# Preparation, Crystal and Molecular Structure of a Hydrocarbon Soluble, Volatile Oxo-alkoxide of Barium: $H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}$

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Barium granules suspended in toluene react rapidly and exothermically with 2-methoxyethanol to yield a hydrocarbon-soluble, volatile (160 °C, $10^{-1}$ Torr; 1 Torr = 133.322 Pa), crystalline oxo-alkoxide $H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}$ which has been characterized by a single-crystal X-ray study; a central octahedral $Ba_6(\mu_6\text{-}O)$ unit is supported by eight $\mu_3\text{-}\eta^2\text{-}OCH_2CH_2OCH_3$, four $\eta^2\text{-}OCH_2CH_2OMe$ and two $\eta^1\text{-}OCH_2CH_2OMe$ groups and intermolecular hydrogen bonds.

A number of useful barium-containing oxides are known.[1] Alkoxides of metals provide valuable molecular precursors to oxides by sol-gel and MOCVD processes.[2] We describe herein a facile, high yield preparation and structural characterization of an oxo-alkoxide barium aggregate that is volatile and hydrocarbon soluble, two properties that are valuable with regard to molecular precursor strategy and control of purity. It is likely that this compound was present as the barium source in the previously reported[3] preparation of $YBa_2Cu_3O_7$ from the molecular precursors described in the reaction sequence given in Scheme 1.

The compound $Y(OCH_2CH_2OCH_3)$ in Scheme 1 has recently been shown to exist as a cyclooligomer in the solid state ($n$ = 10)[4] and a related bismuth derivative of 2-meth-

$$3(CuO)_n + 2nBa(OCH_2CH_2OCH_3)_2 \rightarrow nCu_3O_3Ba_2(OCH_2CH_2OCH_3)_4$$

$$Cu_3O_3Ba_2(OCH_2CH_2OCH_3)_4 + Y(OCH_2CH_2OCH_3)_3 \rightarrow Cu_3O_3Ba_2Y(OCH_2CH_2OCH_3)$$

**Scheme 1**

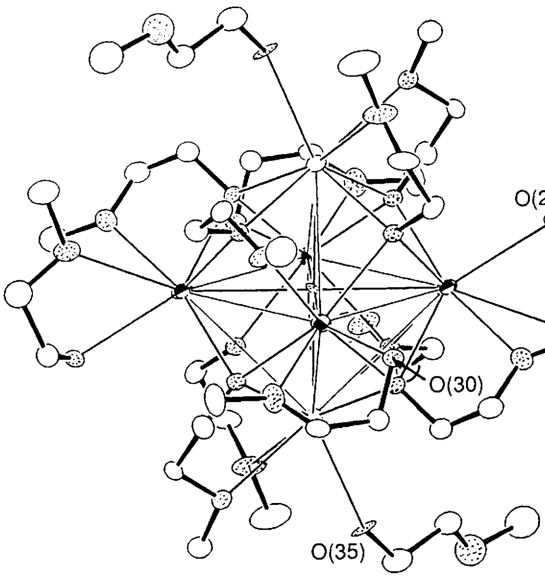

**Fig. 1** An ORTEP drawing of $H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}$. Ba atoms are shown with the thermal ellipsoid principal axis and the oxygen atoms are stippled. Ba–O distances (Å) are 2.90–2.93 (oxo); 2.67–2.82 (Ba–$\mu_3$-O); 2.71–2.81 [Ba–O(H)R (terminal)]; 2.83–2.97 Ba–O (ethers). Lines drawn between Ba atoms are not indicative of M–M bonding but are drawn to emphasize the $Ba_6$ octahedron

oxyethanol was found to have an infinite chain structure $[Bi_2(\mu\text{-}OCH_2CH_2OCH_3)_4(OCH_2CH_2OCH_3)_2]_\infty$.[5]

Barium granules suspended in toluene and 2-methoxyethanol undergo an extremely rapid and exothermic reaction.† The title compound was obtained as crystals by toluene extraction and crystallization from toluene/pentane solutions at −10° C in 90% yield based on barium. It is volatile and may be sublimed at 160 °C, $10^{-1}$ Torr (1 Torr = 133.322 Pa).† The compound has been characterized by IR, $^1H$ and $^{13}C$ NMR spectroscopy, solution cryoscopy, elemental analysis and a single crystal X-ray diffraction study (Fig. 1).‡

The following points are noteworthy. (i) In contrast to the recently reported[6] structures of phenoxide and t-butoxide derivatives which had square pyramidal $Ba_5(\mu_5\text{-}O)$ units, we find here a fully encapsulated oxo ligand. The presence of oxo rather than the hydroxy ligand seems certain in this instance.

(ii) The molecule has a crystallographically imposed centre of inversion; it is useful to refer to the barium atoms that are coordinated by $\eta^1$-$OCH_2CH_2OCH_3$ ligands as apical Ba atoms.

(iii) Each barium is coordinated to eight oxygen atoms: the oxo group, four oxygen atoms from $\mu_3$-*O*R ligands, two ether oxygens and one *O*$CH_2CH_2OCH_3$ oxygen atom that is either a terminal ($\eta^1$) group, (the apical Ba atoms) or a chelating ($\eta^2$) ligand (the four Ba atoms in the equatorial plane). From the eight $\mu$-$OCH_2CH_2OCH_3$ ligands, a total of four ether oxygen atoms are coordinated to the two apical and four to the four equatorial Ba atoms. The difference in ligand sets at the apical and equatorial barium centres arises from a simple mismatch of site populations: an octahedron has eight triangular faces but only six apices. After six $\mu_3$-$OCH_2CH_2OCH_3$ ligands coordinate their ether oxygen atoms to barium, two remain to make two barium centres (the apical ones) unique by coordination of a second ether oxygen. This forces the *terminal* $OCH_2CH_2OCH_3$ on the apical bariums to be $\eta^1$. In solution, by $^1H$ and $^{13}C$ NMR spectroscopy, all fourteen ligands are equivalent on the NMR time-scale.†

(iv) The formulation of the complex as $H_4Ba_6(O)(OCH_2CH_2OCH_3)_{14}$ rests on the assumption that barium is in the +2 oxidation state. Three of the four required hydrogen atoms were located crystallographically involving O(25), O(30) and O(35), and are responsible for the short intermolecular O–O distances (2.4–2.5 Å). It is because these are alcohol, not alkoxide oxygens, that their Ba–O distances are long, *e.g.* comparable to the Ba–$\mu_3$-O distances. There is no obvious place to locate the fourth hydrogen which is presumably disordered over the hexanuclear $Ba_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8(O)_{18}$ moiety.

It seems likely that the volatility of the hexanuclear barium oxoalkoxide would be increased if the interaggregate O···H···O bonding were not present. A number of approaches can be envisaged to eliminate this type of hydrogen bonding and further studies are in progress.

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† All reactions were carried out under a nitrogen atmosphere. Solvents and $CH_3OCH_2CH_2OH$ were dried and deoxygenated. Glassware was flame dried and in some instances silated. The latter did not influence the yield of the $Ba_6$-oxo aggregate. The origin of the oxo oxygen atom has not been determined. The sublimate was obtained in *ca.* 30% yield. Satisfactory elemental analyses were obtained for the crystalline and sublimed samples $[H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}]$. From cryoscopy (benzene, 8.5–25 × $10^{-3}$ mol dm$^{-3}$) $M_o$ = 1880 ± 40; $M_c$ for $H_4Ba_6(O)(OCH_2CH_2OCH_2)_{14}$ = 1895. NMR spectra (500 MHz) were essentially invariant over 220–298 K and 5 × $10^{-2}$ mol dm$^{-3}$. $^1H$ ([$^2H_8$]toluene, 298 K, 500 MHz) δ 3.42 (s, $OCH_3$), 3.62 (s, $CH_2$), 4.16 (s, $OCH_2$), 7.64 (br. s, OH). $^{13}C$ ([$^2H_8$]toluene, 126 MHz, 298 K) δ 58.62 (s, $OCH_3$), 62.91 (s, $CH_2$), 79.54 (s, $OCH_2$).

‡ *Crystal data* for $Ba_6C_{42}H_{102}O_{29}$: $T$ = −171 °C, $a$ = 12.980(2), $b$ = 13.059(2), $c$ = 12.044(2) Å, $\alpha$ = 96.57(1), $\beta$ = 106.51, $\gamma$ = 114.95(1)°, $Z$ = 1, $D_c$ = 1.84 g cm$^{-3}$, space group $P\bar{1}$. Of 5050 reflections collected, Mo-K$\alpha$, 6 ≤ 2θ ≤ 45°, 4437 were unique and those with $F > 2.33\ \sigma(F)$, 3820 reflections, were used in the full least-square refinement leading to the residuals $R(F)$ = 0.044 and $Rw(F)$ = 0.047. Atomic coordinates bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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