Preparation of Monomeric $Ba[O(CH_2CH_2O)_nCH_3]_2$ (n = 2, 3), Ambient Temperature Liquid Barium Compounds

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Reaction of elemental barium with a stoichiometric quantity of the appropriate alcohol in tetrahydrofuran (thf) gives the monomeric $Ba[O(CH_2CH_2O)_nCH_3]_2$ (n = 2, 3).

We report the preparation and characterization of the first *monomeric* barium bisalkoxides. The initial publications in this area all described $Ba(OR)_2$ compounds as insoluble and involatile compositions.[1–4] Recent data have indicated barium hydrido-oxo-alkoxides are hexameric in the solid state.[5,6] A trimeric barium siloxide,[7] the highly hydrogen-bonded $Ba[OCH_2CH_2N(CH_2CH_2OH)_2]_2\cdot 2EtOH$,[8] and a benzene soluble diaryloxide†[9] each recently have been prepared. In this previous work, no evidence has been presented for the existence of monomeric species of the form $Ba(OR)_2$. These discrete molecular alkoxides have the potential to serve as precursors for solid state barium oxide containing compositions of interest in electronic materials.[10–12]

The preparation of $Ba[O(CH_2CH_2O)_nCH_3]_2$, n = 2, **1**, was achieved by the interaction of elemental barium cubes with a stoichiometric quantity of the oligoether alcohol in thf at ambient temperature for one day (Scheme 1).‡ The synthesis of compound **2**, n = 3, was similarly carried out at reflux conditions for five hours.§ Reaction product yields and purities each were high after filtration and solvent removal.¶ Spectroscopic data (^1H, ^{13}C NMR) revealed unique resonance

$$Ba + 2\,HOR \rightarrow H_2 + Ba(OR)_2$$

Scheme 1 $R = (CH_2CH_2O)_nCH_3$; n = 2, **1**; n = 3, **2**

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† NMR data only, postulated as $[Ba(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(OC_4H_8)_4]$, see: ref. 9.

‡ *Preparation of* **1**: under O_2- and H_2O-free N_2, 5.10 ml of $HO(CH_2CH_2O)_2CH_3$ (5.15 g, 42.8 mmol) and 3.10 g of Ba (22.6 mmol) were added to 100 ml of thf (freshly distilled from Na and benzophenone) in a 250 ml oven-dried (130 °C) Schlenk flask equipped with an N_2 inlet, magnetic stir bar, and a water cooled condensor. The reaction visibly commenced after twenty minutes of stirring and was allowed to continue at ambient temperature under N_2 for 24 h; an opaque brown solution resulted. The solution was filtered using a Schlenk frit (30 mm diameter) packed with 4 cm of Celite; the filtrate was a clear brown liquid. The solvent was removed by distillation *in vacuo* to a liquid N_2 cooled receiver and the resulting product, in 87% yield (based on initial Ba charge), was a viscous brown syrup. The product was kept under vacuum (0.05 mmHg) for 12 h at ambient temperature to insure the complete removal of solvent.

§ *Preparation of* **2**: in a preparation identical to that employed for **1**, 2.40 ml of $HO(CH_2CH_2O)_3CH_3$ (2.46 g, 15.0 mmol) and 1.08 g of Ba (7.86 mmol) were utilized. The solution was heated to reflux and after 30 min a visible change commenced and the reaction was allowed to continue at reflux conditions under N_2 for 5 h; an opaque brown solution resulted. The reaction mixture was worked up identical to that described for **1**.

¶ *Spectroscopic data* **1**: ^1H NMR: (300 MHz, positive δ down field referenced to Me_4Si = 0 ppm utilizing residual C_6HD_5 = 7.15 ppm in solvent C_6D_6) 3.23 (s, CH_3), 3.36 (t, CH_2) J 4.6 Hz, 3.54 (t, CH_2) J 4.6 Hz, 3.65 (t, CH_2) J 4.4 Hz, 4.07 (t, CH_2) J 4.4 Hz; $^{13}C\{^1H\}$ NMR: (75 MHz positive δ down field referenced to Me_4Si = 0 ppm utilizing solvent C_6D_6 = 128.0 ppm) 76.1 (CH_2), 72.1 (CH_2), 69.9 (CH_2), 62.3 (CH_3), 58.5 (CH_2); solution IR: ν_{max}/cm^{-1} (in CCl_4 *vs.* CCl_4 reference) 2890vs (CH), 1395w, 1345w, 1245w, 1200w, 1110vs (COC), 1075m (COC), 1025w, 935w, 890w, 540w; M_w: found 418 (calcd. 376). **2**: ^1H NMR: (300 MHz, positive δ down field referenced as for **1**) 3.17 (s, CH_3), 3.37 (t, CH_2), 3.6 unassignable multiplets, 3.93 (t, CH_2); $^{13}C\{^1H\}$ NMR: (75 MHz, positive δ down field referenced as for **1**) 77.0 (CH_2), 72.1 (CH_2), 70.7 (CH_2), 62.7 (CH_3), 58.4 (CH_2); solution IR: (ν_{max}/cm^{-1} in CCl_4 *vs.* CCl_4 reference) 2865vs (CH), 1450w, 1345w, 1300w, 1280w, 1250w, 1200w, 1110vs (COC), 1080m (COC), 935w, 890w, 855w, 545w; M_w: found 489 (calcd. 463). Anal. found (calc. for $Ba_8O_8C_{14}H_{30}$): C 35.89 (36.28) H 6.27 (6.48). Thermogravimetric analysis: (1 atm N_2, 10 °C min^{-1}, 50–650 °C) onset 103 °C, completion to 59% wt. loss by 538 °C, max. wt. loss 243–303 °C, midpoint 278 °C (14–39% wt. loss). MS; {EI, 70 eV, m/z (fragment)} 355 ($BaC_{11}H_{22}O_4$), 281 ($BaC_8H_{16}O_2$), 267 ($BaC_7H_{14}O_2$), 209 (BaC_4H_8O), 133 ($C_6H_{13}O_3$), 119 ($C_5H_{11}O_3$), 103 ($C_5H_{11}O_2$), 89 ($C_4H_9O_2$), 74 ($C_3H_7O_2$), 72 (C_4H_8O), 59 (C_3H_7O), 58 (C_3H_6O), 45 (C_2H_5O), 44 (C_2H_4O).

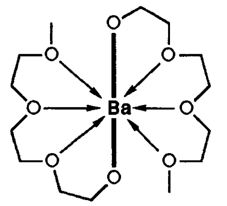

Fig. 1 The proposed solution structure of clam shell oligoether bisalkoxide **2**

frequencies for each methylene group present in the oligoether alkoxide linkages.¶ Solution molecular weight data unambiguously support a monomeric structure for **2**, and strongly indicate the majority presence of a monomer for **1**.¶ Based on all currently available evidence, we propose a 'clam shell' oligoether structure for these discrete $Ba(OR)_2$ compounds as illustrated in Fig. 1. The optimum hinge length for the shell doors was chosen by examination of space filling molecular models, utilizing Pauling's covalent radius for barium of 1.98 Å. A quite recent result should be pointed out regarding hinge length importance. The removal of one ethylene oxide linkage from the ligand present in **1** creates a di-solvated aggregate of $[Ca(OR)_2]_9$ (M_w = 1862 g mol^{-1}).[13] Thus, it would appear at this time that seemingly subtle structural changes in these new clam shell oligoether alkoxide ligands potentially may lead to rather dramatic effects in the molecularity of their subsequent metal complexes.

Perhaps more remarkable than their adoption of monomeric identities in solution is the fact that both **1** and **2** possess an ambient temperature *liquid* state. These compositions are highly soluble in polar aprotic organic solvents (Et_2O, thf, CCl_4, $CHCl_3$, C_6H_6) and, hence, stand in stark contrast to the non-ethereal primary bisalkoxides of barium.‖[14] Although extremely moisture sensitive, neither **1** nor **2** displayed noticeable decomposition after brief exposure to anhydrous air. This kinetic stability presently is attributed to the relative inaccessibility of the stearically crowded central metal to further reaction. Unlike other recent reports[5,7–9,13] of intermolecularly stabilized group 2 alkoxides, generally formed by parasitic attachment either of thf from the reaction medium or of an excess of alcohol molecules present during the preparation, **1** and **2** presumably achieve coordinative saturation of the central metal atom through enforced closure of the clam shell produced by intramolecular coordination of the oxygen atoms located in the oligoether 'doors'.

Studies in progress are directed at (*i*) an expansion of the recently discovered clam shell strategy and an exploration of its generality using these new oligoether alkoxides and related ligands, and (*ii*) extension to other elements known for traditionally forming insoluble and/or involatile aliphatic alkoxides.

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‖ 'The primary alkoxide derivatives of alkaline earth and other metals of group II are generally insoluble, non-volatile compounds . . .' see ref. 14.