Synthesis and Structural Characterization of the First Examples of Molecular Aggregates of Barium supported by Aryloxide and Alkoxide ligands: $[HBa_5(O)(OPh)_9(thf)_8]$ and $[H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]$ (thf = tetrahydrofuran)

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The reaction of barium granules in tetrahydrofuran with either phenol or t-butyl alcohol yields phenoxide and t-butoxide aggregates that have been characterized in the crystalline state; they share a number of novel structural features, including the presence of a square-based pyramidal core $Ba_5(\mu_5\text{-}O)$ supported by μ_3 and μ_2 phenoxide or butoxide ligands.

The current research interest in metal oxides has led to a renaissance in metal alkoxide chemistry since metal alkoxides may provide molecular precursors for the synthesis of the former.[1] Barium is a constituent in oxides of wide ranging properties and utility, *e.g.* $BaTiO_3$,[2] $YBa_2Cu_3O_{7-x}$,[3] and $Ba_{0.6}K_{0.4}BiO_3$,[4] but virtually nothing is known concerning its alkoxides.[5—8] We describe herein our preparation and structural characterization of the first examples of discrete molecular aggregates of barium supported by either phenoxide or t-butoxide ligands.

Barium metal, as granules, suspended in tetrahydrofuran (thf) was allowed to react with either phenol or t-butyl alcohol. The reaction involving phenol was rapid at room temperature and exothermic, being complete in *ca.* 50 min. The reaction involving t-butyl alcohol proceeded over 1 h at 70 °C. Whereas the reaction mixture involving phenol remained colourless, the reaction involving t-butyl alcohol gave highly coloured solutions as the reaction proceeded.† In each case crystallization from toluene–pentane gave colourless crystals. These were formulated as $[HBa_5(O)(OPh)_9(thf)_8]$ (**1**) and $[H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]$, (**2**), based, in part, on single-crystal X-ray studies.‡

The molecular structures of (**1**) and (**2**) are shown in Figures 1 and 2. Common to both is a square-based pyramid of barium atoms and a μ_5-oxo ligand: $Ba_5(\mu_5\text{-}O)$. The apical barium atom is bonded to four μ_3-OR ligands that cap the four triangles of the square-based pyramid. The barium atoms in the basal plane are linked by four μ_3 and four μ_2 OR groups that lie respectively above and below the $Ba_4(\mu\text{-oxo})$ plane. In (**1**) each barium in the basal plane is co-ordinated by two terminal thf ligands to yield a co-ordination number of seven whereas the apical barium atom has one terminal phenoxide and is only six-co-ordinate. The Ba–O bond distances to the apical Ba atom are notably shorter than those involving the seven-co-ordinate Ba atoms in the basal plane.

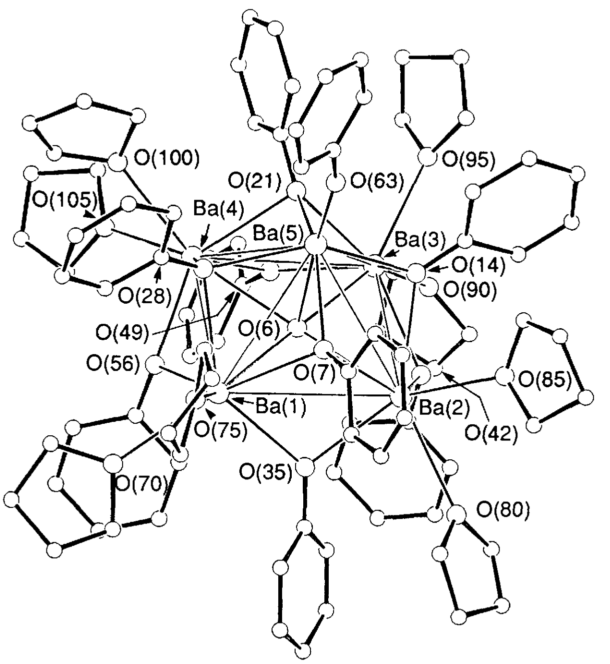

Figure 1. A ball-and-stick drawing of the $[HBa_5(O)(OPh)_9(thf)_8]$ molecule (**1**). Selected distances (Å) averaged where appropriate are Ba(5)–O(63) 2.32(1), Ba(5)–μ_3-OPh 2.54(1), Ba(5)–O(6) 2.68(1), Ba(1—4)–μ_3-OPh 2.75(2), Ba(1—4)–μ_2-OPh 2.65(3), Ba(1—4)–μ_5-O(6) 2.88(2), Ba–O(thf) 2.80(4). Lines are drawn between Ba atoms to emphasize the structural similarities in (**1**) and (**2**) (Figure 2) and are not indicative of M–M bonding.

In (**2**) the apical Ba atom and two of the Ba atoms in the basal plane are each ligated by one terminal thf molecule. The other two Ba atoms are linked to the sixth Ba atom through the agency of three μ-OR bridges. In this manner the Ba atoms in (**2**) that are associated with the $Ba_5(\mu_5\text{-}O)$ pyramid are six-co-ordinate while the sixth Ba atom is ligated to only five oxygen atoms. Such a low co-ordination number for barium is unprecedented.

A number of points are worthy of mention in connection with the syntheses and structures reported here. (i) The pyramidal Ba_5 unit in (**1**) and (**2**) may be viewed as the fusing of four *triangulo* subunits $M_3(\mu_3\text{-}O)_2(\mu\text{-}O)_3L_n$. Triangular subunits of this type are common in cluster compounds and in metal oxide structures. The attachment of the sixth Ba atom in (**2**) to an edge of the Ba_5 unit is reminiscent of the co-ordination of Na^+ to the $W_2(\mu\text{-}H)(OPr^i)_8{}^-$ anion in $NaW_2(\mu\text{-}H)(OPr^i)_8(diglyme)$[9] and to the attachment of a boron-containing moiety to the basal edge of pentaborane.[10]

(ii) The ability of the metal atoms to synthesize and *assemble* a ligand set of their choice is evident from the unexpected appearance of the μ_5-oxo moiety in (**1**) and (**2**) and the diolate ligand in (**2**). The partial encapsulation of the oxide (μ_5-O) finds a parallel with the encapsulation of light main-group atoms (*e.g.*, Be, B, C, or N) in the synthesis of transition metal clusters within extended lattices[11] as well as in the synthesis of the alkoxides $M_5(\mu_5\text{-}O)(OPr^i)_{13}$ where M = In[12] and Y.[13] Common to all these syntheses is the use of the metal in its elemental form.

The occurrence of the diolate ligand $OCEt_2CH_2O$ in (**2**) is

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† $[HBa_5(O)(OPh)_9(thf)_8]$. Ba (10 mmol), PhOH (20 mmol) and thf (10 ml) were added to a Schlenk apparatus cooled to 0 °C. An exothermic reaction resulted in vigorous gas evolution. All the metal was consumed within 50 min. The solution volume was reduced to *ca.* 1 ml and toluene (15 ml) was added. The solute was collected by filtration, layered with pentane (15 ml), and left to crystallize at −20 °C; yield 3.80 g, 81% based on Ba; ν(OH) (Nujol) 3410 cm^{-1}, m.p. 226—228 °C.

$[H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]$. (10 mmol) was suspended in a Bu^tOH (10 ml) and thf (8 ml) solution and heated under reflux at 70 °C for 1 h during which time the metal gradually dissolved to give an orange-red solution. The solvent was removed under a dynamic vacuum to yield a waxy solid. This was dissolved in toluene (7 ml) and filtered hot to yield a clear orange filtrate which was subsequently layered with pentane (15 ml) and placed in a freezer at −20 °C. After 2 days a large crop of crystals had formed and were collected by filtration and dried *in vacuo*; yield 2.82 g, 84% yield based on Ba; ν(OH) 3340 cm^{-1}, m.p. >340 °C.

Satisfactory elemental analyses were obtained for both complexes.

‡ *Crystal data* for (**1**) at −155 °C: a = 22.935(4), b = 17.091(3), c = 22.219(5) Å, β = 90.46(1)°, Z = 4, D_c = 1.61 g cm^{-3}, monoclinic, space group $P2_1/c$. Of the 16 429 reflections collected (Mo-Kα, $6 \leq 2\theta \leq 45°$) 11 425 were unique and the 8654 having $F > 3\sigma(F)$ were used in the full-matrix least-squares refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms on carbon atoms were placed in calculated positions with d_{C-H} = 0.95 Å and the thermal parameters of the hydrogen atoms were set to one plus the isotropic thermal parameter of the parent atom. The final residuals are R = 0.079 and R_w = 0.077. No hydroxy H atoms were located and the μ_5-oxo to μ_3-OR oxygen distances span the range 3.20—3.30 Å.

Crystal data for (**2**) at −130 °C: a = 14.537(5), b = 22.707(7), c = 14.524(5), α = 91.35(1)°, β = 102.64(1), γ = 102.67(1)°, Z = 2, D_c = 1.578 g cm^{-3}, triclinic, space group = $P\bar{1}$. Of 17 176 reflections collected (Mo-Kα, $6 \leq 2\theta \leq 45°$), 11 900 were unique. The R for the averaging was 0.050 for 5036 reflections measured more than once. Four standard reflections measured periodically during the data collection showed no systematic trends. 6762 Reflections with $F > 3\sigma(F)$ were considered observed. 10 882 reflections were non-zero. No correction was made for absorption. The structure was refined by using full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms associated with the Ba_6 aggregate. A solvent toluene molecule in the lattice was disordered, C(86)—C(103), and was refined isotropically and with partial occupancies. The final R was 0.069 using 5036 unique reflections as defined above. Some of the ligand atoms have very large thermal parameters indicating some degree of disorder. This is especially true of the thf ligands. The diol ligand at Ba(6) was modelled with two-position disorder at C(82).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

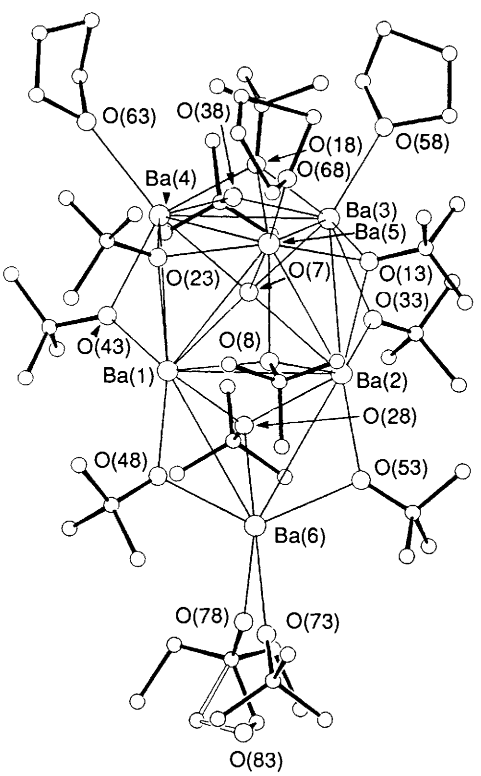
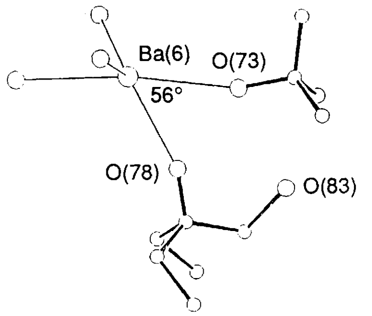


Figure 2. A ball-and-stick drawing of $[H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]$. The metal–oxygen distances (Å) are Ba(1)–O(7), –O(8), –O(23), –O(43), –O(48) 2.85(1), 2.76(1), 2.78(1), 2.67(1), 2.64(2), 2.58(1); Ba(2)–O(7), –O(8), –O(13), –O(28), –O(33), –O(53) 2.86(1), 2.73(1), 2.78(1), 2.67(2), 2.65(1), 2.59(1); Ba(3)–O(7), –O(13), –O(18), –O(33), –O(38), –O(58) 2.74(1), 2.77(1), 2.73(2), 2.58(1), 2.58(2), 2.81(2); Ba(4)–O(7), –O(18), –O(23), –O(38), –O(43), –O(63) 2.73(1), 2.76(1), 2.76(2), 2.64(2), 2.60(1), 2.83(2); Ba(5)–O(7), –O(8). –O(13), –O(18), –O(23), –O(68) 2.78(1), 2.69(1), 2.62(1), 2.64(1), 2.60(2), 2.95(2); Ba(6)–O(28), –O(48), –O(53), –O(73), –O(78) 2.73(1), 2.65(1), 2.64(2), 2.73(2), 2.57(2).

most noteworthy. The ligand is attached to Ba(6) in the manner shown in (**A**).

The presence of the diolate in (**2**) was evident from ^1H and ^{13}C NMR studies in $[^2H_8]$toluene. The free diol $HOCEt_2CH_2OH$ was liberated upon hydrolysis of (**2**) and was identified by comparison with an authentic sample by NMR, mass spectrometry, and gas chromatography. The diol was not present as an impurity in either the thf or Bu^tOH employed in the synthesis of (**2**) but was subsequently found in the mother-liquor as a product of the reaction between metallic Ba and Bu^tOH in thf. Evidently the diol is synthesized during the reaction and despite its low concentration (relative to Bu^tOH and thf), it is selectively co-ordinated by the hexanuclear barium aggregate in the formation of (**2**). Also significant is the observation that the reaction between barium and t-butyl alcohol in toluene does not generate this ligand, which implies that the diolate is formed from a reaction involving tetrahydrofuran.

(iii) Finally, there is the question of the location of the hydrogens in the title compounds. It seems reasonable to assume that barium is present in oxidation state +2 which leads to the formulation of (**1**) and (**2**) as $H^+[Ba_5(O)(OPh)_9(thf)_8]^-$ and $3H^+[Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]^{3-}$. Although the protons themselves were not evident in the *X*-ray diffraction data, they are most surely associated with the oxygen atoms, but an inspection of the O···O and Ba–O distances and Ba–O–C angles in (**1**) does not provide any clue as to their location. This situation is not unlike the problems encountered in high-nuclearity cluster hydride compounds of the transition elements.[14] The structural parameters of (**2**) reveal two short O···O distances around the terminal OBu^t and diolate ligands as shown in (**A**). Note also the relatively acute O–Ba–O angle in (**A**). It is most likely that hydrogen bonding is responsible for these structural features and indeed it is most probable that the hydrogen bonding afforded by the diolate ligand accounts for its preferential binding to the Ba_6 aggregate. The terminal ligands bonded to Ba(6) could be counted as $(^-OCEt_2CH_2OH{\cdot}Bu^tOH)$, a mononegative chelating group. This would be consistent with the observed short and long Ba(6)–oxygen distances: Ba(6)–O(73) = 2.57 Å *vs.* Ba(6)–O(78) = 2.73 Å. This would require that one other hydrogen atom be associated with the ligands attached to the pyramidal Ba_5 moiety. There is then the possibility that the μ_5-oxo group in both (**1**) and (**2**) is actually a μ_5-hydroxy group. This could be hydrogen bonded in a disordered manner to the μ_2-OR ligands that lie below the basal plane.



(**A**)
O(73)–O(78), 2.50; O(73)–O(83), 2.70; O(78)–O(83) 2.71 Å.

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