass spectrometry.