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Structural Relationships between Mono- and Dimeric Bis(alkoxides) and Bis(aryloxides) of Calcium and Barium. X-ray Crystal Structures of $M(OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3\cdot THF$ (M = Ca, Ba) and $[Ca(\mu\text{-}OR)(OR)(THF)]_2\cdot 2(toluene)$ [R = $C(C_6H_5)_2CH_2C_6H_4Cl\text{-}4$]

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Soluble alkoxides and aryloxides of calcium and barium have been prepared from the reaction of potassium salts of the alcohols and phenols with alkaline-earth diiodides. Reaction of the bulky aryloxide ligand $[OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4]^-$ with CaI_2 in THF generates a hydrocarbon-soluble compound of the formula $Ca(OAr)_2(THF)_3\cdot THF$. Single-crystal X-ray diffraction at −172 °C reveals it as a 5-coordinate monomeric species, in which the ligating oxygen atoms form a distorted trigonal bipyramidal arrangement about the calcium. The axis is formed by two THF ligands, with a nearly linear O–Ca–O angle of 177°; the third THF and the two aryloxide ligands lie in the equatorial plane, with an RO–Ca–OR angle of 152°. Use of $[OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4]^-$ with BaI_2 generates the $Ba(OAr)_2(THF)_3\cdot THF$ complex that X-ray crystallography reveals is isostructural with the calcium analog. In the barium aryloxide, the axis is again formed by two THF ligands, with an essentially linear O–Ba–O angle of 179°. The third THF and the two aryloxide ligands lie in the equatorial plane, with an RO–Ba–OR angle of 150°. Reaction of the bulky alkoxide $[OC(C_6H_5)_2CH_2C_6H_4Cl\text{-}4]^-$ with CaI_2 and recrystallization of the product from THF also produces a monomeric 5-coordinate species, analogous to the aryloxides. In the $Ca(OR)_2(THF)_3\cdot THF$ complex, the axis is formed by two THF ligands, with an O–Ca–O angle of 163°. The third THF and the two alkoxide ligands lie in the equatorial plane; the RO–Ca–OR angle of 126° is markedly reduced from that for the analogous aryloxide. Recrystallization of the monomer from toluene partially desolvates the complex and generates a calcium species of the formula $Ca(OR)_2(THF)$. In the solid state it exists as a dimer, $[Ca(\mu\text{-}OR)(OR)(THF)]_2$, with each calcium coordinated by a single terminal and two bridging alkoxide ligands and a single THF. A systematic comparison of structural relationships among these complexes emphasizes the contribution of ligand packing to their structures.

Introduction

Progress in the chemical and structural investigation of alkoxides and aryloxides of the alkaline-earth (Ae) metals, especially Ca, Sr, and Ba, has depended critically on the size of the OR^- and OAr^- ligands used. Historically the first alkoxides to be prepared were those containing sterically compact groups (OMe^-, OEt^-, etc.), which formed $Ae(OR)_2$ derivatives of low solubility and volatility.[1-3] Presumably oligomeric or polymeric, the constitution and structures of many of these materials are still not well defined.[4]

In the last several years, interest in compounds that might be relevant to materials development has reinvigorated the study of alkaline-earth alkoxides and aryloxides. Several of these compounds are large molecular aggregates, such as $Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2$,[5] the oxo–alkoxides and –aryloxides $[Ba_4(\mu_4\text{-}O)(\mu_2\text{-}OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6)_6]\cdot 3(toluene)$,[6] $HBa_5(O)(OPh)_9(THF)_8$,[7] $H_3Ba_6(O)(O\text{-}t\text{-}Bu)_{11}(OCEt_2CH_2O)(THF)_3$,[7] and $H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}$,[8] and the trinuclear siloxide $[Ba_3(OSiPh_3)_6(THF)]\cdot 0.5THF$.[9]

Our interest in the heavy pretransition elements[10-12] has lead us to examine mono- and dinuclear $Ae(OR)_2$ complexes of Ca, Sr, and Ba. Detailed understanding of the formation and reactions of these simpler compounds might then help illuminate the chemistry of more complex systems. Toward that end we report here the synthesis, structural characterization, and geometric relationships of several monomeric and dimeric complexes, including the structures of a monomeric and dimeric calcium alkoxide and monomeric calcium and barium aryloxides. While this work was in progress, the room-temperature structure of one of these molecules ($Ca(OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me)_2(THF)_3\cdot THF$) was reported,[13] and the preparation of its strontium and barium analogues has been described.[13,14] For ease of comparison with the other systems, we include our low-temperature determination of the calcium structure.

Experimental Section

All manipulations were performed with the exclusion of air and moisture. Chemicals were handled with high-vacuum or Schlenk techniques or in a Vacuum Atmospheres HE-143 drybox equipped with an MO40-1 recirculating purifier. Proton NMR spectra were obtained at 300 MHz with a Bruker AC-300 spectrometer and were referenced

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to the residual proton resonances of C_6D_6 (δ 7.15) or THF-d_8 (δ 3.58); carbon (^{13}C) NMR spectra were recorded at 50.3 MHz on a Bruker AC-200 spectrometer, respectively, and were referenced to the residual ^{13}C resonances of C_6D_6 (δ 128.0) or THF-d_8 (δ 25.0).

Infrared data were obtained on Perkin-Elmer 1430 or 1600 spectrometers; the KBr pellets were prepared as previously described.[15] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or Oneida Research Services, Whitesboro, NY.

Materials. Anhydrous calcium iodide and barium iodide (95%) were commercial samples (Strem Chemicals or Cerac) heated under vacuum to remove residual free iodine. Potassium hydride was obtained from Strem Chemicals or Aldrich as a dispersion in oil; it was washed with hexane and dried before use. HOC_6H_2-*t*-Bu_2-2,6-Me-4 (referred to as HBHT) and $HOC(Ph_2)_2CH_2C_6H_4Cl$-4 (referred to as Hclox) were purchased from Aldrich and used without further purification. They were converted into their potassium salts by reaction with excess KH in THF. Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were stirred over sodium or potassium and vacuum transferred before use.

Preparation of $Ca(BHT)_2(THF)_2$. KBHT (1.57 g, 6.06 mmol) and CaI_2 (0.751 g, 2.56 mmol) were added to a 125-mL Erlenmeyer flask. Tetrahydrofuran (75 mL) was added, and the mixture stirred for 24 h during which time a white solid precipitated. Filtration of the mixture through a fritted funnel and evaporation of the solvent yielded a white solid (1.40 g, 88%). Anal. Calc for $C_{38}H_{62}CaO_4$: C, 73.26; H, 10.03; Ca, 6.43. Found: C, 72.58; H, 10.24; Ca, 6.23. ^1H NMR (C_6D_6): δ 7.29 (s, 2H, C_6H_2), 3.54 (m, 8H, α-C_4H_8O), 2.45 (s, 3H, CH_3), 1.64 (s, 18H, C_4H_9), 1.19 (m, 8H, β-C_4H_8O). ^{13}C NMR data (50.3 MHz, C_6D_6): δ 136.6 (s, C_6-2,6), 125.5 (d, C_6-3,5), 120.2 (s, C_6-4), 69.7 (m, α-C_4H_8O), 35.1 (s, $C(CH_3)_3$), 31.4 (q, $C(CH_3)_3$), 25.1 (m, β-C_4H_8O), 21.7 (q, CH_3-4). Major IR bands (KBr pellet, cm^{-1}): 2883 (v br), 1415, 1381, 1279, 1221, 1031, 890, 820, 804, 509. Slow recrystallization of $Ca(BHT)_2(THF)_2$ from THF produces crystals of the $Ca(BHT)_2(THF)_3 \cdot THF$ solvate, which were used for X-ray analysis.

Preparation of $Ba(BHT)_2(THF)_2$. HBHT (0.880 g, 4.00 mmol) and KH (0.166 g, 4.15 mmol) were added to a 125-mL Erlenmeyer flask. Tetrahydrofuran (50 mL) was added with stirring, and during the next 30 min gas evolved and the initial pale yellow color of the mixture disappeared. Upon addition of BaI_2 (0.786 g, 2.01 mmol), the solution became cloudy, and filtration through a fritted funnel removed a white precipitate. The solvent was removed from the filtrate under vacuum until ca. 5 mL was left. Slow evaporation of the remaining solvent yielded a white solid (1.20 g, 83%). Anal. Calc for $C_{38}H_{62}BaO_4$: C, 63.37; H, 8.68; Ba, 19.07. Found: C, 63.59; H, 9.15; Ba, 18.28. ^1H NMR (C_6D_6): δ 7.27 (s, 2H, C_6H_2), 3.55 (m, 8H, α-C_4H_8O), 2.45 (s, 3H, CH_3), 1.66 (s, 18H, C_4H_9), 1.34 (m, 8H, β-C_4H_8O). Major IR bands (KBr pellet, cm^{-1}): 2886, 1424, 1372, 1290, 1216, 1035, 862, 817, 800, 495. Recrystallization of $Ba(BHT)_2(THF)_2$ from THF produces crystals of the $Ba(BHT)_2(THF)_3 \cdot THF$ solvate, which were used for X-ray analysis.

Preparation of $Ca(clox)_2(THF)_3 \cdot THF$. Potassium hydride (70 mg, 1.7 mmol) and Hclox (0.442 g, 1.43 mmol) were added to a 125-mL Erlenmeyer flask. THF (20 mL) was added and the mixture stirred for 70 min, during which time gas was evolved and the solution became yellow. Upon addition of CaI_2 (0.216 g, 0.735 mmol), a white precipitate formed, and the reaction mixture was allowed to stir overnight. After being allowed to settle, the supernatant liquid was removed by pipet and was evaporated to dryness under vacuum, leaving a fluffy white solid (0.51 g, 75%). Anal. Calc for $C_{56}H_{64}CaCl_2O_6$: C, 71.24; H, 6.83; Ca, 4.25; Cl, 7.51. Found: C, 71.51; H, 6.88; Ca, 6.75; Cl, 6.78. ^1H NMR (C_6D_6): δ 7.31 (d, 8H, J = 7.7 Hz), 7.10–7.01 (m, 12H), 6.84 (d, 4H, J = 8.4 Hz), 6.58 (d, 4H, J = 8.4 Hz) 3.41 (m, 20H, CH_2, α-C_4H_8O), 1.36 (m, 16 H, β-C_4H_8O). ^1H NMR (THF-d_8): δ 7.50 (d, 8H, J = 7.5 Hz), 7.12 (t, 8H, J = 7.3 Hz), 6.99 (m, 4H), 6.63 (m, 8H), 3.48 (s, 4H, CH_2). ^{13}C NMR (THF-d_8): δ 133.1, 127.8, 127.7, 127.5, 125.3 (methylene and quaternary carbons not observed). Major IR bands (KBr pellet, cm^{-1}): 3056, 2919, 1490, 1444, 1230, 1097, 1065, 1031, 1015, 823, 776, 754, 727, 700, 671, 617, 512.

Preparation of $[Ca(clox)_2(THF)]_2 \cdot 2(toluene)$. The preparation of $Ca(clox)_2(THF)_3 \cdot THF$ was repeated using 80 mg (2.0 mmol) of KH and 0.632 g (2.0 mmol) of Hclox in 75 mL of THF. After the mixture was stirred for 1 h and CaI_2 (0.294 g, 1.0 mmol) added, the reaction was allowed to stir for an additional 24 h. The isolated $Ca(clox)_2(THF)_3 \cdot THF$ was dissolved in an excess of toluene and the solution reduced in volume. Small aliquots of toluene were occasionally added during the evaporation to remove THF/toluene azeotropes. The solvent volume was eventually reduced to below 20 mL and placed in a vial for slow evaporation. Colorless crystals suitable for X-ray analysis formed. Yield: 0.57 g (68%). Anal. Calc for $C_{51}H_{48}CaCl_2O_3$: C, 74.71; H, 5.90; Ca, 4.89; Cl, 8.65. Found: C, 73.34; H, 5.47; Ca, 4.78; Cl, 9.70. ^1H NMR (C_6D_6): δ 7.33 (br), 7.25 (br), 7.15–6.91 (br m), 6.72 (d, J = 7.8 Hz), 6.57 (d, J = 6.1 Hz), 6.37 (d, J = 7.5 Hz), 3.40 (m, α-C_4H_8O), 3.29 (br s, CH_2), 2.10 (s, $CH_3C_6H_3$), 1.25 (br, β-C_4H_8O). ^{13}C NMR (C_6D_6): δ 147.5, 135.9, 132.5, 125.2, 68.1 (β-C_4H_8O), 51.4 (CH_2), 25.5 (β-C_4H_8O) (quaternary carbons not observed). Major IR bands (KBr pellet, cm^{-1}): 3000 (v br), 1595, 1490, 1444, 1406, 1232, 1065, 956, 885, 825, 778, 706, 671, 616, 576, 513.

Table I. Crystallographic Data for $Ca(BHT)_2(THF)_3 \cdot THF$

chem formula $C_{46}H_{78}CaO_6$	fw 767.21
a = 9.703 (2) Å	space group $P2_1$ (No. 4)
b = 15.209 (4) Å	λ = 0.710 69 Å
c = 15.360 (2) Å	ρ_{calcd} = 1.128 g cm^{-3}
β = 94.80 (1)°	μ = 1.76 cm^{-1}
V = 2259 (2) Å^3	$R(F_o)$ = 0.046
Z = 2	$R_w(F_o)$ = 0.044
T = −172 °C	

Table II. Crystallographic Data for $Ba(BHT)_2(THF)_3 \cdot THF$

chem formula $C_{46}H_{78}BaO_6$	fw 864.45
a = 10.034 (5) Å	space group $P2_1/c$ (No. 14)
b = 15.529 (5) Å	λ = 1.54178 Å
c = 31.355 (15) Å	ρ_{calcd} = 1.181 g cm^{-3}
β = 95.69 (5)°	μ = 67.73 cm^{-1}
V = 4862 (7) Å^3	$R(F_o)$ = 0.067
Z = 4	$R_w(F_o)$ = 0.069
T = 20 °C	

X-ray Crystallography of $Ca(BHT)_2(THF)_3 \cdot THF$. General procedures for data collection and reduction in use at Indiana University have been described previously.[16] A suitable colorless crystal measuring 0.25 × 0.30 × 0.30 mm was located and transferred using standard inert-atmosphere techniques to a Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator. The crystal was cooled to −172 °C for characterization and data collection. Relevant crystal and data collection parameters for the present study are given in Table I.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a monoclinic space group with a 2_1 axis along b—either $P2_1$ or $P2_1/n$. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric choice $P2_1$.

Data collection was performed using standard moving-crystal/moving-detector techniques with fixed backgrounds. Data were reduced to a unique set of intensities and associated errors in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. False symmetry in the E-maps proved to be somewhat troublesome in the initial solution, but by placement of the Ca atom and a fragment, the remainder of the structure was easily located. A difference Fourier synthesis revealed the location of most, but not all, hydrogen atoms. The hydrogen atom positions were therefore calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement. A final difference Fourier was featureless, and no absorption correction was performed. Positional parameters are supplied in Table IV; selected bond distances and angles are listed in Table V.

X-ray Crystallography of $Ba(BHT)_2(THF)_3 \cdot THF$. Crystals of $Ba(BHT)_2(THF)_3 \cdot THF$ were grown from THF. A prism measuring 0.40 × 0.45 × 0.10 mm was located and sealed in a quartz capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer at Vanderbilt University with graphite-monochromated Cu Kα radiation. Data were collected at 20 ± 1 °C. Relevant crystal and data collection parameters for the present study are given in Table II.

Although visually the crystal appeared to be well formed, examination on the diffractometer proved it to be twinned. The diffraction maxima located for the crystal during initial examination were deconvoluted using the program INDEX TWIN of the TEXSAN crystallographic package, and a primitive monoclinic unit cell was determined for the sample. Cell

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Table III. Crystallographic Data for $[Ca(\mu\text{-clox})(clox)(THF)]_2 \cdot 2(toluene)$

chem formula $C_{102}H_{96}Ca_2Cl_4O_6$	fw 819.92
$a = 13.517\ (2)$ Å	space group $P\bar{1}$ (No. 2)
$b = 15.782\ (2)$ Å	$T = 20$ °C
$c = 12.129\ (2)$ Å	$\lambda = 1.54178$ Å
$\alpha = 111.282\ (8)°$	$\rho_{calcd} = 1.242$ g cm^{-3}
$\beta = 107.205\ (9)°$	$\mu = 26.87$ cm^{-1}
$\gamma = 99.49\ (1)°$	$R(F_o) = 0.053$
$V = 2193\ (1)$ Å^3	$R_w(F_o) = 0.064$
Z (dimers/cell) = 1	

constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $9° < 2\theta < 20°$. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.65°. Although this represents a higher mosaicity than is normally desirable, no more suitable crystal could be found, and data collection was begun with this sample.

Data collection was performed using a continuous ω–2θ scan with stationary backgrounds. The intensities of three representative reflections measured after every 150 reflections showed no decay. On the basis of systematic absences, the space group was uniquely determined to be $P2_1/c$ (No. 14). Subsequent solution and refinement of the structure confirmed this choice. Data were reduced to a unique set of intensities and associated σ values in the usual manner. The barium atom was located in a Patterson map, and the structure was expanded with a combination of direct methods (DIRDIF) and Fourier techniques. An empirical absorption correction, using the program DIFABS, was applied that resulted in transmission factors ranging from 0.72 to 1.37. All non-hydrogen atoms associated with the $Ba(OR)_2(THF)_3$ unit were refined anisotropically; the lattice THF molecule, which displayed higher thermal parameters, was refined isotropically. As not all the hydrogens of the aryloxide were evident on a difference Fourier map, their positions were calculated using idealized geometries based on packing considerations and d(C–H) = 0.95 Å. The positions were fixed for the final cycles of refinement. A final difference map was featureless. Positional parameters are supplied in Table IV; selected bond distances and angles are listed in Table VI.

X-ray Crystallography of $[Ca(\mu\text{-clox})(clox)(THF)]_2 \cdot 2(toluene)$. Crystals of $[Ca(\mu\text{-clox})(clox)(THF)]_2 \cdot 2(toluene)$ were grown from toluene. A suitable prism measuring 0.20 × 0.40 × 0.40 mm was located and sealed in a quartz capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer at Vanderbilt University using the system described above with graphite-monochromated Cu Kα radiation. Data were collected at 20 ± 1 °C. Crystal and data collection parameters for the present study are given in Table III.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $60 < 2\theta < 80°$ corresponded to a triclinic cell. Subsequent solution and refinement of the structure confirmed the choice of $P\bar{1}$ (No. 2). The data were collected using the ω–2θ scan technique. The intensities of three representative reflections that were measured after every 200 reflections declined by −6.5%. A linear correction factor was applied to the data to account for this phenomena. An empirical absorption correction, based on azimuthal scans of several reflections, was applied that resulted in transmission factors ranging from 0.90 to 1.00. The calcium atoms were located from a Patterson map, and the structure was expanded using the program DIRDIF. All non-hydrogen atoms were refined anisotropically. As not all the hydrogen atoms were evident in difference maps, hydrogen atom positions were calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement. A final difference Fourier was featureless, and no absorption correction was performed. Positional parameters are supplied in Table IV; selected bond distances and angles are listed in Table VII.

Results

Synthesis of Alkoxides and Aryloxides. Reaction of the potassium salts of HBHT or Hclox with CaI_2 or BaI_2 in THF results in the precipitation of KI and the formation of bis(alkoxides) or –(aryloxides) (eq 1). The success of the reaction

$$2KOR + AeI_2 \xrightarrow{THF} Ae(OR)_2(THF)_n + 2KI\downarrow \qquad (1)$$

is insensitive to whether the potassium salt is preformed or formed in situ. It also is stoichiometrically precise, and complications do not seem to arise from incorporation of free alcohol or phenol into the product, as has been observed in systems involving direct reaction with the metals.[5,7,8] As KI is virtually insoluble in THF, halide contamination is minimal. The method is not suited, however, to the formation of alkoxides that are only slightly soluble in ethers, as their separation from the residual alkali halide would be difficult.

Although complexes containing BHT have been previously described for several s-, p-, and f-block metals,[17–19] we are unaware of any prior use of the $[OC(C_6H_5)_2CH_2C_6H_4Cl\text{-}4]^-$ ("clox") ligand to form alkoxide complexes. It is a usefully bulky alkoxide, as the parent alcohol is inexpensive and the anion readily forms crystalline complexes.[20]

The complex originally isolated from the reaction of K[clox] with CaI_2 in THF is a white, thermally stable, hydrocarbon-soluble solid with the empirical formula $Ca(clox)_2(THF)_4$. The ^1H NMR spectrum contains the expected signals for the $[clox]^-$ ligand; although the crystal structure of the solid indicates that only three of the THF molecules are coordinated in the solid state (see below), there is no evidence of more than one type of THF in the NMR spectrum. In solution, all four ligands could be interchanging rapidly on the NMR time scale.

The complex readily loses THF on recrystallization from toluene and produces a new material with the empirical formula $Ca(clox)_2(THF)(toluene)$. The material is stable in the absence of air and moisture and displays no tendency to desolvate further. Assuming that the toluene is not coordinated to the metal center, this material would have the unusually low coordination number of 3 for the calcium center. An X-ray crystal structure revealed that this degree of undersaturation is relieved in the solid state by dimerizing, raising the coordination number to 4. The dimer may persist in solution as well, as the resonances for the clox ligand in the ^1H NMR spectrum in C_6D_6 are not well resolved; this may reflect the existence of more than one type of alkoxide and/or slow tumbling in solution.

Solid-State Structures. $Ca(BHT)_2(THF)_3 \cdot THF$. As previously observed at room temperature,[13] the $Ca(BHT)_2(THF)_3$ complex crystallizes as a monomer, with two THF ligands on the axis and the third THF and the aryloxides in the equatorial plane of a distorted trigonal bipyramid (Figure 1). The Ca and three equatorial oxygen atoms are planar to within 0.05 Å. The axial O–Ca–O angle is nearly linear at 177.2 (1)°, but the equatorial RO–Ca–OR angle of 152.0 (1)° is markedly opened over the 120° expected for an ideal trigonal bipyramid. The C_6 planes of the BHT ligands form an angle of 11.9° with each other, and the "mean plane" of the equatorial THF ligand is turned 75.9° from the CaO_3 plane.

The Ca–O–C(aryloxide) angles are almost linear, with Ca(1)–O(2)–C(3) and Ca(1)–O(18)–C(19) being 171.3 (3) and 173.9 (3)°, respectively. The reason for the commonly-observed linearity of M–O–C angles (and shortened M–O bonds) of aryloxides of electropositive metals has been much discussed,

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Table IV. Fractional Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms

$Ca(BHT)_2(THF)_3 \cdot THF$

atom	x/a ($\times 10^4$)	y/b ($\times 10^4$)	z/c ($\times 10^4$)	B_{iso} ($\times 10$ Å^2)[a]	atom	x/a ($\times 10^4$)	y/b ($\times 10^4$)	z/c ($\times 10^4$)	B_{iso} ($\times 10$ Å^2)[a]
Ca(1)	5145 (1)	2244[b]	2816 (1)	13	C(28)	4535 (6)	256 (4)	1193 (4)	23
O(2)	6630 (3)	1701 (2)	3834 (2)	16	C(29)	352 (6)	1680 (5)	−1525 (4)	33
C(3)	7381 (5)	1285 (4)	4480 (3)	18	C(30)	2689 (6)	3698 (4)	735 (3)	21
C(4)	7630 (5)	361 (3)	4433 (3)	15	C(31)	4263 (5)	3875 (4)	824 (4)	24
C(5)	8448 (5)	−39 (3)	5113 (3)	17	C(32)	2097 (6)	3883 (4)	1612 (4)	25
C(6)	8987 (5)	400 (3)	5841 (3)	16	C(33)	2090 (6)	4406 (4)	88 (4)	28
C(7)	8725 (5)	1298 (4)	5883 (3)	18	O(34)	5116 (3)	3767 (2)	3149 (2)	18
C(8)	7943 (5)	1750 (3)	5227 (3)	11	C(35)	4118 (5)	4230 (4)	3651 (3)	20
C(9)	7060 (5)	−186 (4)	3649 (3)	19	C(36)	4468 (7)	5185 (4)	3586 (5)	42
C(10)	5469 (5)	−115 (4)	3550 (3)	21	C(37)	5926 (7)	5206 (4)	3430 (5)	40
C(11)	7671 (5)	116 (4)	2815 (3)	22	C(38)	6161 (5)	4390 (4)	2909 (3)	21
C(12)	7388 (6)	−1170 (4)	3762 (4)	27	O(39)	3280 (3)	2030 (2)	3737 (2)	17
C(13)	9827 (5)	−53 (4)	6585 (3)	21	C(40)	1824 (5)	2168 (4)	3478 (3)	21
C(14)	7743 (5)	2746 (4)	5333 (3)	19	C(41)	1054 (6)	1415 (4)	3861 (3)	24
C(15)	6202 (5)	2977 (4)	5289 (4)	24	C(42)	2119 (6)	957 (4)	4479 (4)	33
C(16)	8417 (6)	3233 (4)	4598 (4)	23	C(43)	3317 (5)	1599 (4)	4568 (3)	19
C(17)	8409 (5)	3119 (4)	6198 (3)	20	O(44)	6970 (3)	2389 (3)	1868 (2)	19
O(18)	3650 (3)	2102 (2)	1683 (2)	16	C(45)	8433 (5)	2442 (4)	2140 (3)	24
C(19)	2851 (5)	2014 (3)	939 (3)	17	C(46)	9167 (5)	1939 (4)	1467 (4)	28
C(20)	2456 (5)	1149 (4)	619 (3)	19	C(47)	8128 (8)	1872 (9)	716 (5)	97
C(21)	1629 (5)	1077 (4)	−157 (4)	21	C(48)	6884 (5)	2257 (6)	937 (3)	36
C(22)	1182 (5)	1790 (4)	−652 (3)	21	O(49)	5926 (5)	1266 (3)	8648 (3)	48
C(23)	1546 (5)	2615 (4)	−341 (3)	18	C(50)	4563 (6)	1543 (4)	8796 (4)	35
C(24)	2377 (5)	2762 (4)	443 (3)	16	C(51)	4385 (7)	2455 (5)	8417 (5)	48
C(25)	2947 (5)	307 (4)	1105 (3)	20	C(52)	5460 (6)	2483 (4)	7764 (4)	35
C(26)	2438 (6)	−537 (4)	653 (4)	29	C(53)	6576 (7)	1929 (4)	8186 (4)	38
C(27)	2404 (5)	284 (4)	2018 (4)	24					

$Ba(BHT)_2(THF)_3 \cdot (THF)$

atom	x/a	y/b	z/c	B_{iso} (Å^2)[a]	atom	x/a	y/b	z/c	B_{iso} (Å^2)[a]
Ba(1)	0.4941 (1)	0.23714 (7)	0.86215 (4)	4.29 (5)	C(28)	0.230 (2)	0.454 (2)	0.858 (1)	9 (2)
O(2)	0.652 (1)	0.248 (1)	0.9236 (4)	5.3 (7)	C(29)	0.013 (3)	0.467 (2)	0.6710 (8)	10 (2)
C(3)	0.726 (2)	0.252 (1)	0.961 (1)	6 (2)	C(30)	0.244 (3)	0.196 (1)	0.736 (1)	7 (2)
C(4)	0.759 (3)	0.329 (2)	0.977 (1)	6 (2)	C(31)	0.185 (2)	0.149 (1)	0.7719 (9)	7 (2)
C(5)	0.846 (3)	0.341 (2)	1.018 (1)	7 (2)	C(32)	0.386 (2)	0.183 (1)	0.7378 (8)	8 (2)
C(6)	0.900 (3)	0.277 (2)	1.043 (1)	8 (2)	C(33)	0.169 (3)	0.157 (1)	0.695 (1)	8 (2)
C(7)	0.865 (3)	0.196 (2)	1.027 (1)	8 (2)	O(34)	0.496 (2)	0.066 (1)	0.8428 (6)	8 (1)
C(8)	0.786 (2)	0.183 (2)	0.987 (1)	5 (2)	C(35)	0.397 (3)	0.006 (2)	0.8573 (8)	8 (2)
C(9)	0.715 (3)	0.418 (2)	0.955 (1)	7 (2)	C(36)	0.397 (3)	−0.060 (2)	0.823 (2)	20 (4)
C(10)	0.767 (2)	0.424 (1)	0.912 (1)	8 (2)	C(37)	0.530 (4)	−0.062 (2)	0.809 (1)	15 (3)
C(11)	0.565 (2)	0.425 (1)	0.950 (1)	8 (2)	C(38)	0.588 (3)	0.023 (2)	0.820 (1)	10 (2)
C(12)	0.773 (3)	0.503 (2)	0.982 (1)	12 (2)	O(39)	0.698 (1)	0.259 (1)	0.8115 (5)	7.2 (9)
C(13)	0.982 (3)	0.282 (2)	1.0843 (9)	14 (2)	C(40)	0.690 (3)	0.312 (2)	0.774 (1)	12 (2)
C(14)	0.746 (2)	0.093 (2)	0.9713 (8)	5 (2)	C(41)	0.817 (3)	0.357 (3)	0.776 (1)	18 (3)
C(15)	0.591 (3)	0.080 (1)	0.963 (1)	8 (2)	C(42)	0.907 (3)	0.316 (2)	0.807 (1)	14 (3)
C(16)	0.794 (3)	0.075 (2)	0.927 (1)	10 (2)	C(43)	0.838 (2)	0.241 (2)	0.8255 (8)	10 (2)
C(17)	0.788 (3)	0.018 (2)	1.001 (1)	14 (3)	O(44)	0.287 (1)	0.215 (1)	0.9121 (6)	7 (1)
O(18)	0.341 (1)	0.3027 (8)	0.8072 (5)	4.9 (8)	C(45)	0.294 (3)	0.237 (3)	0.956 (1)	18 (3)
C(19)	0.266 (2)	0.339 (2)	0.7778 (9)	5 (2)	C(46)	0.164 (4)	0.264 (3)	0.966 (1)	14 (3)
C(20)	0.233 (2)	0.432 (2)	0.7761 (8)	5 (1)	C(47)	0.078 (3)	0.256 (3)	0.927 (1)	15 (3)
C(21)	0.145 (2)	0.465 (2)	0.742 (1)	7 (2)	C(48)	0.149 (3)	0.212 (2)	0.8957 (9)	11 (2)
C(22)	0.102 (2)	0.414 (3)	0.7067 (8)	8 (2)	O(49)	0.354 (4)	0.264 (3)	0.588 (1)	29 (1)
C(23)	0.134 (3)	0.328 (2)	0.708 (2)	13 (3)	C(50)	0.443 (3)	0.325 (2)	0.567 (1)	13 (1)
C(24)	0.213 (2)	0.291 (1)	0.7388 (9)	4 (1)	C(51)	0.583 (5)	0.274 (3)	0.586 (1)	22 (1)
C(25)	0.284 (3)	0.484 (1)	0.8171 (8)	7 (2)	C(52)	0.537 (4)	0.201 (3)	0.562 (1)	18 (1)
C(26)	0.244 (3)	0.582 (1)	0.8107 (9)	11 (2)	C(53)	0.459 (4)	0.186 (3)	0.603 (1)	20 (1)
C(27)	0.443 (3)	0.483 (1)	0.823 (1)	10 (2)					

$[Ca(\mu\text{-clox})(clox)(THF)]_2 \cdot 2(toluene)$

atom	x/a	y/b	z/c	B_{iso} (Å^2)[a]	atom	x/a	y/b	z/c	B_{iso} (Å^2)[a]
Ca(1)	0.06532 (6)	0.12633 (5)	0.07876 (7)	4.40 (2)	C(29)	0.4018 (4)	0.0113 (3)	0.2864 (5)	6.3 (2)
O(2)	0.0098 (2)	0.2461 (2)	0.0996 (2)	4.69 (8)	Cl(29)	0.5334 (1)	0.0443 (1)	0.2919 (2)	10.29 (7)
C(3)	−0.0326 (3)	0.3224 (3)	0.1345 (3)	4.6 (1)	C(30)	0.3852 (4)	0.0420 (3)	0.3990 (4)	6.8 (2)
C(4)	−0.0484 (3)	0.3644 (3)	0.0344 (4)	5.3 (1)	C(31)	0.2801 (4)	0.0166 (3)	0.3925 (4)	6.1 (2)
C(5)	0.0519 (3)	0.3949 (3)	0.0110 (3)	4.7 (1)	C(32)	−0.1131 (3)	−0.0486 (3)	0.2086 (4)	5.0 (1)
C(6)	0.1363 (3)	0.4781 (3)	0.0977 (4)	5.1 (1)	C(33)	−0.1955 (3)	−0.0308 (3)	0.1294 (4)	5.7 (1)
C(7)	0.2285 (3)	0.5041 (3)	0.0751 (4)	5.7 (1)	C(34)	−0.3034 (4)	−0.0648 (3)	0.1106 (5)	7.2 (2)
C(8)	0.2356 (3)	0.4467 (3)	−0.0369 (4)	5.8 (2)	C(35)	−0.3299 (5)	−0.1186 (4)	0.1716 (6)	8.4 (2)
Cl(8)	0.3531 (1)	0.4780 (1)	−0.0642 (2)	9.35 (6)	C(36)	−0.2491 (5)	−0.1380 (4)	0.2492 (6)	8.4 (2)
C(9)	0.1534 (4)	0.3655 (3)	−0.1250 (4)	6.4 (2)	C(37)	−0.1420 (4)	−0.1029 (3)	0.2681 (4)	6.5 (2)
C(10)	0.0619 (4)	0.3403 (3)	−0.1012 (4)	5.8 (1)	C(38)	0.0486 (3)	0.0982 (3)	0.3430 (3)	4.6 (1)
C(11)	−0.1434 (3)	0.2862 (3)	0.1425 (4)	4.9 (1)	C(39)	−0.0056 (3)	0.1317 (3)	0.4236 (3)	5.3 (1)
C(12)	−0.1481 (3)	0.2315 (3)	0.2089 (4)	5.7 (1)	C(40)	0.0358 (4)	0.2246 (3)	0.5200 (4)	6.5 (2)
C(13)	−0.2441 (4)	0.1963 (3)	0.2194 (5)	6.7 (2)	C(41)	0.1318 (5)	0.2852 (3)	0.5398 (4)	6.9 (2)

Table IV (Continued)

[Ca(μ-clox)(clox)(THF)]$_2$·2(toluene)

atom	x/a (×10^4)	y/b (×10^4)	z/c (×10^4)	B_{iso} (×10 Å^2)^a	atom	x/a (×10^4)	y/b (×10^4)	z/c (×10^4)	B_{iso} (×10 Å^2)^a
C(14)	−0.3366 (4)	0.2152 (4)	0.1641 (5)	7.3 (2)	C(42)	0.1871 (4)	0.2528 (3)	0.4624 (4)	6.1 (2)
C(15)	−0.3326 (4)	0.2705 (4)	0.0999 (5)	7.6 (2)	C(43)	0.1456 (3)	0.1606 (3)	0.3649 (4)	5.2 (1)
C(16)	−0.2372 (4)	0.3061 (3)	0.0883 (4)	6.3 (2)	O(44)	0.2530 (2)	0.2167 (2)	0.1578 (3)	5.6 (1)
C(17)	0.0430 (3)	0.4034 (3)	0.2679 (4)	4.8 (1)	C(45)	0.3593 (4)	0.2227 (4)	0.2385 (5)	7.6 (2)
C(18)	0.1451 (4)	0.4023 (3)	0.3308 (4)	5.6 (1)	C(46)	0.4337 (5)	0.3154 (5)	0.2692 (7)	11.7 (3)
C(19)	0.2144 (4)	0.4767 (3)	0.4509 (4)	6.9 (2)	C(47)	0.3818 (5)	0.3481 (5)	0.1809 (7)	12.3 (3)
C(20)	0.1811 (5)	0.5525 (3)	0.5083 (4)	7.5 (2)	C(48)	0.2698 (4)	0.2840 (3)	0.1033 (4)	6.2 (2)
C(21)	0.0798 (5)	0.5548 (3)	0.4463 (5)	7.4 (2)	C(49)	0.7555 (7)	0.2388 (5)	0.5972 (8)	13.1 (4)
C(22)	0.0110 (4)	0.4812 (3)	0.3273 (4)	6.2 (2)	C(50)	0.6611 (5)	0.2618 (4)	0.6309 (5)	8.4 (2)
O(23)	0.0109 (2)	0.0016 (2)	0.1207 (2)	4.43 (8)	C(51)	0.6310 (7)	0.2314 (5)	0.7102 (7)	11.5 (3)
C(24)	0.0054 (3)	−0.0030 (3)	0.2324 (3)	4.5 (1)	C(52)	0.5474 (8)	0.2560 (8)	0.7423 (8)	13.6 (5)
C(25)	0.0771 (4)	−0.0654 (3)	0.2689 (4)	5.6 (1)	C(53)	0.4898 (6)	0.3100 (9)	0.700 (1)	14.2 (5)
C(26)	0.1922 (3)	−0.0390 (3)	0.2767 (4)	5.1 (1)	C(54)	0.5235 (6)	0.3399 (6)	0.6186 (7)	12.4 (4)
C(27)	0.2132 (3)	−0.0711 (3)	0.1657 (4)	5.6 (1)	C(55)	0.6063 (5)	0.3172 (5)	0.5868 (5)	8.7 (2)
C(28)	0.3179 (4)	−0.0458 (3)	0.1703 (4)	6.3 (2)					

^{a} Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610. ^{b} Not varied.

Table V. Selected Bond Lengths (Å) and Angles (deg) in Ca(BHT)$_2$(THF)$_3$·THF

Distances			
Ca(1)–O(2)	2.197 (3)	Ca(1)–O(44)	2.395 (3)
Ca(1)–O(18)	2.181 (3)	O(2)–C(3)	1.340 (6)
Ca(1)–O(34)	2.373 (4)	O(18)–C(19)	1.333 (6)
Ca(1)–O(39)	2.411 (3)		
Angles			
O(2)–Ca(1)–O(18)	152.03 (14)	O(18)–Ca(1)–O(44)	90.00 (11)
O(2)–Ca(1)–O(34)	103.47 (13)	O(34)–Ca(1)–O(39)	88.99 (12)
O(2)–Ca(1)–O(39)	90.65 (12)	O(34)–Ca(1)–O(44)	93.68 (13)
O(2)–Ca(1)–O(44)	89.63 (12)	O(39)–Ca(1)–O(44)	177.17 (13)
O(18)–Ca(1)–O(34)	104.46 (13)	Ca(1)–O(2)–C(3)	171.3 (3)
O(18)–Ca(1)–O(39)	88.43 (12)	Ca(1)–O(18)–C(19)	173.9 (3)

Table VI. Selected Bond Lengths (Å) and Angles (deg) in Ba(BHT)$_2$(THF)$_3$·THF

Distances			
Ba(1)–O(2)	2.38 (1)	Ba(1)–O(44)	2.75 (1)
Ba(1)–O(18)	2.42 (1)	O(2)–C(3)	1.32 (3)
Ba(1)–O(34)	2.72 (1)	O(18)–C(19)	1.26 (3)
Ba(1)–O(39)	2.73 (1)		
Angles			
O(2)–Ba(1)–O(18)	150.8 (5)	O(18)–Ba(1)–O(44)	89.8 (5)
O(2)–Ba(1)–O(34)	103.5 (5)	O(34)–Ba(1)–O(39)	88.4 (5)
O(2)–Ba(1)–O(39)	89.1 (4)	O(34)–Ba(1)–O(44)	91.5 (5)
O(2)–Ba(1)–O(44)	91.6 (5)	O(39)–Ba(1)–O(44)	179.3 (6)
O(18)–Ba(1)–O(34)	105.7 (5)	Ba(1)–O(2)–C(3)	172 (1)
O(18)–Ba(1)–O(39)	89.6 (5)	Ba(1)–O(18)–C(19)	177 (1)

Table VII. Selected Bond Lengths (Å) and Angles (deg) in [Ca(μ-clox)(clox)(THF)]$_2$·2(toluene)

Distances			
Ca(1)···Ca(1)′	3.581 (2)	O(2)–C(3)	1.400 (4)
Ca(1)–O(2)	2.105 (2)	O(23)–C(24)	1.405 (4)
Ca(1)–O(23)	2.268 (2)	Cl(8)–C(8)	1.746 (4)
Ca(1)–O(23)′	2.299 (2)	Cl(29)–C(29)	1.744 (4)
Ca(1)–O(44)	2.401 (3)		
Angles			
O(2)–Ca(1)–O(23)	129.77 (9)	O(23)–Ca(1)–O(44)	118.85 (9)
O(2)–Ca(1)–O(23)	117.01 (9)	Ca(1)–O(23)–Ca(1)	103.23 (9)
O(2)–Ca(1)–O(44)	93.91 (9)	Ca(1)–O(2)–C(3)	167.4 (2)
O(23)–Ca(1)–O(23)′	76.77 (9)	Ca(1)–O(23)–C(24)	132.2 (2)
O(23)–Ca(1)–O(44)	122.67 (9)	Ca(1)–O(23)–C(24)	123.9 (2)

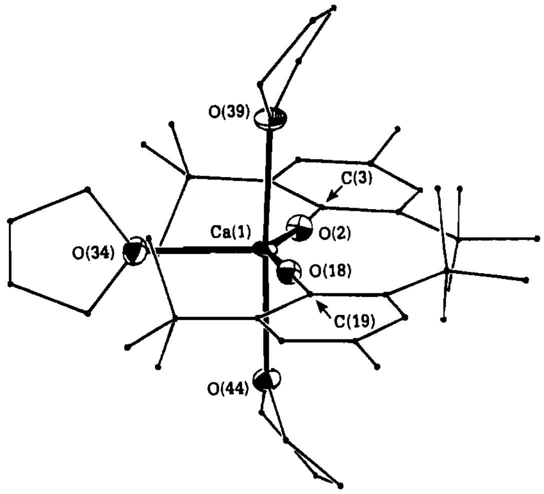

Figure 1. ORTEP diagram of Ca(BHT)$_2$(THF)$_3$·THF, displaying the numbering scheme used in the text. Thermal ellipsoids are shown at the 50% level, and the parts of the ligands not directly bonded to the metal center are presented as lines. The hydrogen atoms and lattice solvent have been omitted for clarity.

and both steric effects and π-bonding (i.e., $\mathrm{M}\overset{\cdot\cdot}{-}\mathrm{O}\overset{\cdot\cdot}{-}\mathrm{C}$)have been suggested as contributors.[22,23] The latter is not as unlikely for the alkaline-earth metals as it might first appear, as alkoxides and aryloxides are good π-donor ligands,[24] and calcium has been shown to possess low-lying d orbitals that can influence the structure of molecules.[25-27] In practice, steric and electronic effects can be difficult to separate experimentally, although clearly linearization does occur in aryloxide complexes even when steric influences can be ruled out.[22] Rothwell has demonstrated, however, that the M–O–C angle is a "soft" parameter that has no simple correlation with the degree of π-bonding in d^0 complexes.[22]

It is instructive to note the changes in the present low-temperature structure (−172 °C) from that reported at room temperature.[13] As expected, there is a small shrinkage in the average bond lengths (approximately 1%) on lowering the temperature, although there is no consistent difference in the bond angles. Interestingly, the small changes of the bond distances and angles exert a more noticeable cumulative effect on the nonbonding contacts. For example, the closest nonbonding Ca···CH$_3$ contact to a *tert*-butyl group changes from 3.9 Å at room temperature to 3.77 Å in the present structure. This is of no chemical significance here, but the effect of temperature in

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(25) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 491–497.

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(27) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360–1366.

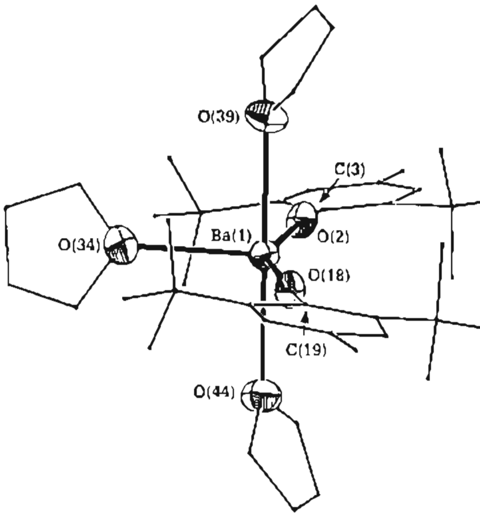

Figure 2. ORTEP diagram of $Ba(BHT)_2(THF)_3{\cdot}THF$, using the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level, and the parts of the ligands not directly bonded to the metal center are represented as lines. For clarity, the hydrogen atoms and lattice solvent have been omitted.

modifying such nonbonded contacts may be important in the structure of larger systems.

$Ba(BHT)_2(THF)_3{\cdot}THF$. Although the barium picrate of Hughes and Wingfield is the first monomeric bis(aryloxide) of barium to be structurally characterized,[28] the $Ba(BHT)_2(THF)_3{\cdot}THF$ barium complex reported here represents the first monomeric barium complex containing only monodentate aryloxides. It crystallizes from THF as the trisolvate as a distorted five-coordinate trigonal bipyramidal monomer (Figure 2). Remarkably, despite the 0.35-Å difference in radii,[29] the calcium and barium aryloxides are isostructural. As with the calcium analog, two THF ligands form the axis and the third THF and the aryloxides lie in the equatorial plane of a trigonal bipyramid. The plane containing the Ba and three oxygen atoms is planar to within 0.04 Å. The axial O–Ba–O angle is almost exactly linear at 179.3 (6)°, but the equatorial RO–Ba–OR angle of 150.8 (5)° is only slightly less than the 152.0 (1)° observed in the calcium analog. The similarity with the calcium complex extends to the orientation of the equatorial THF ligand with respect to the MO_3 plane (83.6°) and to the angle between the rings in the BHT ligands (12.0°). The lattice solvent does not interact with the complex (closest contact > 4.2 Å).

Although it might be reasonable to assume that interligand contacts between the *t*-Bu groups of the BHT ligands are responsible for the wide BHT–Ca–BHT angle in $Ca(BHT)_2(THF)_3$ (closest $C(H_3)\cdots C(H_3)'$ approach = 3.69 Å), the analogous contact in the $Ba(BHT)_2(THF)_3$ structure is 4.15 Å, well outside the sum of the van der Waals radii for two methyl groups.[30] There is no obvious steric constraint that would prevent the BHT ligands from moving more closely to each other and narrowing the RO–Ba–OR angle.

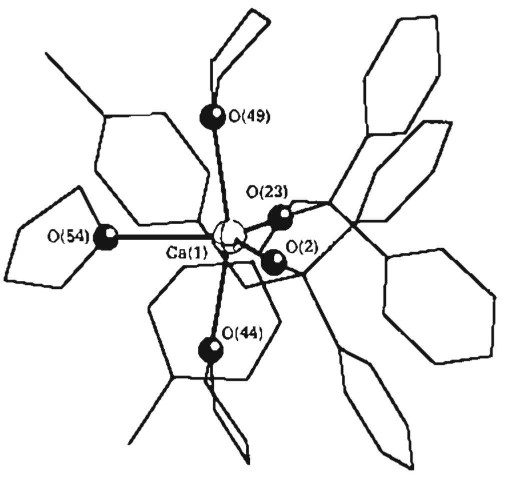

Figure 3. Proposed structure of $Ca(clox)_2(THF)_3{\cdot}THF$, displaying the numbering scheme used in the text.

$Ca(clox)_2(THF)_3{\cdot}THF$. The bis(alkoxide) formed from the clox ligand did not form crystals that diffracted well, and consequently its structure determined by X-ray diffraction was not high-resolution.[31] Although the structure can be discussed only semiquantitatively, it is a five-coordinate species analogous to the calcium and barium BHT structures. It represents the first crystallographically examined mononuclear bis(alkoxide) of calcium. As with the aryloxide complexes, two alkoxide and three THF ligands are coordinated to the metal center; a fourth THF crystallizes in the lattice, but is more than 4.9 Å away from the atoms of the complex (Figure 3). Even qualitatively it can be seen that the axis of a trigonal bipyramid is formed by two THF ligands is bent away from the clox ligands, and the THF–Ca–THF angle is distinctly nonlinear (ca. 163°). Interestingly, the RO–Ca–OR angle of 126° is much closer to the ideal 120° than is the case with the aryloxide complexes. The clox anion evidently has more flexibility in the packing of its rings than does BHT.

$[Ca(clox)_2(THF)]_2{\cdot}2(toluene)$. When $Ca(clox)_2(THF)_3{\cdot}THF$ is recrystallized from toluene, THF ligands are lost, and an alkoxide results with the empirical formula $Ca(clox)_2(THF){\cdot}{}^1/_2(toluene)$. This formula suggested the improbably low (although not unprecedented[32]) coordination number of 3 for calcium. Crystals of the substance proved to be suitable for X-ray diffraction and yielded a higher quality structure than did $Ca(clox)_2(THF)_3{\cdot}THF$.

In the solid state, the complex is a dimer, with each calcium coordinated by one terminal alkoxide ligand and one THF and the two metals joined by two slightly asymmetrically bridging alkoxide groups (Figure 4). This is the first structurally characterized example of a dinuclear calcium alkoxide. The coordination number of the calcium centers is 4, and a crystallographically imposed inversion center relates the two halves of the dimer. A molecule of toluene was found in the crystal lattice, but it is more than 3.7 Å away from the dimer and displays no interaction with it.

The $Ca\cdots Ca'$ separation of 3.581 (2) Å is the shortest found thus far in a molecular alkoxide; the only shorter $Ca\cdots Ca'$ separation in a molecular species is observed in $\{Ca[N(SiMe_3)_2]_2\}_2$ at 3.521 (2) Å.[32] These distances can be compared to the Ca–Ca' distance in the metal of 3.95 Å.[33] The four oxygen atoms around the calcium centers describe a distorted tetrahedron, with an O(2)–Ca(1)–O(44) angle of 93.91 (9)° and an O(23)–Ca(1)–O(23)' angle of 76.77 (9)°. The calcium–oxygen distances follow an expected progression from 2.105 (2) Å (Ca–terminal alkoxide)

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(28) Hughes, D. L.; Wingfield, J. N. *J. Chem. Soc., Chem. Commun.* **1977**, 804–805.

(29) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(30) Pauling, L. *The Nature of the Chemical Bond*; 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 261.

(31) Attempts were made to grow crystals from THF that would be suitable for X-ray, but only poorly diffracting samples could be obtained. The best of these was triclinic, space group $P\bar{1}$ (No. 2), with a = 13.546 (7) Å, b = 19.583 (8) Å, c = 10.824 (4) Å, α = 99.03 (3)°, β = 110.00 (3)°, γ = 73.36 (4)°, and D_{calcd} = 1.215 g cm^{-3} for $Z = 2$. Of the 5320 unique reflections that were collected at 20 °C, only 1326 were considered observed ($I > 3\sigma(I)$). Although the structure was readily solved with a combination of Patterson maps and direct methods, the large number of atoms in the structure combined with the paucity and relatively low quality of the data yielded a high residual ($R = 0.11$). The structure is clearly monomeric and appears to be isomorphous with the BHT analog, but obviously bond distances and angles are not as accurate.

(32) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 127–140.

(33) In CRC Handbook; Weast, R. C., Ed.; Chemical Rubber Co.: Cleveland, OH, 1986; Vol. 67, p F-159.

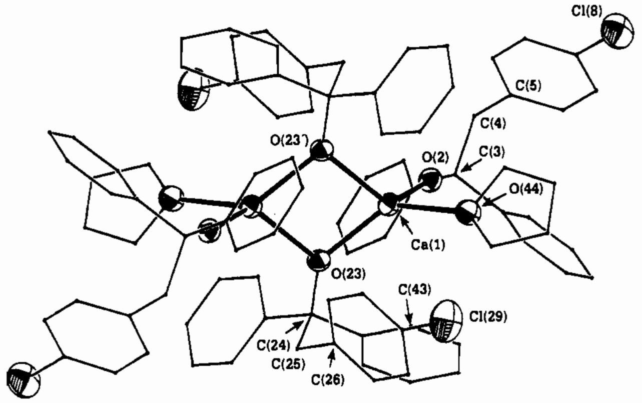

Figure 4. ORTEP diagram of $[\mathrm{Ca}(\mu\text{-clox})(\mathrm{clox})(\mathrm{THF})]_2\cdot 2(\mathrm{toluene})$, giving the numbering scheme used in the text. Thermal ellipsoids are drawn at the 30% level, and except for chlorine, the parts of the ligands not directly bound to the metal are shown as lines. For clarity, the hydrogen atoms and lattice solvent have been omitted.

to 2.268 (2) and 2.299 (2) Å (Ca–bridging alkoxides) to 2.401 (3) Å (Ca–THF). The difference between the Ca–(μ-OR) distances is 0.03 Å, statistically (>7σ) but not chemically significant. A carbon atom of one phenyl ring (C43) lies within 3.12 Å of the metal center, but the tipped orientation of the ring does not suggest that any significant Ca···C interaction is present.

The geometry of the clox ligand can be examined more quantitatively in this molecule than in the monomer. For example, atoms attached to the quaternary carbons (C(3) and C(24)) form normal tetrahedra, but the ipso carbons of the benzyl groups do not lie in planes bisecting the angle between the phenyl rings (see Figure 4). In the terminal alkoxide, the torsion angle O(23)–C(24)–C(25)–C(26) is 51.4°, and in the bridging alkoxide the O(2)–C(3)–C(4)–C(5) angle is 55.5°.

Discussion

Structural Relationships in Alkaline-Earth Alkoxides. The paucity of structural data on alkaline-earth alkoxides has hindered attempts at systematizing the available experimental data, although Bradley's structural theory[34] and the distinction between "primary" and "secondary" (dative) bonding developed by Alcock[35] and Haaland[36] have been used in some cases.[5] The need for such elaborations has become greater in recent years, as simple interligand repulsion theories such as VSEPR[37] are not always completely adequate to predict the structures of molecular alkoxides. This was discussed in detail for the unusual cadmium complex $\mathrm{Cd(BHT)_2(THF)_2}$, which adopts a square-planar geometry, rather than one based on a tetrahedron as expected on the basis of VSEPR.[18]

The monomeric and dimeric structures described here offer an unusual chance to compare the structures of the molecules with other alkoxides containing low-coordinate metal centers and to attempt a ranking of the relative importance of various influences on the structures of these systems. Several comparisons can be drawn among the BHT structures alone, including the occurrence of trigonal bipyramidal structures with axial THF ligands and the facts that the Ca and Ba compounds are isostructural and that the isoleptic ytterbium(II) structure reported by Lappert[38] is square pyramidal, rather than trigonal bipyramidal.

That the $\mathrm{Ca(BHT)_2(THF)_3}$ structure is trigonal bipyramidal would have been predicted on simple electrostatic grounds. The observed arrangement of the two BHT ligands and a THF group in the equatorial plane allows the BHT ligands to avoid as many sterically unfavorable 90° interactions as they would experience if they were on the axis. An M–O–Ar angle near 180° is often observed in compounds of electropositive elements,[22] and even two coordinated THF groups would encounter high steric resistance from axial BHT ligands. It is worth noting that in the square planar $\mathrm{Cd(BHT)_2(THF)_2}$ complex,[18] the Cd–O–BHT angles are bent at 127.6 (4)°, thus preventing steric interference between the *t*-Bu groups.

If the primary geometry-determining feature in the $\mathrm{Ae(OAr)_2(THF)_3}$ complexes is the arrangement of two BHT ligands and a THF group in a distorted trigonal arrangement, other features of the structure become understandable. Relative to the plane defined by the metal atom and three oxygen atoms (two from the OAr groups, one from THF), the THF ligand must lie nearly perpendicularly to them; this configuration is observed in $\mathrm{Ca(BHT)_2(THF)_3}$, $\mathrm{Ba(BHT)_2(THF)_3}$, and, despite the differences in ligands, the $\mathrm{Ca(clox)_2(THF)_3}$ complex. In the aryloxides, the BHT ligands twist somewhat to avoid each other's *t*-Bu groups. The two additional THF groups can then be inserted above and below the $\mathrm{MO_3}$ plane in the pockets between the OR groups and the equatorial THF. With the $\mathrm{Ca(BHT)_2(THF)_3}$ and $\mathrm{Ba(BHT)_2(THF)_3}$ complexes, the additional THF groups form nearly linear RO–M–OR angles.[39]

The unusual square pyramidal geometry of the $\mathrm{Yb(BHT)_2(THF)_3}$ complex[38] should be analyzed further here, especially since the radii of $\mathrm{Ca^{2+}}$ and $\mathrm{Yb^{2+}}$ differ only by 0.02 Å,[29] the ions both possess noble gas electron configurations, and the elements are similarly electropositive. We note that the RO–Yb–OR angle of 154.8 (10)° is close to that observed in the $\mathrm{Ca(BHT)_2(THF)_3}$ complex (152.0 (1)°), and as with the calcium species, the equatorial THF is oriented perpendicularly to the BHT plane. The major difference comes from the smaller angle between the two additional THF ligands of 163.8 (7)°. This amount of bending places the O atoms of the THF ligands in a plane with the oxygens of the BHT groups. Interestingly, this THF–Yb–THF angle (163.8 (7)°) is indistinguishable from that found in $\mathrm{Ca(clox)_2(THF)_3}$ (163°).

The reason for the THF–Yb–THF bending observed in the Yb complex is not obvious. As $\mathrm{Yb^{2+}}$ has a closed-shell f^{14} electron configuration, there is no orbital support for a square planar geometry. Lappert identified a long-range interaction (3.4 Å) between the Yb and one of the methyl groups of the BHT ligands, but this distance is outside the sum of the radii of $\mathrm{Yb^{2+}}$ and the methyl group (2.95 Å),[30] and it seems unlikely that this is a *cause* of the bending. The contact does have the effect of providing the molecule with a distorted pseudooctahedral geometry. Evidently there is some flexibility possible in the arrangement of the THF groups around the metal centers. In any case, it has long been recognized that the energetic difference between trigonal bipyramidal and square-based pyramidal geometries is small enough that crystal packing forces can affect it.[40]

Metal–Oxygen Distances. Some indication of the nature of the bonding between the metal and O-donor ligands in the alkoxides and aryloxides can be had by calculating the differences between the M–O distances and the metal radii. This provides an "effective radius" for oxygen, which is tabulated for a variety of complexes in Table VIII. It is noteworthy that the effective O radius for $\mathrm{Ca^{2+}}$ complexes with monodentate ligands is between 1.18 and 1.28 Å (average 1.25 Å), and the values for the Ca–

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[34] Bradley, D. C. *Nature* **1958**, *182*, 1211–1214.

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[36] Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1007.

[37] Bader, R. F. W.; Gillespie, R. J.; MacDougall, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7329–7336.

[38] Deacon, G. B.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; MacKinnon, P.; Newnham, R. H. *J. Chem. Soc., Chem. Commun.* **1989**, 935–937.

[39] A reviewer has noted that the three THF ligands and the four *t*-Bu groups of the BHTs could be viewed as generating a distorted pentagonal bipyramidal geometry around the metal centers; the BHTs could even be considered a type of "chelating" ligand. Although it interleaves elements of the primary and secondary coordination spheres, this description emphasizes the importance of nonbonding ligand groups to the coordination environment of the metals.

[40] Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p 146.

Table VIII. M–O Distances and Effective Oxygen Radii of Terminal and Doubly Bridging Alkoxide, Siloxide, and Aryloxide Ligands and Ethers in Calcium and Barium Complexes

complex	μ_x-O[a]	M–OR[b]	CN at M	eff O radius[c]	M–O_{ether}[b]	CN at M	eff O radius[c]	ref
Calcium Complexes								
$Ca(BHT)_2(THF)_3 \cdot THF$	1	2.19 (av)	5	1.26	2.39 (av)	5	1.46	this work
$Ca(BHT)_2(THF)_3 \cdot THF$	1	2.21 (av)	5	1.28	2.41 (av)	5	1.48	13
$Ca_9(O(CH_2)_2OMe_{18}(O(CH_2)_2OMe)_2$	2	2.29 (av)	6.74 (av)	1.24	2.60 (1)	*d*		5
$Ca(OC_6H_3(NO_2)_2\text{-}2,4)(H_2O)_6(OC_6H_3(NO_2)_2\text{-}2,4)$	1	2.361 (5)	8	1.18	2.478 (5) (av)	8	1.30	42
$[Ca(\mu\text{-clox})(clox)(THF)]_2$	1	2.105 (2)	4	1.27	2.401 (3)	4	1.56	this work
	2	2.28 (av)	4	1.44				
Barium Complexes								
$Ba(BHT)_2(THF)_3 \cdot THF$	1	2.40 (av)	5	1.10	2.73 (av)	5	1.43	this work
$Ba_4(O)[OC_6H_2(CH_2NMe_2)_3 2,4,6]_6$	2	2.72 (av)	7	1.34				this work
$Ba_3(OSiPh_3)_6(THF)$	1	2.472 (4)	5	1.17	2.75 (1)	5	1.45	9
	2	2.64 (4) (av)	4.67	1.36				28
$Ba(O_2CC_6H_3(NO_2)_3\text{-}2,4,6)_2(C_{24}H_{32}O_8)$	1	2.67, 2.71	10	1.15, 1.19				
$HBa_5(O)(OPh)_9(THF)_8$	1	2.32 (1)	6	0.97	2.80 (4) (av)	6	1.45	7
	2	2.65 (3)	7	1.27				
$H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(THF)_3$	1	2.57 (2), 2.73 (2)[e]	5		2.81 (2), 2.83 (2), 2.95 (2)	6	1.46, 1.48, 1.60	7
	2	2.58 (1)–2.65 (1)	5,6	1.26–1.30				

[a] x is the number of metal atoms that the atom bridges. [b] Distances are from the metal to anionic oxygen atoms (Å). [c] "Effective radii" (in Å) are calculated as described in the text. Radii of calcium and barium less than six-coordinate are not well-defined. Extrapolation of the six-coordinate values to lower numbers can be made using Pauling's formula (ref 30, pp 537 ff) and gives the values 0.93 Å (5-coordinate), 0.84 Å (4-coordinate), and 0.74 Å (3-coordinate) for Ca^{2+} and 1.30 Å (5-coordinate), 1.24 Å (4-coordinate), and 1.16 Å (3-coordinate) for Ba^{2+}. These values are only rough approximations but are useful for comparisons. [d] The ether functionalities are part of the alkoxide group and cannot be directly compared with terminal ethers. [e] These distances may be distorted by hydrogen bonding and cannot reliably be used to calculate oxygen radii.

THF distances are approximately 0.20 Å greater. This difference is approximately the same as the values in the $Zn(BHT)_2(THF)_2$ complex,[17] and both the M–OR and M–THF bonds in these complexes qualify as "primary" or structure determining.[36]

It is interesting that the average oxygen (terminal-OR) radius for the barium complexes is smaller than that found for calcium, i.e., 1.10 Å, ranging from a minimum of 0.97 Å with $HBa_5(O)(OPh)_9(THF)_8$[7] to 1.19 Å in the barium picrate complex.[28] These values mean that the increase in Ae–OR distance on going from calcium to barium is smaller than the increase in metal radii. The Ba–ether distances have increased as expected, however, and thus the difference between the radii has grown to an average of 0.36 Å. On the basis of the observed geometries, the Ba–ether interactions must still be considered when analyzing the structures. They may be approaching "dative" status,[36] however, and if so, they follow the trend of increasing length (=decreasing strength) of "dative" bonds relative to "primary" bonds of the heavier main-group elements.[18] It also might be noted that the trends identified for the mononuclear Ca and Ba systems also apply to the aggregated species, at least in those cases where terminally-bound ligands are involved. Distances in the bridging ligands appear to be more variable, and analogous patterns are not as evident.

$[Ca(\mu\text{-clox})(clox)(THF)]_2 \cdot 2(toluene)$. Although the structure of "$Ca(clox)_2(THF)_2$" has not been determined, there is no reason to think that it should not adopt a tetrahedral geometry, analogous to that found for the $Yb(BHT)_2(THF)_2$ species.[38] With only one THF ligand available, however, the hypothetical 3-coordinate monomeric "$Ca(clox)_2(THF)$" species is apparently unstable and dimerizes to raise the coordination number of the calcium to 4.

Despite the substantial difference in the metals and the donor ligands, the bis(clox) calcium structure is paralleled in the series of cobalt alkoxides and siloxides studied by Power, particularly the species $[Co(\mu\text{-}OSiPh_3)(OSiPh_3)THF]_2]$.[41] For the terminal ligands, the effective oxygen radius can be calculated as the difference between the average Co–(O) length of 1.85 (1) Å and the 4-coordinate radius of Co^{2+} (0.58 Å). The value of 1.27 Å is identical with the value found for the Ca complex. A similar calculation for the bridging ligands (average Co–(μ-O) length = 1.99 (1) Å) leads to an oxygen radius of 1.41 Å, nearly identical with the value of 1.44 Å found for the Ca complex. Interestingly, the close parallelism does not apply to the THF ligands: the average Co–THF distance of 2.03 Å for the cobalt siloxide complex translates into an oxygen radius of 1.45 Å, whereas the corresponding value is 1.56 Å in the calcium alkoxide. The similar oxygen radii for the bridging siloxide and the THF ligands emphasize that the distinction between "primary" and "secondary" bonding observed in main-group alkoxides may not apply with equal force in transition metal complexes.

Conclusion

This study of monomeric and dimeric alkaline-earth alkoxides has served to highlight distinctive features of their formation and structures. They are available by means of a relatively straightforward metathetical preparation, and their structures are generally understandable in terms of interligand repulsion theories. Although metal radii have been thought in the past to play a key role in fixing metal–ligand distances, it appears that the *packing* of ligands around the metal may be just as critical and can lead to isostructural molecules even with large change in radii, as with the $M(BHT)_2(THF)_3$ molecules. We expect that a similar global ligand analysis will be important in defining the structures of polymetallic alkoxides, although the variety of ligand bonding modes typically found there will make the analysis less straightforward.

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Supplementary Material Available: Tables of hydrogen atom fractional coordinates, bond distances and angles involving hydrogen atoms, and anisotropic thermal parameters (19 pages). Ordering information is given on any current masthead page.

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(41) Sigel, G. A.; Bartlet, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773–1780.

(42) Cole, L. B.; Holt, E. M. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1997–2002.

(43) Two other monomeric barium complexes that should be mentioned in this regard are the hydrogen-bonded $Ba(2,6\text{-}t\text{-}Bu_2C_6H_3O)_2(HOCH_2CH_2NMe_2)_4$ (Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Folting, K. *Inorg. Chem.* **1991**, *30*, 1500–1503) and the alkoxide $Ba[N(OC_2H_4)(OHC_2H_4)_2]_2 \cdot EtOH$ (Poncelet, O.; Hubert-Pfalzgraf, L. G.; Toupet, L.; Daran, J. C. *Polyhedron* **1991**, *10*, 2045–2050). Neither of these can be easily compared to the complexes here; the former lacks direct Ba–OAr interactions, and the long effective oxygen radius calculated for the latter (1.33 Å) may be a consequence of restrictions imposed by the chelating ethanolamine and the uncertainty in distinguishing Ba–OR and Ba–O(H)R distances in the structure.