Cite this: Chem. Commun., 2011, 47, 5467–5469



## *tert*-Butylzinc hydroxide as an efficient predesigned precursor of ZnO nanoparticles<sup>†</sup>

Wojciech Bury,<sup>a</sup> Elżbieta Krajewska,<sup>a</sup> Michał Dutkiewicz,<sup>a</sup> Kamil Sokołowski,<sup>b</sup> Iwona Justyniak,<sup>b</sup> Zbigniew Kaszkur,<sup>b</sup> Krzysztof J. Kurzydłowski,<sup>c</sup> Tomasz Płociński<sup>c</sup> and Janusz Lewiński<sup>\*ab</sup>

Received 7th March 2011, Accepted 24th March 2011 DOI: 10.1039/c1cc11328c

The reaction of <sup>t</sup>Bu<sub>2</sub>Zn with water was investigated which led to isolation of the novel hexameric *tert*-butylzinc hydroxide. The resulting zinc hydroxide cluster appears to be an ideal predesigned single-source precursor which decomposes smoothly in one step at only *ca*. 120 °C into ZnO nanoparticles.

The homoleptic main-group metal alkyls, including zinc alkyls, are extremely reactive toward water. To avoid side reaction in the preparation and handling of these compounds organometallic chemists commonly use anaerobic conditions and moisture free reaction media in daily laboratory work. Simultaneously, it is a big challenge to bring the hydrolysis reactions under control to favor the more rapid design and implementation of H<sub>2</sub>O-based reaction systems. For instance, Barron et al. made a significant breakthrough in the hydrolysis of Group 13 trialkyl compounds almost two decades ago, providing the first structurally characterized  $[R_2AIOH]_n$  clusters and alumoxanes, when <sup>t</sup>Bu<sub>3</sub>Al was applied as a basic reagent for systematic studies.<sup>1,2</sup> Surprisingly, interactions of R<sub>2</sub>Zn compounds with water remain a largely unexplored area,<sup>3</sup> despite their rich history<sup>4</sup> and potential application of alkylzinc hydroxides in materials chemistry (vide infra) or as initiators in polymerization processes.<sup>5</sup> There are only two structurally characterized RZnOH-type compounds, the dimeric complex  $[(Me_2PhSi)_3CZn(\mu-OH)]_2^6$  and the tetrameric arylzinc hydroxide  $[ArZn(\mu_3-OH)]_4$  (Ar = 2,4,6- $(CF_3)_3C_6H_2$ .<sup>7</sup> Interestingly, early studies implied that EtZnOH species are relatively unstable and tend to form ethylzinc oxo(hydroxides).<sup>8</sup> These suggestions are in line with more recent studies which have demonstrated that the exposition

of an  $R_2Zn$  precursor in a donor solvent toward water or air at ambient temperature affords organozinc oxo clusters<sup>9</sup> or crystalline ZnO nanoparticles of controlled size and shape.<sup>10</sup>  $R_2Zn$  compounds have also been employed in combination with water for the preparation of ZnO thin films by atomic layer deposition.<sup>11,12</sup> Thus, systematic investigations on the hydrolysis of zinc alkyls are undoubtedly highly desirable and there are still challenges left for chemists concerning a more fundamental structural perspective.

In the course of our very successful investigations on the structure and reactivity of  ${}^{t}Bu_{2}Zn$  and its derivatives<sup>13</sup> we extended this chemistry to the controlled hydrolysis reactions. Herein, we report on the synthesis, structure characterization and thermal stability of the unprecedented example of alkylzinc hydroxide, *i.e.* hexameric alkylzinc hydroxide [( ${}^{t}BuZnOH$ )<sub>6</sub>], as well as its application as a predesigned precursor in the solid-state synthesis of ZnO nanoparticles.

After considerable investigation it was discovered that the two-phase reaction system involving  ${}^{t}Bu_{2}Zn$  with 1 equivalent of degassed water in toluene afforded reproducibly the alkylzinc hydroxide cluster, [ ${}^{t}BuZn(\mu-OH)$ ]<sub>n</sub> (1), in an essentially quantitative yield after 4 h of vigorous stirring.‡ Compound 1 is stable at ambient temperature under an inert atmosphere in the solid state but in solution it slowly decomposes with a concomitant yellowing of the solution and finally with the formation of a yellow insoluble solid.<sup>14</sup> Compound 1 was characterized by <sup>1</sup>H NMR and IR spectroscopy. The presence of a hydroxyl group in 1 is substantiated in the <sup>1</sup>H NMR spectrum (in thf-[D8]) by a singlet resonance at 4.40 ppm and in the IR spectrum (CH<sub>2</sub>Cl<sub>2</sub> solution) by a sharp O–H stretch at 3642 cm<sup>-1</sup>.‡

Colorless crystals of **1** suitable for X-ray single-crystal determination were obtained by crystallization from a concentrated toluene solution at -25 °C. Compound **1** crystallizes in the monoclinic space group  $P2_1/c$  as a hexamer [<sup>t</sup>BuZn( $\mu$ -OH)]<sub>6</sub> and represents an unprecedented example of an alkylzinc hydroxide complex (Fig. 1).§ The association of six <sup>t</sup>BuZnOH molecules results in a drum-like structure comprised of two six-membered and six four-membered Zn–O rings. Each hydroxide ligand bridges up three zinc centers and adopts the  $\mu_3$ -OH coordination mode. The Zn<sub>6</sub>O<sub>6</sub> core can be described as a hexagonal prism with alternating Zn and O atoms.

<sup>&</sup>lt;sup>a</sup> Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. E-mail: lewin@ch.pw.edu.pl; Web: http://lewin.ch.pw.edu.pl; Fax: +48-22-234-7279

<sup>&</sup>lt;sup>b</sup> Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

<sup>&</sup>lt;sup>c</sup> Faculty of Materials Science and Engineering, Warsaw University of Technology, Wołoska 141, 02-507 Warsaw, Poland

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Details of the structural solutions and X-ray data for 1, details of experimental procedures and TGA/DTA profiles for 1 and 2. CCDC 812506. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11328c



**Fig. 1** Molecular structure of **1**; hydrogen atoms of *tert*-butyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–O1, 2.044(7); Zn2–O1, 2.037(7); Zn2–O2, 2.019(8); Zn1'–O2, 2.183(8); Zn2–O3', 2.147(8); Zn3–O1', 2.113(8); O3–Zn1–O1, 100.9(3); Zn1–O1–Zn2, 139.7(4); O3–Zn1–O2', 82.5(3); Zn1–O1–Zn3', 95.6(3).

The Zn<sub>3</sub>O<sub>3</sub> hexagonal faces are essentially planar with significant trigonal distortion  $[O-Zn-O_{av} = 104^{\circ}, Zn-O-Zn_{av} = 136^{\circ}]$ . The Zn–O distances are of two types, those within [2.019–2.044 Å] and those linking [2.113–2.183 Å] the two Zn<sub>3</sub>O<sub>3</sub> rings. Interestingly, the noticeable elongation of two Zn–O linking bonds (namely Zn1–O2' and Zn1'–O2) suggests that this core structure is labile and prone to structural modifications.

Amongst the discrete organozinc complexes investigated as precursors for ZnO nanomaterials, alkylzinc alkoxides (RZnOR') with heterocubane structures have received the most attention, and their 'Zn<sub>4</sub>O<sub>4</sub>' heterocubane core has been regarded as a 'preorganized ZnO'.<sup>15</sup> Therefore we were wondering how the presence of hydroxide groups will influence the thermal behavior of **1** in comparison with a zinc alkoxide complex and in the next step we performed thermogravimetric analyses for **1** and the *tert*-butoxide cluster (<sup>1</sup>BuZnO<sup>1</sup>Bu)<sub>4</sub> (**2**) which was extensively studied by our group very recently.<sup>13c</sup> Thermogravimetric analysis of **1** showed only one sharp weight loss step with a maximum at 122 °C (Fig. 2), which can be attributed to the quantitative elimination of isobutane with the concomitant formation of a pure ZnO phase as confirmed by PXRD studies (*vide infra*) and elemental analysis.<sup>16</sup>



**Fig. 2** Thermogravimetric analysis (TGA, DTG) traces showing the decomposition of compounds **1** and **2** in an inert (Ar) atmosphere.



Fig. 3 VT PXRD profiles of the grinded sample of compound 1.

TGA studies of 2 showed a significantly more complex nature of its decomposition than that observed for 1 (Fig. 2). In the TGA profile of 2 two main decomposition steps are present with a maximum decomposition rate at 168 °C and 239 °C. The decomposition process is finished at around 260 °C with a total weight loss of 58.5% which is in a very good agreement with a theoretical value of 58.4%. Moreover, in situ variable temperature PXRD analysis under an inert atmosphere (He) of a fresh sample of 1 (Fig. 3) demonstrated a rapid conversion of 1 into nanosized Wurtzite-type ZnO. The decomposition process of 1 can be observed even at temperatures as low as 60 °C with the formation of ZnO nanoclusters with an average particle size of 2.0 nm as determined by the Scherrer equation (Fig. 3). Further heating of the sample leads to a slow sintering of as-formed nanoparticles to higher aggregates reaching the mean diameter of nanoparticles of 3.4 nm at 150 °C and finally 6.2 nm at 450 °C. The HRTEM micrographs of the sample of 1 heated to 150 °C show aggregates of nanoparticles with a narrow size distribution and a mean diameter of 5.0 nm which is in acceptable agreement with PXRD analysis (Fig. 4).

Thus, the decomposition of **1** appears to be a clean process and the use of the alkylzinc hydroxide complexes as ZnO precursors is very promising. To our knowledge, the observed value of the decomposition temperature for **1** is extremely low in comparison to the recently reported data for single-source precursors of the type of [RZnOR']<sub>4</sub>; the latter precursors exhibited multi-step decomposition pathways to ZnO nanoparticles in a relatively wide temperature range with the upper limit above 260 °C. This transformation of **1** to ZnO under such mild conditions can be rationalized in terms of a mild cluster to sub-nanoparticle transformation of the predesigned cluster as presented in Scheme 1. The molecular drum-like structure of **1** clearly resembles those observed as a







Fig. 4 HRTEM micrographs of ZnO nanoparticles obtained by thermal decomposition of 1 at 150 °C under a nitrogen atmosphere; images shown at  $\times 1.5$  M (top-left) and  $\times 4.5$  M (top-right) and particle size distribution diagram (bottom).

basic unit in a Wurtzite-type ZnO, so one can consider breaking of three Zn–O bonds in **1** resulting in the formation of a flexible quasi-molecule (transition state) which can be further easily stabilized as a sub-nanometre scale ZnO cluster with a concomitant evolution of isobutane.

In conclusion, we have successfully synthesized and characterized the novel hexameric *tert*-butylzinc hydroxide **1** which was then used as a predesigned precursor in the solid-state synthesis of ZnO nanoparticles. Strikingly, the decomposition of **1** was found to be a clean process with one sharp weight loss step with a maximum at 122 °C and the use of the alkylzinc hydroxide complexes as ZnO precursors appears very attractive. Further studies on the reactivity of Zn–OH in various coordination environments towards small molecules are in progress.

The authors would like to acknowledge the Ministry of Science and Higher Education (Grant N N204 164336) (W.B., J.L.) and the European Union within European Regional Development Fund (grant Innovative Economy, POIG.01.01.02-00-008/08) (E.K., M.D., K.S., I.J., J.L.) for financial support.

## Notes and references

‡ Synthesis of 1: <sup>1</sup>Bu<sub>2</sub>Zn (0.718 g, 4.00 mmol) in toluene (4 mL) was added dropwise to a suspension of water (72 µL, 4.00 mmol) in toluene (4 mL) at -10 °C. After the addition was completed the reaction mixture was allowed to warm to room temperature and stirred for further 4 h. Compound 1 was obtained as colourless plate crystals after crystallization from the toluene/hexane mixture at 4 °C. Yield: 0.435 g (78%). Elemental analysis (%) calcd for C<sub>24</sub>H<sub>60</sub>O<sub>6</sub>Zn<sub>6</sub>: C, 34.44; H, 7.23%; found: C, 34.30; H, 7.27%; IR (CH<sub>2</sub>Cl<sub>2</sub>, KBr):  $\nu$  = 3642s, 2939s, 2920s, 2863m, 2817s, 2756w, 2698w, 1496w, 1464m, 1358w, 1011w, 816m, 522w cm<sup>-1</sup>; <sup>1</sup>H NMR (THF-d<sub>8</sub>, 400.10 MHz, 298 K):  $\delta$  = 4.40 (s, 1H, OH)), 0.97 (s, 9H, ZnC(CH<sub>3</sub>)<sub>3</sub>) ppm.

§ Crystal data for 1:  $C_{24}H_{60}O_6Zn_6$ : M = 837.06, monoclinic space group  $P2_1/c$  (no. 14), a = 9.9031(3) Å, b = 10.5542(5) Å,

c = 18.1019(7) Å,  $\beta = 108.814(2)^\circ$ , U = 1790.89(12) Å<sup>3</sup>, Z = 2, F(000) = 864,  $D_c = 1.552$  g m<sup>-3</sup>, T = 100(2) K,  $\mu$ (Mo-K $\alpha$ ) = 3.983 mm<sup>-1</sup>. Final residuals (for 172 parameters) were  $R_1$  [ $I > 2\sigma(I)$ ] = 0.061, w $R_2$  (all data) = 0.141. CCDC 812506. Diffraction data were collected on a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and an Oxford Cryostream low-temperature device.

- (a) M. R. Mason, J. M. Smith, S. G. Bott and A. R. Barron, J. Am. Chem. Soc., 1993, 115, 4971–4984; (b) C. J. Harlan, M. R. Mason and A. R. Barron, Organometallics, 1994, 13, 2957–2969.
- 2 For seminal account on the hydrolysis of Group 13 organometallics, see: H. W. Roesky, M. G. Walawalkar and R. Murugavel, *Acc. Chem. Res.*, 2001, 34, 201–211.
- 3 For computational studies on the gas-phase hydrolysis of Et<sub>2</sub>Zn, see: S. M. Smith and H. B. Schlegel, *Chem. Mater.*, 2003, **15**, 162–166.
- 4 D. Seyferth, Organometallics, 2001, 20, 2940–2955.
- 5 W. Kuran, *Principles of Coordination Polymerisation*, Wiley, Chichester, 2001, ch. 9.
- 6 S. S. Al-Juaid, N. H. Buttrus, C. Eaborn, P. B. Hitchcock, A. T. L. Roberts, J. D. Smith and A. C. Sullivan, J. Chem. Soc., Chem. Commun., 1986, 908–909.
- 7 C. Agnew, K. B. Dillon, A. E. Goeta and A. L. Thompson, *Inorg. Chim. Acta*, 2009, **362**, 4260–4262.
- 8 (a) R. J. Herold, S. L. Aggarwal and V. Neff, Can. J. Chem., 1963, 41, 1368–1380; (b) W. Kuran and M. Czarnecka, J. Organomet. Chem., 1984, 263, 1–7.
- 9 A. Pettersen, A. Lennartson and M. Håkansson, Organometallics, 2009, 28, 3567–3569.
- (a) M. Monge, M. L. Kahn, A. Maisonnat and B. Chaudret, Angew. Chem., Int. Ed., 2003, 42, 5321–5324; (b) M. L. Kahn, M. Monge, V. Colliere, F. Senocq, A. Maisonnat and B. Chaudret, Adv. Funct. Mater., 2005, 15, 458–468; (c) M. L. Kahn, M. Monge, E. Snoeck, A. Maisonnat and B. Chaudret, Small, 2005, 1, 221–224; (d) C. Pages, Y. Coppel, M. L. Kahn, A. Maisonnat and B. Chaudret, ChemPhysChem, 2009, 10, 2334–2344; (e) M. L. Kahn, A. Glaria, C. Pages, M. Monge, L. Saint Macary, A. Maisonnat and B. Chaudret, J. Mater. Chem., 2009, 19, 4044–4060.
- (a) A. B. F. Martinson, J. W. Elam, J. T. Hupp and M. J. Pellin, Nano Lett., 2007, 7, 2183–2187; (b) T. W. Hamann, A. B. F. Martinson, J. W. Elam, M. J. Pellin and J. T. Hupp, Adv. Mater., 2008, 20, 1560–1564; (c) A. Pourret, P. Guyot-Sionnest and J. W. Elam, Adv. Mater., 2008, 20, 1–4; (d) J. A. Libera, J. W. Elam and M. J. Pellin, Thin Solid Films, 2008, 516, 6158–6166; (e) A. Pourret, P. Guyot-Sionnest and J. W. Elam, Adv. Mater., 2009, 21, 232–235.
- 12 For a recent review on solution-based synthesis of ZnO thin films, see: B. Weintraub, Z. Zhou, Y. Li and Y. Deng, *Nanoscale*, 2010, 2, 1573–1587.
- 13 (a) J. Lewiński, W. Śliwiński, M. Dranka, I. Justyniak and J. Lipkowski, Angew. Chem., Int. Ed., 2006, 45, 4826–4829; (b) J. Lewiński, M. Dranka, W. Bury, W. Śliwiński, I. Justyniak and J. Lipkowski, J. Am. Chem. Soc., 2007, 129, 3096–3098; (c) J. Lewiński, M. Dutkiewicz, M. Lesiuk, W. Śliwiński, K. Zelga, I. Justyniak and J. Lipkowski, Angew. Chem., Int. Ed., 2010, 49, 8266–8269.
- 14 Due to a low stability of **1** in benzene solution more detailed cryoscopic studies of the degree of association were unsuccessful.
- (a) C. G. Kim, K. Sung, T.-M. Chung, D. Y. Jung and Y. Kim, *Chem. Commun.*, 2003, 2068–2069; (b) S. Polarz, A. Roy, M. Merz, S. Halm, D. Schroeder, L. Schneider, G. Bacher, F. E. Kruis and M. Driess, *Small*, 2005, 1, 540–552; (c) S. Polarz, F. Neues, M. van den Berg, W. Grunert and L. Khodeir, *J. Am. Chem. Soc.*, 2005, 127, 12028–12034; (d) S. Polarz, A. Roy, M. Lehmann, M. Driess, F. E. Kruis, A. Hoffmann and P. Zimmer, *Adv. Funct. Mater.*, 2007, 17, 1385–1391; (e) C. Lizandara-Pueyo, M. W. E. van den Berg, A. De Toni, T. Goes and S. Polarz, *J. Am. Chem. Soc.*, 2008, 130, 16601–16610; (f) N. Reuge, R. Bacsa, P. Serp and B. Caussat, *J. Phys. Chem. C*, 2009, 113, 19845–19852.
- 16 Elemental analysis of the obtained ZnO confirmed the absence of any carbon impurities.