Mechanochemistry

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Solid-State Conversion of the Solvated Dimer $[\{t\mathrm{BuZn}(\mu\text{-O}t\mathrm{Bu})(\mathrm{thf})\}_2]$ into a Long Overlooked Trimeric $[\{t\mathrm{BuZnO}t\mathrm{Bu}\}_3]$ Species**

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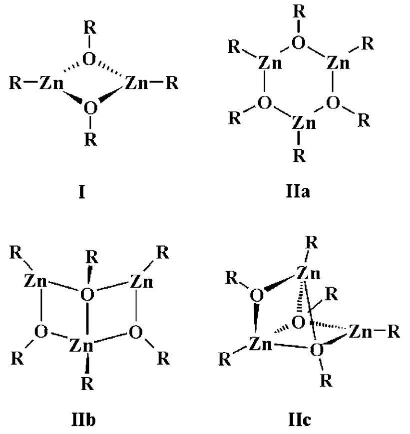
Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday

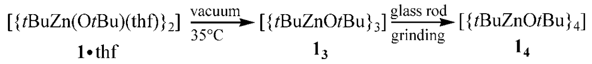
Interest in zinc alkoxides originated with the pioneering studies of Frankland.[1] Alkylzinc alkoxides have attracted much attention because of their rich structural diversity[2] and potential practical applications as versatile single-source precursors for the preparation of nanosized ZnO particles.[3] Detailed structural information concerning the extent of coordination and association in these species is important in understanding their physical behavior and chemical reactivity. For unsolvated RZnOR species, dimeric (**I**), cyclic (**IIa**) or roof-like trimeric (**IIb**) (Scheme 1), and tetrameric cubane structures have been considered.[2,4] Until now, only two basic structural motifs have been crystallographically confirmed, the dimer $[\{\mathrm{RZn}(\mu\text{-OR}')\}_2]$[3d,5] and tetrameric cubane $[\{\mathrm{RZn}(\mu_3\text{-OR}')\}_4]$.[3b,c,d,e,6] In some instances, ligand redistribution takes place, and the formation of trinuclear $[(\mathrm{RZn})_2\mathrm{Zn}(\mathrm{OR}')_4]$ aggregates with a linear chain arrangement[2,3a,5,7] or double-cubes $[(\mathrm{RZn})_6\mathrm{Zn}(\mathrm{OR})_8]$ has been observed.[6d,8]



Scheme 1.

Crucially, no examples of structurally characterized trimeric $[\{\mathrm{RZnOR}\}_3]$ forms have been previously reported, although the related well-characterized heavier sulfur and selenium analogues with six-membered $\mathrm{Zn_3S_3}$ or $\mathrm{Zn_3Se_3}$ rings are known.[2a,9] Already almost two decades ago, Power and co-workers wrote: "*It is the present rarity of its occurrence, in comparison to the dimer or tetramer, that is the most striking feature. […] Conclusive proof of the existence of alkylzinc alkoxide or aryloxide trimers still awaits a structural determination of such a compound*".[2a] Furthermore, the character of RZnOR species in noncoordinating solvents is a matter for conjecture, and studies on the aggregation state of $[t\mathrm{BuZnO}t\mathrm{Bu}]$ (**1**) are a classic example of inconsistency in the reported data: cryoscopic molecular weight studies by Coates and Roberts[10] indicated that **1** exists as a mixture of dimers and trimers in benzene, whereas Noltes and Boersma[11] concluded that only a trimer exists.[12]

In the course of our studies on the structure and reactivity of $[\mathrm{Zn}t\mathrm{Bu}_2]$,[13,14] we isolated and structurally characterized the solvated dimeric alkoxide $[\{t\mathrm{BuZn}(\mu\text{-O}t\mathrm{Bu})(\mathrm{thf})\}_2]$ (**1**·thf).[14] Herein, we report on a solid-state transformation of **1**·thf under mild conditions to give trimer $[\{t\mathrm{BuZnO}t\mathrm{Bu}\}_3]$ ($\mathbf{1_3}$) with an overlooked unique cluster structure **IIc**, which upon grinding is converted into tetrameric cubane $[\{t\mathrm{BuZnO}t\mathrm{Bu}\}_4]$ ($\mathbf{1_4}$) (Scheme 2). In addition, we examine the solution behavior of $[\{t\mathrm{BuZnO}t\mathrm{Bu}\}_n]$ species. Solid-state reactions are of extreme interest both for technological applications and from the point of view of basic science.[15] To our knowledge, the possibility to obtain new metastable metal alkoxide structures by solid-state conversions based on solvent loss remains virtually unexplored.[16]



$$\underset{\mathbf{1\cdot thf}}{[\{t\mathrm{BuZn}(\mathrm{O}t\mathrm{Bu})(\mathrm{thf})\}_2]} \xrightarrow[35^\circ\mathrm{C}]{\text{vacuum}} \underset{\mathbf{1_3}}{[\{t\mathrm{BuZnO}t\mathrm{Bu}\}_3]} \xrightarrow[\text{grinding}]{\text{glass rod}} \underset{\mathbf{1_4}}{[\{t\mathrm{BuZnO}t\mathrm{Bu}\}_4]}$$

Scheme 2.

The trimeric alkoxide $\mathbf{1_3}$ can be reproducibly isolated by desolvation of solid **1**·thf employing reduced pressure at a slightly elevated temperature, followed by recrystallization of

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the resulting amorphous material from toluene at −20 °C. Single-crystal X-ray analysis revealed that **1_3** crystallizes in the $P\bar{1}$ space group with 12 unique trinuclear molecules in the unit cell. All independent molecules have almost identical geometry, but in one molecule some disorder was observed. Complex **1_3** is perhaps best considered as a dimeric aggregate assembled with one monomeric unit of **1** (Figure 1 a). The monomeric unit is associated above the oxygen-bridged dimer by the simultaneous coordination of the Zn3 atom to both bridging oxygen atoms and the O3 atom to one of Zn atom in the parent dimer. In the resulting cluster, two distinct sets of both organozinc centers and bridging alkoxide groups are present. Two four-coordinate Zn centers are linked by two μ_3- and one μ_2-oxygen atoms, and one three-coordinate Zn center binds to two μ_3-oxygen atoms. The Zn−O bond lengths within this cluster fall into two groups: four long and four short Zn−O distances at 2.164–2.234 Å and 1.927–1.965 Å, which are drawn on Figure 1 a by dotted and solid lines, respectively. The revealed trimeric core for **1_3** is unprecedented in the field of coordination chemistry of group II heteroleptic RMX compounds.

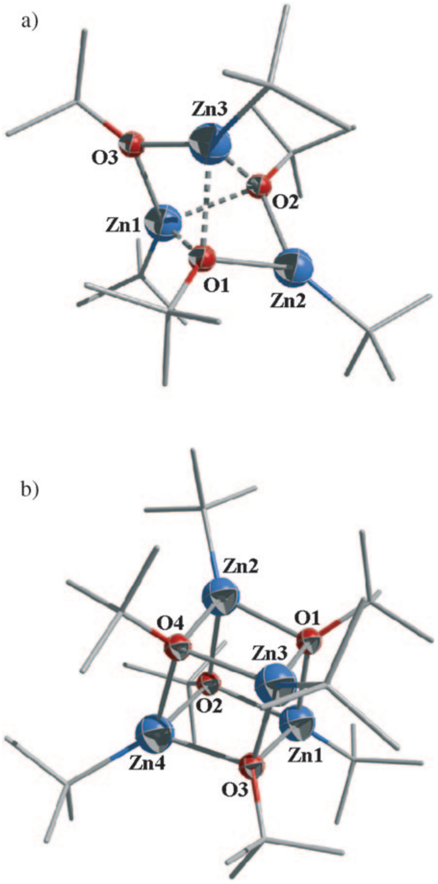

Figure 1. Molecular structures of a) **1_3** and b) **1_4** with thermal ellipsoids drawn at the 30 % probability level; hydrogen atoms omitted for clarity.

Surprisingly, a completely different crystallization outcome was observed when this process was conducted in a solution of **1** in toluene conventionally synthesized by direct reaction of [Zn*t*Bu$_2$] with *t*BuOH. In this case, crystallization led exclusively to tetramer **1_4**. Moreover, we also found that the tetramer can be reproducibly prepared by crystallization from any solution of **1** in toluene incubated for 1–2 h at ambient temperature. Strikingly, we found that **1_4** can be also prepared without recourse to solution chemistry simply by grinding solid **1_3** with a glass rod [Eq. (1)] as judged by its X-ray powder patterns (Figure S1 in the Supporting Information). The observed mechanochemical cluster-to-cluster transformation is rather unusual as there are very few known examples of mechanochemical reactions involving clusters. Typically, aggregation into polymers or breaking down of coordination polymers into smaller units occurs.[15–17]

Single-crystal X-ray analysis revealed that the second distinct aggregate **1_4** possesses a typical heterocubane structure with four-coordinate zinc centers bridged by μ_3-oxygen atoms (Figure 1 b) and displays basic geometric parameters (the average Zn−O bond length distance is 2.109 Å) typical for this type of alkylzinc alkoxide clusters.[3b,c,d,e,6] Thus, these findings indicate that the solid-state desolvation of **1**·thf is a key process in the creation of **1_3** as a metastable form not accessible by conventional solution methods.

We reasoned that the observed discrepancy in the crystallization outcomes (i.e., **1_3** vs. **1_4**) results from a different composition of the parent solution. To clarify this issue, we set out to investigate the solution behavior of **1** by using ^{1}H NMR spectroscopy and cryoscopy. The room-temperature ^{1}H NMR spectrum of a freshly prepared solution of **1** in [D$_8$]toluene derived by the desolvation of **1**·thf is dominated by two slightly broadened singlets with equal intensities ($\delta = 1.18$ and 1.34 ppm) associated with the Zn–*t*Bu and Zn–O*t*Bu protons, which were assigned to trimer **1_3** (Figure 2 a). The related second pair of sharp signals with relatively low intensities ($\delta =$ 1.25 and 1.35 ppm) was assigned to **1_2**. The spectroscopic details are more apparent at low temperatures (Figure 2 b), whereby upon cooling the solution to −40 °C the signals of **1_2** remain unchanged while both broadened singlets of **1_3** split into a 1:2 ratio of signals [note that the spectrum contains

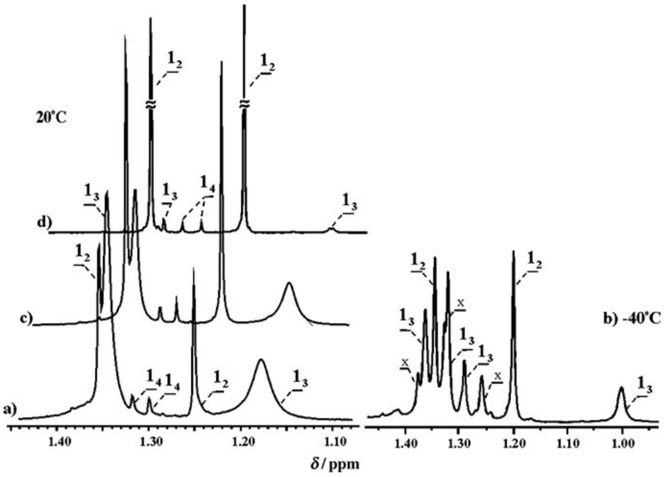

Figure 2. ^{1}H NMR spectra (in [D$_8$]toluene) of a) freshly dissolved **1** at 20 °C, b) at −40 °C, c) after 20 min at 20 °C, and d) after 1.5 h at 20 °C.

some additional signals (marked as x) which indicate the presence of trace amounts of other species, likely another trimeric form and tetramer $\mathbf{1}_4$; see below]. The observed splitting is apparently consistent with the trimeric structure found in the solid state and reflects the asymmetry and fluxionality of the trimer in solution. Interestingly, at 20°C over time the resonances associated with $\mathbf{1}_3$ decrease and those from $\mathbf{1}_2$ increase, while two singlets associated with $\mathbf{1}_4$ remain essentially weak (Figure 2c,d). A slow equilibration between aggregates is completed in approximately 1.5 h, and under these conditions higher aggregates remain minor relative to $\mathbf{1}_2$. Cryoscopic studies confirmed that **1** occurs predominantly as dimeric species in benzene ($n=2.3$, over the concentration range 1.3–2.9 % by weight), thus our data concur with that reported by Coates and Roberts.[10]

The above data clearly indicate that in the presence of bulky substituents as in [*t*BuZnO*t*Bu], the dimeric structure **I** is more stable in solution than higher aggregates, and it is likely that the trimeric forms are of comparable stability to the tetrameric structure. To provide a fuller basis for discussion of the relative stability of the revealed trimeric cluster structure in relation to the previously considered dimeric, and cyclic or roof-like trimeric of methylzinc methoxide structures,[4] density functional theory (DFT) calculations were carried out on all three [{MeZnOMe}$_3$] isomers using GAMESS program package using M06 functional and the 6-311+G(d,p) basis set level of theory.[18] The energy difference among the structural isomers is about 11.3 kJ mol^{-1}, which indicates that a multitude of species could be simultaneously present in equilibrium. We found that the cluster-like trimer has the lowest absolute energy value (after correction for zero-point energy) and is stabilized over the roof-like trimer by only 1.3 kJ mol^{-1} and over the cyclic (planar) trimer by 11.3 kJ mol^{-1} (Figure S4 in the Supporting Information). Dissociation of the cluster-like trimer into 3/2 dimer is endothermic ($\Delta E_{\mathrm{ZPC}} = 33.5$ kJ mol^{-1}) rather than exothermic as is observed experimentally for $\mathbf{1}_3$, but this difference can be attributed to the steric bulk of the substituents.

In summary, the reported results provide a new direction in solid-state transformation of metal alkoxides. Further systematic studies will be aimed at elucidating the relationship between alkylzinc alkoxides structure and the character of resulting ZnO based materials. Moreover, the elucidated two distinct solid-state aggregates for **1**, including a nontrivial trimeric structure of $\mathbf{1}_3$, as well as the observed solution behavior of [{*t*BuZnO*t*Bu}$_n$] species may shed new light on aggregation processes of not only alkylzinc alkoxides but also various heteroleptic RMX compounds.

Experimental Section

$\mathbf{1}_3$: Colorless block-shaped crystals of [{Zn*t*Bu(μ-O*t*Bu)(thf)}$_2$] (1.071 g, 2 mmol) were gently heated in a vacuum line for 1 h (35°C, approximately 5×10^{-2} mmHg). The resulting amorphous residue (confirmed by the PXRD data) was dissolved in 4 mL of toluene and stored at −25°C. Colorless crystals of $\mathbf{1}_3$ deposited after several hours; yield of isolated product 61 %. Elemental analysis (%) calcd for $C_{24}H_{54}O_3Zn_3$: C 49.12, H 9.28; found: C 48.93, H 9.41; cryoscopic molecular weight (benzene, 2.936, 1.939, 1.306 wt % at an equilibrium state) formula weight calcd for $C_8H_{18}OZn$: 195.6, found: 459 ± 4, 457 ± 5, 456 ± 8 amu, respectively; ^{1}H NMR ([D$_8$]toluene, 400.10 MHz) at 298 K: $\delta = 1.34$ (s, 9H, OC(CH$_3$)$_3$), 1.18 ppm (s, 9H, ZnC(CH$_3$)$_3$), at 240 K: $\delta = 1.36$ (s, 9H, OC(CH$_3$)$_3$), 1.32 (s, 9H, OC(CH$_3$)$_3$), 1.29 (s, 9H, ZnC(CH$_3$)$_3$), 1.00 ppm (s, 9H, ZnC(CH$_3$)$_3$).

$\mathbf{1}_4$: Colorless rhomboidal crystals were obtained from toluene/hexane mixture at 4°C; yield of isolated product 84 %. Elemental analysis (%) calcd for $C_{32}H_{72}O_4Zn_4$: C 49.12, H 9.28; found: C 49.04, H 9.40; molecular mass measurements gave the same results as for $\mathbf{1}_3$; ^{1}H NMR ([D$_8$]toluene, 400.10 MHz, 298 K): $\delta = 1.32$ (s, 9H, OC(CH$_3$)$_3$), 1.30 ppm (s, 9H, ZnC(CH$_3$)$_3$).

Crystal data for $\mathbf{1}_3$: $C_{24}H_{54}O_3Zn_3$: $M = 586.78$, triclinic, space group $P\bar{1}$ (no. 2), $a = 19.5071(3)$, $b = 22.6871(7)$, $c = 22.7469(6)$ Å, $\alpha = 92.3640(10)$, $\beta = 104.2720(10)$, $\gamma = 107.1750(10)°$, $U = 9250.1(4)$ Å^3, $Z = 12$, $F(000) = 3744$, $\rho_{\mathrm{calcd}} = 1.264$ g m^3, $T = 100(2)$ K, $R1 = 0.0715$, $wR2 = 0.1764$ for 20543 reflections with $I_o > 2\sigma(I_o)$); crystal data for $\mathbf{1}_4$: $C_{32}H_{72}O_4Zn_4$: $M = 782.43$, monoclinic, space group $P2/c$ (no. 13), $a = 19.5361(4)$, $b = 12.2459(4)$, $c = 16.8481(6)$ Å, $\beta = 109.316(2)°$, $U = 3803.8(2)$ Å^3, $Z = 4$, $F(000) = 1664$, $\rho_{\mathrm{calcd}} = 1.366$ g m^3, $T = 100(2$ K, $R1 = 0.0435$, $wR2 = 0.0872$ for 5413 reflections with $I_o > 2\sigma(I_o)$); the structures were solved by direct methods using the program SHELXS-97[19] and refined by full-matrix least-squares analysis on F^2 using the program SHELXL-97.[20] The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. CCDC 784978 ($\mathbf{1}_3$) and 784979 ($\mathbf{1}_4$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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