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Notes

A Soluble Alkoxide of Barium with a Cubane Structure

Björn Borup, John A. Samuels, William E. Streib, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

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Introduction

There has been recent interest in alkaline earth metal alkoxides and aryloxides in an effort to make volatile precursors for the preparation of superconducting thin films using organometallic chemical vapor deposition (OMCVD).[1] This has been especially true for barium, as it is an important metal in many of the high-temperature superconductors ($YBa_2Cu_3O_7$, $HgBa_2CuO_4$, $HgBa_2Ca_2Cu_3O_8$).[2] A problem in the attempted synthesis of a well-defined $[Ba(OR)_2]_n$ species has been the formation of oxo complexes[3-7] as in $[H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}]$,[3] $[Ba_4(\mu_4\text{-}O)(\mu_2\text{-}OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6)_6]$,[5] and $[H_2Ba_8(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6]$.[6] The high nuclearity of these compounds decreases their volatility and thus their usefulness for OMCVD. The origin of the oxo ligand has not yet been determined with certainty but is unlikely to stem from adventitious water.[5] The absence of an oxo ligand appears to decrease the nuclearity of the complexes synthesized. More recently, the synthesis of oxo-free silyloxides,[8-10] aryloxides,[11-14] and alkoxides[15,16] was reported. The nuclearity of these compounds is usually not more than 3 with the exception of $[Ba_6(OPh)_{12}(TMEDA)_4]$.[14] The compounds $[Ba_3(OSiPh_2O)_3(tetraglyme)_2]$,[9] $[Ba_2(OCPh_3)_4(THF)_3]$,[10] $[Ba_2(OSi^tBu_3)_4(THF)]$,[10] and $[Ba(BHT)_2(THF)_3]$[13] exemplify the use of bulky ligands to prevent a high degree of oligomerization. Another approach has been the use of multidentate ligands such as in $[Ba(OAr)_2(18\text{-crown-}6)]$[11] and $[N(C_2H_4O)(C_2H_4OH)_2]_2Ba$.[15] The high coordination number required by the large barium has thus far always been achieved by added neutral donor ligands such as THF,[9,11-13] TMEDA,[6,14] or the pendant arm of an amine alkoxide.[15] We now report the first structurally-characterized homoleptic alkoxide with an unusual cubic structure.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk and glovebox techniques. All solvents were purchased from Fisher Scientific and dried over alkali metal/benzophenone. They were then distilled and stored under nitrogen. Barium metal was purchased from Alfa Chemicals and was stored in a glovebox under nitrogen. All other reagents were from Aldrich. ^1H NMR spectra were recorded on a Varian XL-300 spectrometer, and chemical shifts were referenced to residual protio solvent peaks. The starting material $Ba[N(SiMe_3)_2]_2(THF)_2$ was synthesized according to literature methods.[17] The compound $\{Ba[N(SiMe_3)_2]_2\}_2$ was sublimed at a pressure of 10^{-3} Torr and a temperature of 160 °C.[17] The *tert*-butyl alcohol/heptane azeotrope was prepared by refluxing the mixture over calcium hydride and distilling under 1 atm of nitrogen, resulting in a concentration of 5.8 M, determined by ^1H NMR.

Synthesis of $[Ba(O^tBu)_2(HO^tBu)_2]_4$. In 5 mL of pentane was dissolved 0.55 g (0.91 mmol) of $Ba[N(SiMe_3)_2]_2(THF)_2$. To the solution was added 0.95 mL of 5.8 M (5.5 mmol) *tert*-butyl alcohol azeotrope. After 1 h of stirring at room temperature, the small amount of solid at the bottom of the reaction flask was removed by filtration. The resulting solution was put into a freezer (−15 °C). After 4 days, cube-shaped crystals suitable for X-ray diffraction had formed. Isolated yield: 70%. (By ^1H NMR, the yield is quantitative.) ^1H NMR (tol-d_8): 0.67 (s, OH), 1.18 (s, ^{t}Bu) ppm. $^{13}C\{^1H\}$ NMR: 36.2, 68.5 ppm.

The stoichiometries of both the ^{t}BuOH adduct (recrystallized from pentane) and the $[Ba(O^tBu)_2]_n$ polymer (see Results) were established by (reproducible) thermogravimetric analysis (up to 700 °C); melting points, in contrast, were not reversible or reproducible. The ^{t}BuOH adduct shows a two-step weight-loss profile. The first step begins already at 20 °C, and by 100 °C, the full (35%) mass loss corresponding to two ^{t}BuOH per Ba is observed. After a plateau, a second abrupt weight loss (31%) occurs centered around 360 °C, to leave BaO, together with some $BaCO_3$. The insoluble material shows only the second step (this confirms that the low-temperature process above is alcohol loss), and at essentially the same temperature.

X-ray Structure Determination of $[Ba(O^tBu)_2(HO^tBu)_2]_4$. A crystal of suitable size was obtained by cleaving a large piece of the sample in a nitrogen atmosphere glovebag. The crystal was mounted using silicone grease, and it was then transferred to a goniostat where it was cooled to −155 °C for characterization and data collection (Table 1). A selective search of a limited hemisphere of reciprocal space revealed a primitive cubic cell. Following the complete data collection ($6° < 2\theta < 45°$),[18] the condition $k = 2n$ for $0kl$ uniquely determined space group $Pa3$ (No. 205). Fourteen data were removed because of excessively high background counts. Data processing then gave a residual of 0.078 for the averaging of 3195 unique intensities which had been observed more than once. Four standards measured every 300 data points showed no significant trends. No correction was made for absorption. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the barium atoms were obtained from an initial E map. The positions of the remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and different Fourier calculation. Hydrogen atoms bonded to carbon atoms were included in fixed calculated positions with thermal parameters fixed at 1 plus the thermal parameters of the atoms to which they were bonded. A difference Fourier then revealed two of the anticipated hydrogens bonded to oxygen atoms in the asymmetric unit. The remaining hydrogens bonded to oxygen were necessarily disordered because the molecule lies on a crystallographic 3-fold axis. They were not observed in the difference maps and were not included in the refinement of the structure. In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal

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Table 1. Crystallographic Data[a] for $Ba_4(O^tBu)_8(HO^tBu)_8$

formula	$C_{64}H_{152}Ba_4O_{16}$	T, °C	−155
space group	$Pa3$	λ, Å	0.710 69
a, Å	25.766(4)	ρ_{calcd}, g cm^{-3}	1.34
V, Å^3	17 106.60	μ(Mo K$_\alpha$), cm^{-1}	18.7
Z	8	R	0.0582
fw	1727.26	R_w	0.0476

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^3/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected Bond Distances and Angles (deg) for $[Ba(O^tBu)_2(HO^tBu)_2]_4$

Ba(1)–O(3)	2.675(7)	O(8)–C(9)	1.412(23)
Ba(1)–O(3)B	2.703(7)	O(11)–C(12)	1.413(14)
Ba(1)–O(8)	2.728(6)	O(16)–C(17)	1.438(15)
Ba(1)–O(11)	2.673(8)	O(21)–C(22)	1.424(13)
Ba(1)–O(16)	2.798(8)	O(26)–C(27)	1.432(17)
Ba(1)–O(21)	2.773(8)	O(11)–H(49)	1.79(16)
Ba(2)–O(3)	2.706(7)	O(11)–H(50)	1.61(11)
Ba(2)–O(26)	2.698(9)	O(16)–H(49)	0.93(16)
O(3)–C(4)	1.458(13)	O(21)–H(50)	1.06(11)

O(3)–Ba(1)–O(3)B	77.5(3)	Ba(1)–O(3)–Ba(2)	101.53(24)
O(3)–Ba(1)–O(8)	76.19(23)	Ba(1)A–O(3)–Ba(2)	100.81(24)
O(3)B–Ba(1)–O(8)	75.73(23)	Ba(1)–O(3)–C(4)	118.1(6)
O(3)–Ba(1)–O(11)	113.03(24)	Ba(1)A–O(3)–C(4)	114.9(6)
O(3)B–Ba(1)–O(11)	157.99(23)	Ba(2)–O(3)–C(4)	115.3(6)
O(3)–Ba(1)–O(16)	109.42(25)	Ba(1)–O(8)–Ba(1)A	101.7(3)
O(3)B–Ba(1)–O(16)	103.67(24)	Ba(1)–O(8)–C(9)	116.42(24)
O(3)–Ba(1)–O(21)	164.49(24)	Ba(1)–O(11)–C(12)	148.6(8)
O(3)B–Ba(1)–O(21)	115.73(23)	Ba(1)–O(16)–C(17)	170.2(8)
O(8)–Ba(1)–O(11)	124.72(27)	Ba(1)–O(21)–C(22)	169.2(7)
O(8)–Ba(1)–O(16)	174.19(24)	Ba(2)–O(26)–C(27)	162.8(10)
O(8)–Ba(1)–O(21)	98.5(3)	Ba(1)–O(11)–H(49)	65.(5)
O(11)–Ba(1)–O(16)	55.10(25)	Ba(1)–O(11)–H(50)	71.(4)
O(11)–Ba(1)–O(21)	57.76(25)	C(12)–O(11)–H(49)	142.(5)
O(16)–Ba(1)–O(21)	76.44(26)	C(12)–O(11)–H(50)	127.(4)
O(3)–Ba(2)–O(3)A	76.95(24)	Ba(1)–O(16)–H(49)	62.(10)
O(3)–Ba(2)–O(26)	106.2(3)	C(17)–O(16)–H(49)	124.(10)
O(3)A–Ba(2)–O(26)	167.98(27)	Ba(1)–O(21)–H(50)	71.(6)
O(3)B–Ba(2)–O(26)	115.00(27)	C(22)–O(21)–H(50)	119.(6)
O(26)–Ba(2)–O(26)A	61.9(4)	O(11)–H(49)–O(16)	135.(14)
Ba(1)–O(3)–Ba(1)	103.76(25)	O(11)–H(50)–O(21)	160.(9)

parameters and H(49) and H(50) were varied with isotropic thermal parameters. The largest peak in the final difference map was 1.0 e/Å^3, and the deepest hole was −1.2 e/Å^3. The results of the structure determination are shown in Tables 1 and 2 and in Figure 1.

Results

Synthesis. The amide ligands in either $Ba(NR_2)_2(THF)_2$ or $Ba_2(NR_2)_4$ ($R = SiMe_3$) undergo immediate alcoholysis by ^tBuOH in pentane. Cooling of a concentrated solution gives a good yield of cubic crystals which were initially identified by X-ray diffraction (see below). We briefly defer discussion of NMR data but note that these crystals easily lose alcohol *in vacuo* or upon their removal from the mother liquor to give a material which is insoluble in benzene. The material is easily redissolved in pentane upon addition of *tert*-butyl alcohol. The process is thus simple alcohol loss, not the formation of some oxo complex (e.g., by accidental hydrolysis or ether formation).

Structural Description of $[Ba(O^tBu)_2(HO^tBu)_2]_4$. The X-ray study reveals a cubane-type structure, which was only recently observed for a barium phosphazene compound.[19] The cube is composed of four barium atoms linked together by four μ_3-alkoxy oxygen atoms, giving it approximate T_d symmetry (Figure 1). One terminal alkoxide and two alcohols are also coordinated to each of the barium atoms, giving a total of eight alkoxides and eight alcohols in the molecule. This results in each barium center having a distorted octahedral geometry.

A crystallographic C_3 axis passes through Ba(2) and O(8), resulting in four independent Ba–(μ_3-O) distances (2.675(7)–2.728(6) Å) which average 2.702 Å. The protons on the alcohols coordinated to Ba(1) were located and refined. The hydrogen atoms are in bonding distance to O(16) and O(21), at 0.93(16) and 1.06(11) Å, respectively. The Ba–O distances are longer for the oxygen atoms that are directly bound to a hydrogen atom as compared to the barium–terminal alkoxide distance (Ba–O(11) = 2.67 Å). The distances from Ba(1) to O(16) and O(21) (2.798(8) and 2.773(8) Å, respectively) are the longest in this molecule and are identical to within 3σ. It is of interest that the two hydrogen atoms form hydrogen bonds with the same oxygen atom, alkoxide oxygen O(11) (**A**). As a result, the distances from O(11) to O(16) and O(21) are shortened to 2.53 and 2.63 Å, respectively. Also, the angles O(11)–Ba(1)–O(16) and O(11)–Ba(1)–O(21) are compressed to 55.1(3) and 57.8(3)°, respectively. This is much smaller than the angle O(16)–Ba(1)–O(21) with 76.4(3)°. The Ba(1)–O–C angles to the alcohols (170.2(8) and 169.2(7)°) are more linear than to the hydrogen-bond acceptor O(11) (148.6(8)°). There is a crystallographic C_3 symmetry axis, so the protons on the alcohols bound to Ba(2) are disordered. All bond lengths and angles to Ba(2) are observed to be the average of those found at Ba(1). Alcohols that form dative bonds to the metal normally have longer O–M bonds than alkoxides. In general, alkoxide bonds to early transition and main group metals are believed to have some multiple-bond character, resulting in larger C–O–M bond angles as well as shorther M–O distances. The bond angle bound in the title compound is thus unusual, as the shorter Ba(1)–O distance involves the more bent ligand.

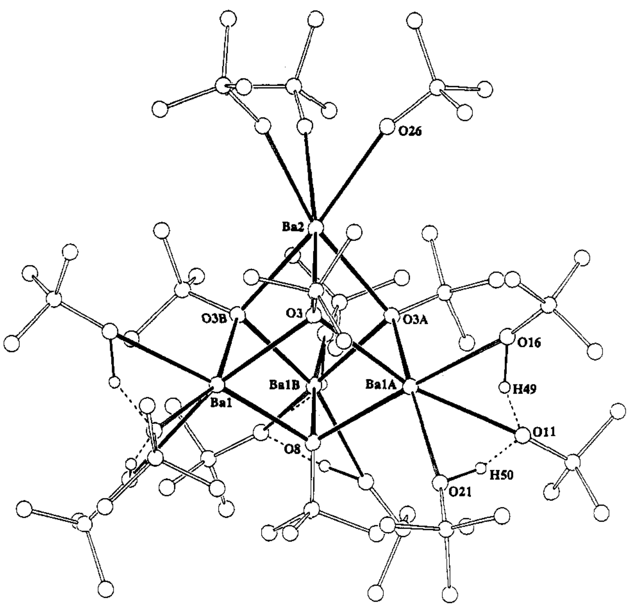
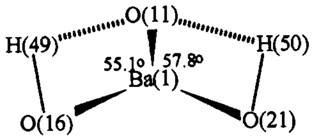


Figure 1. ORTEP drawing of the non-hydrogen atoms of $[Ba(O^tBu)_2(^tBuOH)_2]_4$ showing selected atom labeling. The C_3 axis lies vertically in this drawing, and the hydrogen bonding is shown around Ba(1) as dashed lines.



A

The angles of the distorted Ba_4O_4 cube are compressed at the metals with (μ_3-O)–Ba–(μ_3-O) bond angles ranging from 75.7(2) to 77.5(3)°. They are expanded at the μ_3-O with Ba–(μ_3-O)–Ba bond angles ranging from 100.8(2) to 103.8(3)°.

Solution Studies. To determine if the cubic structure found in the solid state persists in solution, two reactions were carried out in flame-sealed NMR tubes in toluene-d_8.

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(a) 1:4 Ba:^{t}BuOH Ratio. This is the same ratio as was found in the solid-state structure. In the NMR tube, 8 mol equiv of *tert*-butyl alcohol was reacted with $\{Ba[N(SiMe_3)_2]_2\}_2$. At room temperature only one *tert*-butyl peak was visible (1.23 ppm) together with a broad peak (2.26 ppm) assigned as the hydroxyl proton. At lower temperatures, the *tert*-butyl resonances shifted downfield to 1.46 ppm at −112 °C.[20] The hydroxyl peak disappeared at lower temperatures until it reappeared at −112 °C at 6.38 ppm. As only one chemical shift was observed for the *tert*-butyl peaks, the molecule is fluxional even at −112 °C. The exchange between bridging and terminal groups can thus not be frozen out.

(b) 1:8 Ba:^{t}BuOH Ratio. Since the above experiment showed all *tert*-butyl groups *within* the cube to be equivalent on the NMR time scale even at low temperatures, we attempted to freeze out the exchange *between* free and coordinated alcohol. This should give two separate *tert*-butyl resonances. Unfortunately, this was not realized since the observed chemical shift of the *tert*-butyl protons at each temperature was identical to that of the above 1:4 reaction. On the other hand, the hydroxyl protons did split at lower temperatures (at −112 and −117 °C). The hydroxyl proton of the coordinated alcohol had the same chemical shift as in the 1:4 reaction. The hydroxyl proton of the free alcohol had a chemical shift of 10.0 ppm. The integration of these two peaks showed a ratio of 1:2 (coordinated:free) that was expected for formation of the cube unaltered by the presence of free alcohol. The equivalence of the *tert*-butyl resonances must therefore be a case of accidental degeneracy.

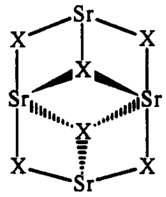
A white precipitate forms immediately upon addition of only 2 equiv of *tert*-butyl alcohol to $Ba[N(SiMe_3)_2]_2(THF)_2$. The precipitate redissolves upon addition of another 2 equiv of *tert*-butyl alcohol. This suggests that a polymeric barium *tert*-butoxide $[Ba(O^tBu)_2]_n$ is formed at the Ba:^{t}BuOH = 1:2 stoichiometry, but this reacts to form $[Ba(O^tBu)_2(HO^tBu)_2]_4$ upon addition of more *tert*-butyl alcohol. These two compounds are conveniently identified by their thermogravimetric behavior (see Experimental Section). Neither THF nor DME ($MeOC_2H_4OMe$) are able to break up the polymer, and thus the alcohol must be able to stabilize the cube in a way that DME as well as THF cannot. Furthermore, ^{1}H NMR experiments show that neither 2,2′-bipyridyl nor DME displaces the alcohol once the cubane structure has formed.

Discussion

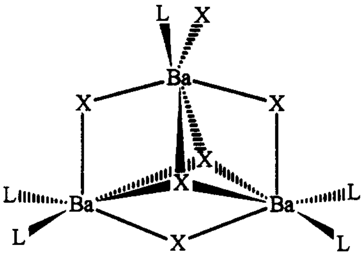
The synthesis of a hydrocarbon-soluble barium alkoxide devoid of oxo or hydroxo groups has been achieved by the simple procedure of alcoholysis of the amide ligands in $Ba[N(SiMe_3)_2]_2(THF)_2$. The use of relatively gentle Brønsted acid–base chemistry in this system minimized alternative (oxo-producing) reaction pathways which appear to be present in the redox chemistry involving bulk barium metal. A second advantage of this technique is that by using an isolable intermediate, $(Ba(NR_2)_2(L)_x)_y$, one avoids bulk metal impurities (oxides, hydroxides, etc.). The limited quantity of THF thereby introduced by the amide starting material does not bind detectably to the products. While the product from a 2:1 ^{t}BuOH:Ba ratio is insoluble in hydrocarbon solvent (i.e., is presumably polymeric), simple addition of more ^{t}BuOH to a benzene slurry of the insoluble product causes solubilization and formation of the product $[Ba(O^tBu)_2(^tBuOH)_2]_4$. This alcohol is apparently especially suited for forming a small aggregate. Not only does it complete coordinate number 6 for each metal, but it suppresses the Lewis basicity of each terminal $^tBuO^-$ group via *two* hydrogen bonds (thus preventing this terminal alkoxide from bridging to another cubane, with the consequence of diminished solubility). Such hydrogen bonding increases the thermodynamic stability of a ^{t}BuOH adduct, giving this Lewis base an advantage over other ligands lacking an acidic proton. The importance of the latter in the energetic balance between (soluble) cubane and (insoluble) polymer is evidently crucial, since even vacuum-drying is sufficient to remove ^{t}BuOH and return the insoluble polymer. It is also interesting to note that excess *tert*-butyl alcohol does not appear to split the cubane to dimeric or monomeric species (i.e., $Ba(O^tBu)_2(HO^tBu)_4$).

The ^{t}BuOH loss/addition is evidently also the cause of the rather uninformative ^{1}H NMR data. Not only is exchange with free ^{t}BuOH rapid at reduced temperature, but the (accidentally) small chemical shift difference between those of pure, intact $[Ba(O^tBu)_2(^tBuOH)_2]_4$ and free ^{t}BuOH in toluene aggravates the problem of achieving a decoalesced spectrum.

The cubane structure is frequently adopted by alkali metal alkoxides, $(MOR)_4$.[21] Noteworthy is the fact that this is its first determination for a heavier group 2 element. In marked contrast, $[Sr(OPh)_2]_4(PhOH)_2(THF)_6$ (another example of the $M_4(OR)_8L_8$ class) adopts the alternative structure **I**. The choice between the cube and **I** is subtle, since both produce the same metal coordinate number (6) and approximate octahedral geometry. There is not currently any basis for predicting when one of these two structures will be preferred. For a slightly different metal-to-neutral donor stoichiometry (1.67 rather than the 2.0 of **I**), the triangular form $Ba_3(\mu_3\text{-}X)_2(\mu_2\text{-}X)_3XL_5$ (**II**) is found.[14,22]



I



II

Conclusion

A soluble, oxide-free barium alkoxide is easily available via Brønsted acid–base chemistry between a barium amide and alcohol. This complex contains coordinated alcohols which should permit further chemistry at the metal center via reactions with Brønsted basic species.

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Supplementary Material Available: Tables of full crystallographic details, atom positional parameters, and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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