Heterometallic Fluoroalkoxides of Barium and Copper(I). Syntheses and Structures of $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$ and $[(THF)_2Ba_2Cu_2(HFTB)_6]$

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

Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405-4001

Received February 27, 1997[⊗]

Reaction of HOR_F and *in situ* synthesized $[Ba(OR_F)_2]$ (from $Ba[N(SiMe_3)_2]_2(THF)_2$ and HOR_F) with CuMes yields, in THF, $[(THF)_2Ba_2Cu_2(OCMe(CF_3)_2)_6]$. In the case of $HOR_F = HOCMe_2CF_3$, only upon addition of Me_3NO is a soluble product obtained: $[(Me_3NO)_2Ba_2Cu_4(OCMe_2CF_3)_8]$. $[(THF)_2Ba_2Cu_2(OCMe(CF_3)_2)_6]$ has a square-planar $Ba_2Cu_2O_4$ core structure with two additional alkoxides bridging the two bariums, giving the barium a tbp coordination environment. The structure of $[(Me_3NO)_2Ba_2Cu_4(OCMe_2CF_3)_8]$ is markedly different in that it has one more Cu−(OR) unit inserted into the Ba−(OR)−Ba unit. This gives the Ba_2Cu_4 core structure the shape of an octahedron and barium a square-pyramidal coordination environment. These structures are compared and contrasted with the structures of $[Ba_2Cu_4(OCEt_3)_8]$, $[(Et_3PO)_2Ba_2Cu_4(O^tBu)_8]$, and $[(Me_3NO)_2Ba_2Cu_4(O^tBu)_8]$.

Introduction

Solubility of barium alkoxides in hydrocarbon solvents and even donor solvents such as the parent alcohol is often very poor.[1] This is in part due to the large size of the barium metal center, which requires a large number of ligands; coordination numbers as large as 11 are known.[2] Two possible methods have been used to circumvent this solubility problem. One is to use a neutral ligand that will coordinate to the barium metal center, preventing polymerization by bridging to an alkoxide of a neighboring molecule. A second method is to prevent polymerization with an even more bulky ligand. A variation on this theme is the use of fluorinated alkoxides, which are bulkier than their fluorine-free analogs.[3] Another advantage of fluorinated ligands is the possibility that intramolecular barium−fluorine interactions help to increase the metal coordination number, leading to less aggregated, more soluble compounds. Heterometallic alkoxides of barium should also follow this trend, because even these compounds are often insoluble. In addition to solubility, the increased volatility displayed by fluorinated alkoxides (over the nonfluorinated analogs) has been exploited by other workers.[4] Heterometallic fluoroalkoxides are thus of interest for their potentially increased volatility and solubility. Examples include $[Pb_2Li_2(HFIP)_6]$,[5] $[Tl_2Zr(HFIP)_6]$,[6] $[Na_2Y(HFTB)_5(THF)_3]$,[7] $[Na_2Zr(HFIP)_6](C_6H_6)$,[6] $[Na_3Y(HFIP)_6(THF)_3]$,[7] $[Na_2Cu(HFIP)_4]$,[8] $[YNa_3(HFIP)_6(THF)_3]$,[9] and $[NaCu(HFIP)_2(2,2,6,6\text{-tetramethylheptane-3,5-dionate})]_n$.[9] A systematic study of a particular dimetal system with a set of different fluorinated alkoxides has not yet been carried out. We have therefore investigated a system of barium copper heterometallic alkoxides which allows us to study the relationship of fluorination to structure, as well as metal stoichiometry.

Experimental Section

All manipulations were carried out under an inert atmosphere (argon, nitrogen, helium) or *in vacuo* using standard Schlenk techniques. All solvents were purchased from Fisher Scientific and dried over alkali metal/benzophenone. They were distilled and stored under argon. In reactions involving monovalent copper, the solvents were degassed in three consecutive freeze−pump−thaw cycles. Barium metal was purchased from Alfa/Aesar Chemicals and was stored in a glovebox under argon. The fluorinated alcohols trifluoro-*tert*-butyl alcohol (HTFTB) and hexafluoro-*tert*-butyl alcohol (HHFTB) were purchased from Oakwood Research Chemicals, dried over molecular sieves, and stored under argon. Hexamethyldisilazane was purchased from Janssen Chimica, and all other reagents were obtained from Aldrich. The starting materials $Ba[N(SiMe_3)_2]_2(THF)_2$[10] and CuMes (copper mesityl)[11] were synthesized according to literature methods. ^1H (300 MHz) and ^{19}F NMR (282 MHz) spectra were run on a Varian Gemini 2000 spectrometer. Samples were run in C_6D_6, $CDCl_3$, and/or C_6F_6 (internal references for ^{19}F NMR $C_6F_6 = -164.9$ ppm, and perfluorotoluene (methyl) $= -59.0$ ppm; internal reference for ^1H NMR $C_6D_6 = 7.15$ ppm). Elemental analyses were performed in-house using a Perkin-Elmer PE2400 CHNS/O elemental analyzer. X-ray diffraction experiments were carried out on a Scintag XDS-2000 diffractometer using Cu K radiation and a solid-state Ge detector. Mass spectra were carried out on a Kratos MS-80 RFA mass spectrometer, calibrated from 169 to 1961 amu with Ultramark 2500F. Samples were introduced using a direct-insertion probe, and they were never heated above 130 °C to avoid decomposition. Thermogravimetric analyses (TGA) were carried out on a Dupont 2100 instrument inside a helium-filled glovebox. TGA profiles were run under a flow of helium (1 atm, 70 cm^3/min) at a heating rate of 5 °C/min to a final temperature of 1000 °C. Sample sizes were 7−15 mg.

Synthesis of $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (1). To a solution of 4.0 g (6.7 mmol) of $Ba[N(SiMe_3)_2]_2(THF)_2$ in 30 mL of pentane was added

---

* Corresponding author. E-mail: caulton@indiana.edu.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) Mehrotra, R. C.; Singh, A.; Sojani, S. *Chem. Soc. Rev.* **1994**, 215.
(2) Drozdov, A.; Troyanov, S. *Main Group Met. Chem.* **1996**, *19*, 547.
(3) Banks, R. E. *Fluorocarbons and their Derivatives*; American Elsevier Publishing Co., Inc.: New York, 1970.
(4) (a) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978. (b) Samuels, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Chem. Mater.* **1995**, *7*, 929.
(5) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.*, in press.
(6) Samuels, J. A.; Lobkovsky, E. B.; Streib, W. E.; Folting, K.; Huffman, J. C.; Zwanziger, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5093.
(7) Laurent, F.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 3980.
(8) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.* **1991**, *30*, 2812.
(9) Labrize, E.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1995**, *14*, 881.
(10) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121.
(11) Mayer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

S0020-1669(97)00234-6 CCC: $14.00

Table 1. Crystallographic Data

	$[(THF)_2Ba_2Cu_2[OCMe(CF_3)_2]_6]$	$[(Me_3NO)_2Ba_2Cu_4(OCMe_2CF_3)_8]$
formula	$C_{32}H_{34}Ba_2Cu_2F_{36}O_8$	$C_{38}H_{66}Ba_2Cu_4F_{24}N_2O_{10}$
fw	1632.31	847.87
space group	$P\bar{1}$	$C2/c$
T, °C	−169	−58
a, Å	11.280(2)	28.001(8)
b, Å	20.086(3)	11.312(3)
c, Å	11.175(2)	22.221(7)
α, deg	92.24(1)	
β, deg	92.22(1)	117.11(1)
γ, deg	85.87(1)	
V, Å^3	5240.14	6264.92
λ,[a] Å	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	2.150	1.798
μ, cm^{-1}	25.5	26.875
Z	2	8
R[b]	0.0557	0.0643
R_w[c]	0.0574	0.0659

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

1.8 mL (14.3 mmol) of HHFTB. The solution was stirred for 2 h, after which all volatiles were removed *in vacuo*. Toluene (30 mL) and 5 mL of THF were then added to the solid, and 900 μL (7.2 mmol) of HHFTB was syringed into the resulting solution. Via a solids addition tube, 1.2 g (6.7 mmol) of CuMes was added. After 2 h of reflux, the solvent was removed *in vacuo*. Crystallization from Et_2O resulted in 3.6 g (4.5 mmol, 72%) of product. X-ray-quality crystals could be obtained from an NMR tube reaction in a mixed (70% benzene and 30% THF) solvent system. ^{1}H NMR (F_8tol/THF-d_8, 80:20%; −20 °C): 1.79 (6H, s, Ba−HFTB−Ba), 1.70 (18H, s, Ba−HFTB−Cu) 1.83 (8H, m, THF), 3.67 (8H, m, THF) ppm. ^{19}F NMR (F_8tol, THF-d_8, 80:20%; 20 °C): −80.6 (24F, s, Ba−HFTB−Cu), −77.7 (12F, s, Ba−HFTB−Ba) ppm. Anal. Calcd for $Ba_2Cu_2F_{36}O_8C_{32}H_{34}$: C, 23.32; H, 2.10. Found: C, 23.55; H, 2.00.

Synthesis of $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$ (2). To a solution of 4.0 g (6.7 mmol) of $Ba[N(SiMe_3)_2]_2(THF)_2$ in 30 mL of pentane was added 1.6 mL (14.3 mmol) of HTFTB. The solution was stirred for 2 h, after which all volatiles were removed *in vacuo*. THF (30 mL) was then added to the solid, and 1.6 mL (14.3 mmol) of HTFTB was syringed into the resulting solution. Via a solids addition tube, 2.4 g (13.1 mmol) of CuMes was added. A solid formed after several minutes, and 500 mg (6.66 mmol) of Me_3NO was then added. After reflux for 1 h, the solvent was removed *in vacuo*, and the solid was crystallized from Et_2O, to yield 3.0 g (4.56 mmol, 69%) of product. X-ray-quality crystals could be obtained from reaction in an NMR tube in a mixed (70% benzene and 30% THF) solvent system. ^{1}H NMR (C_6F_6/THF-d_8, 80:20%): 1.66 (48H, s), 3.55 (18H, s) ppm. ^{19}F NMR (C_6F_6/THF-d_8, 80:20%): −81.2 (s) ppm. Anal. Calcd for $Ba_2Cu_4F_{24}O_{10}C_{38}H_{66}$: C, 27.14; H, 3.98; N, 0.83. Found: C, 28.04; H, 4.32; N, 1.08.

Solid-State Structure of $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (1). The compound was air-sensitive and was handled in a nitrogen-atmosphere glovebag. The crystals used were mounted using silicone grease and were then transferred to a goniostat where they were cooled to −169 °C for characterization and data collection (1° < 2θ < 50°). Characterization led to a triclinic cell (Table 1), and an initial choice of space group $P\bar{1}$ was later proven correct by the successful solution of the structure. Data processing after an analytical absorption correction (0.52−0.73) produced a set of 8911 unique intensities and an $R_{av} = 0.068$ for the averaging of 3094 of these which had been observed more than once. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the Ba and Cu atoms were obtained from an initial E map. The positions of the remaining non-hydrogen atoms were obtained from iterations of a least-squares refinement and a difference Fourier calculation. The two molecules in the unit cell are each at a crystallographic center of symmetry; i.e., the asymmetric unit contains two half-molecules. Two $(CF_3)_2CH_3CO$ ligands, one bridging the barium and copper atoms in the first molecule (atoms 1−43) and one bridging the two barium atoms in the second molecule (atoms 44−86), are disordered. The two CF_3 groups and the CH_3 group appear as three CF_3 groups at partial occupancy. The fluorine occupancies were initially refined and then were normalized and fixed, the nine partial fluorines then having occupancies which add up to 6. Hydrogens on ordered carbons were included in fixed calculated positions with thermal parameters of the parent carbon. In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to give a final $R(F) = 0.056$ for the 776 total variables using all of the unique data. The results of the structure determination are shown in Table 2 and Figures 1 and 2, as well as the Supporting Information.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(THF)_2Ba_2Cu_2[OCMe(CF_3)_2]_6]$

	molecule 1	molecule 2
Ba1−O3	2.751(4)	2.784(5)
Ba1−O8	2.625(5)	2.630(5)
Ba1−O8′	2.6644(21)	2.669(3)
Ba1−O19	2.699(3)	2.6572(13)
Ba1−O30	2.685(4)	2.6703(21)
Cu2−O19	1.849(5)	1.851(5)
Cu2−O30′	1.858(5)	1.845(5)

	molecule 1	molecule 2
O3−Ba1−O8′	155.52(15)	123.24(16)
O3−Ba1−O8	131.98(10)	165.01(18)
O3−Ba1−O19	92.97(11)	97.75(10)
O3−Ba1−O30	99.08(11)	101.28(8)
O8−Ba1−O8′	72.50(12)	71.41(14)
O8′−Ba1−O19	89.50(8)	90.04(12)
O8−Ba1−O19	83.78(14)	77.85(9)
O8′−Ba1−O30	80.10(8)	86.66(13)
O8−Ba1−O30	87.15(15)	81.58(7)
O19−Ba1−O30	167.88(13)	159.14(9)
Ba1−O3−C4	130.0(5)	128.1(7)
Ba1−O3−C7	121.71(13)	124.0(4)
C4−O3−C7	108.3(5)	107.8(7)
Ba1−O8−Ba1′	107.50(12)	108.59(14)
Ba1′−O8−C9	126.2(5)	128.7(4)
Ba1−O8−C9	126.1(4)	122.7(4)
Ba1−O19−Cu2	96.93(19)	100.82(18)
Ba1−O19−C20	141.3(4)	135.89(28)
Cu2−O19−C20	120.57(25)	122.96(20)
Ba1−O30−Cu2′	101.69(13)	100.29(10)
Ba1−O30−C31	136.2(4)	134.6(4)
Cu2′−O30−C31	121.6(5)	125.0(4)

Solid-State Structure of $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$ (2). Because the crystals undergo a destructive phase transition at about −138 °C, data were collected at −58 °C. A preliminary search for peaks and then analysis using the programs DIRAX and TRACER revealed a C-centered monoclinic cell (Table 1). After intensity data collection, the condition $l = 2n$ for $h0l$ limited the space groups to Cc and $C2/c$. The choice of $C2/c$ was later proven correct by the successful solution of the structure. Four standards measured every 200 data showed a significant decline in intensity. Following correction for this drift and

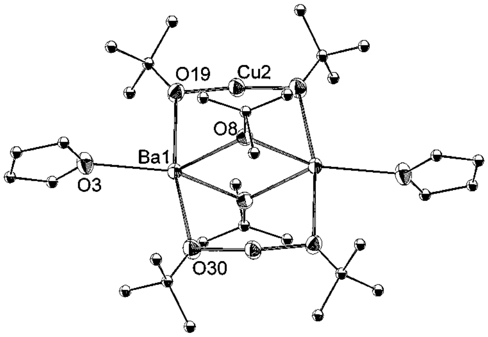


Figure 1. ORTEP plot of molecule A of $[(THF)_2Ba_2Cu_2(HFTB)_6]$. Hydrogen and fluorine atoms have been omitted for clarity.

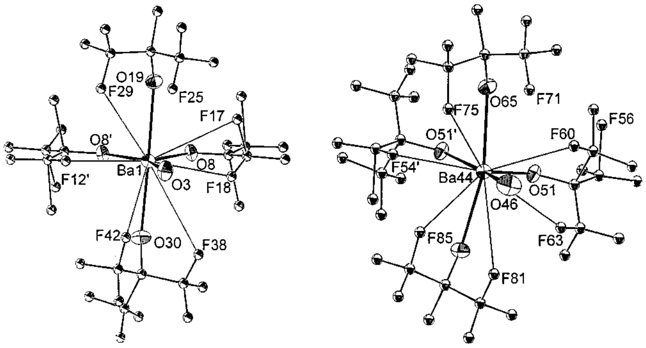


Figure 2. ORTEP plot of barium−fluorine interactions in molecules A and B of $[(THF)_2Ba_2Cu_2(HFTB)_6]$. Barium−fluorine interactions closer than 3.8 Å have been drawn as lines. Hydrogen atoms have been omitted for clarity, and oxygens O3 and O46 are those of THF.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(Me_3NO)_2Ba_2Cu_4(OCMe_2CF_3)_8]$

Ba1−O4	2.651(16)	Cu3−O20′	1.834(10)
Ba1−O12	2.680(15)	Cu3−O28	1.827(10)
Ba1−O20	2.632(10)	O4−C5	1.384(8)
Ba1−O28	2.656(20)	O12−C13	1.43(5)
Ba1−O36	2.480(14)	O20−C21	1.410(14)
Cu2−O4	1.840(14)	O28−C29	1.40(4)
Cu2−O12′	1.818(14)	O36−N37	1.361(24)

O4−Ba1−O12	85.0(5)	Ba1−O4−C5	132.6(16)
O4−Ba1−O20	136.7(4)	Cu2−O4−C5	116.7(13)
O4−Ba1−O28	80.7(5)	Ba1−O12−Cu2′	108.0(9)
O4−Ba1−O36	118.6(4)	Ba1−O12−C13	128.4(9)
O12−Ba1−O20	83.8(4)	Cu2′−O12−C13	121.1(11)
O12−Ba1−O28	141.7(4)	Ba1−O20−Cu3	110.7(5)
O12−Ba1−O36	113.4(7)	Ba1−O20−C21	130.0(8)
O20−Ba1−O28	82.6(5)	Cu3′−O20−C21	118.5(8)
O20−Ba1−O36	104.2(5)	Ba1−O28−Cu3	103.5(7)
O28−Ba1−O36	104.6(6)	Ba1−O28−C29	130.4(13)
O4−Cu2−O12	177.8(6)	Cu3−O28−C29	122.7(21)
O20′−Cu3−O28	176.6(7)	Ba1−O36−N37	175.1(20)
Ba1−O4−Cu2	108.0(4)		

an analytical correction for absorption, the structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the Ba and Cu atoms were obtained from an initial *E* map. The positions of the remaining non-hydrogen atoms were obtained from iterations of a least-squares refinement, followed by a difference Fourier calculation. Hydrogen atoms were included in fixed calculated positions with thermal parameters fixed at 1 plus the isotropic thermal parameter of the parent carbon atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. The largest peak in the final difference map was 1.4, and the deepest hole was −1.7 e/Å^3. The results of the structure determination are shown in Table 3 and Figures 3 and 4, as well as the Supporting Information.

Results

Syntheses of $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$ and $[(THF)_2Ba_2Cu_2(HFTB)_6]$. Synthesis of the barium alkoxides proceeds via a Brønsted acid−base reaction which occurs upon addition of the alcohol to a pentane solution of $Ba[N(SiMe_3)_2]_2$. A reasonable mechanism is an associative one involving precoordination of the alcohol to the barium metal center, followed by proton transfer to the amide, forming the amine. All volatiles, including the free amine, are removed in vacuo to prevent unwanted reactivity with copper mesityl. Addition of more alcohol and copper mesityl to a THF suspension of the barium alkoxide yields a solid in the case of $HOR_F = HOCMe_2(CF_3) = HTFTB$, while, in the case of $HOR_F = HOCMe(CF_3)_2 = HHFTB$, the reaction mixture remains homogeneous. Again, Brønsted acid−base chemistry is involved in this reaction, as a proton transfers from the alcohol to the mesityl group, forming mesitylene.

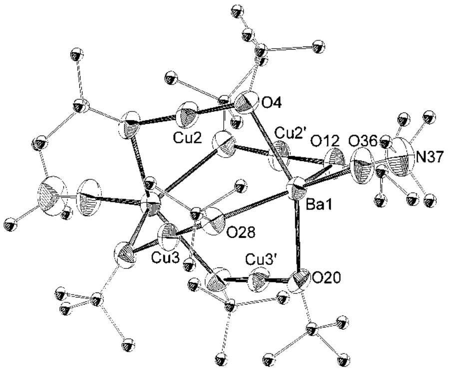


Figure 3. ORTEP plot of $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$. Hydrogen and fluorine atoms have been omitted for clarity.

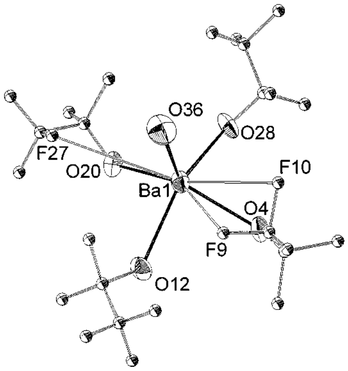
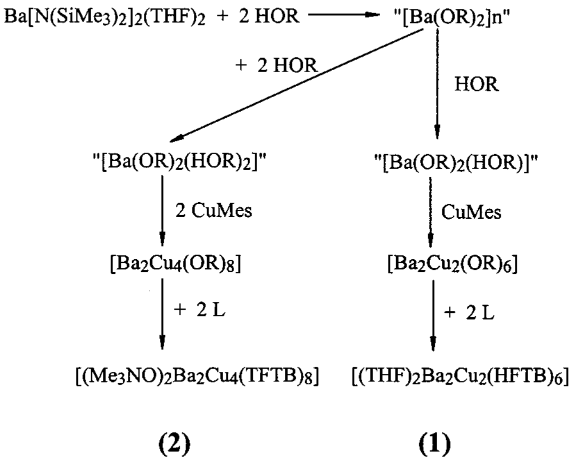


Figure 4. ORTEP plot of barium−fluorine interactions in $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$. Barium−fluorine interactions closer than 3.8 Å have been drawn as open lines. O36 is the oxygen of Me_3NO.

Identity of the intermediates ($[Ba(OR)_2]$ and $[Ba(OR)_2(HOR)_n]$) in Scheme 1 was not pursued. Removal of amine is ensured, as the ^1H NMR in THF-d_8 no longer shows any amine peaks. Because excess alcohol is used in the alcoholysis reaction, it is reasonable that some alcohol is still present in the $[Ba(OR)_2]$ product. This is substantiated by the large excess of carbon (4−7%) and hydrogen (0.5−1.0%) found in the elemental analysis of this compound (even after a 2-h exposure to vacuum). In the case that a stoichiometric amount of alcohol is used in this reaction, THF remains in the product (^1H NMR evidence). It is important to realize that, due to the electronegativity of the fluorines, the fluorinated alcohols will be less nucleophilic than HO^{t}Bu. Counteracting this effect, Ba is more Lewis acidic due to its electronegative ligands and thus will prefer more rather than less ligands. Since THF is no longer present in the solid state when excess alcohol is used during the reaction, we can infer that, in solution, alcohol is coordinated to barium. These alcohol adducts $[Ba(OR)_2(HOR)_n]$ would thus

Scheme 1



L = THF, Me_3NO; OR = TFTB, HFTB

be analogues of $[Ba(O^tBu)_2(HO^tBu)_2]_4$, which has already been described elsewhere.[12]

Solid-State Structure of $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (1). The structure, which has a center of symmetry (Figure 1), consists of a square planar center containing all four metal atoms (two barium and two copper atoms) and four oxygen atoms. Each of the four oxygen atoms is part of an alkoxide ligand and bridges between one barium and one copper atom. Copper is in its preferred linear coordination environment and has only alkoxide ligands. Barium, on the other hand, is in a trigonal-bipyramidal environment, which is completed by a second pair of $Ba_2(\mu\text{-}OR)$ (bridging) alkoxides and one terminal THF (for each barium). The coordination number at barium is increased by fluorine contacts (*vide infra*). Barium−oxygen distances to alkoxides (ranging from 2.625(5) to 2.685(4) Å) are not much shorter than those to the neutral THF (2.751(4) and 2.784(5) Å in the two crystallographically-independent molecules). All copper−oxygen distances are within 2σ of one another. Distortion of the central $Cu_2Ba_2O_4$ square is evident, as all of the M−O−M angles are larger than 90° (ranging from 96.93(19) to 101.69(13)°). Also, the O−Cu−O angles are not exactly linear (170.51(8) and 173.41(16)°). Thus, another way to view the core structure is as an octagon which has been distorted toward a square.

Fluorine contacts augment the coordination number at barium. It is problematic to set a limit on barium−fluorine distances which are "noninteracting". In cases where the van der Waals radii of the elements are known, a simple sum of the two will yield a distance beyond which one can reasonably assume that no interaction takes place. In the case of barium, for which no van der Waals radius is known, it has been suggested that a van der Waals interaction is about 1.5 Å longer than the equivalent single-bond distance.[13] Since a single Ba−F bond is about 2.3 Å,[14] significant interactions between barium and fluorine are on the order of 3.8 Å or shorter. Each of the two crystallographically-independent $[(THF)_2Ba_2Cu_2(HFTB)_6]$ molecules has six such interactions. It is important to note that there are no intermolecular fluorine interactions, but only intramolecular interactions. Barium−fluorine distances on the order of 2.94−3.14 Å have been observed before and have been used to explain the volatility of $[BaCu^{II}_2(HFTB)_6]$.[15]

In molecule A (Figure 2), the sub-3.8 Å Ba−F distances fall into two groups of three. One group ranges from 2.91 to 3.27 Å (involving fluorines F12′, F18, F42). Since there is a site disorder in one of the ligands (the CF_3 and CH_3 groups are disordered), site F42 only has 78% fluorine occupancy. A longer group ranges from 3.48 to 3.75 Å (F17, F29, F38). Fluorine occupancy at site F38 is 87%. One distance (3.90 Å to F25) is just outside the "bonding threshold".

In molecule B (Figure 2), there are five relatively short Ba−F distances (ranging from 3.01 to 3.17 Å to F54′, F60, F63, F75, and F85). A possible reason for the larger number of short contacts (in comparison to molecule A) may be that three of the shorter Ba−F distances are with fluorines that only have partial occupancy (F54′, 44%; F60, 81%; F63, 75%). A sixth fluorine (F81) is 3.66 Å from the barium. Two other fluorine atoms (F71 and F56) are 3.87 and 3.96 Å from the barium.

Solid-State Structure of $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$ (2). The overall structure of the molecule (Figure 3) is that of a paddlewheel. Each of the paddles is composed of linear O−Cu−O rungs (where the copper is in a linear coordination environment), four of which link the two barium metals. All of the Cu−O distances are within 1σ of one another. The barium alkoxide−oxygen distances are within 2σ of one another and average 2.66 Å, whereas the $Ba-ONMe_3$ distance is significantly shorter at 2.480(14) Å. Around the Ba−Ba vector, the molecule has a slight twist, giving the central $Ba_2Cu_4O_{10}$ core S_4 symmetry around the Ba−Ba vector. This molecule has a crystallographic C_2 axis which bisects the Ba−Ba vector but passes through no atoms. Each of the bariums has a square-pyramidal environment, with the Me_3NO ligand in the axial positions and the O−Cu−O paddles making up the base of the pyramid. This pentacoordination is supplemented (Figure 4) by three Ba−F contacts (to F9, F10, and F27) which are 3.12, 3.70, and 3.91 Å, respectively, from the barium. This is within or close to the van der Waals bonding threshold of 3.8 Å (*vide supra*). The other isostructural alkoxides of this system, $[(Me_3NO)_2Ba_2Cu_4(O^tBu)_8]$[16] and $[(Et_3PO)_2Ba_2Cu_4(O^tBu)_8]$,[17] lack rigorous crystallographic symmetry.

NMR spectroscopic data support the solid-state structure of these compounds. $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (Figure 1) has two different alkoxide environments (with a 1:2 integration ratio) and thus displays two chemical shifts with 1:2 integration in both the ^1H and ^{19}F NMR spectra. Upon addition of some (10%) alcohol, the two chemical shifts are no longer observed; instead, one signal is seen at a weighted average of the component chemical shifts. Exchange of alkoxides between environments must thus be facilitated by free alcohol. On the other hand, $[(Me_3NO)_2Ba_2Cu_4(TFTB)_8]$ (Figure 3) has only one alkoxide environment in the solid state. This corresponds well with the two ^1H (Me_3NO and TFTB) and only one ^{19}F NMR chemical shifts observed.

Mass Spectrum and Thermolysis of $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (1). Vacuum thermolysis (at 130 °C) of $[(THF)_2Ba_2Cu_2(HFTB)_6]$ proceeds to form a solid in 30% yield on a cold finger. ^1H NMR (C_6F_6) spectra show a 1:1 integration of alkoxide ligands and no THF signal. Thus, this compound is clearly different from the starting material (the alkoxides for the starting material show 1:2 integration), but all attempts at solving the structure of the compound have been thwarted by

---

[12] Borup, B.; Samuels, J. A.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 994.

[13] Alcock, N. W. *Structure and Bonding*; Ellis Horwood: New York, 1990; p 178.

[14] Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper & Row: Evanston, IL, 1972; p 696.

[15] Purdy, A. P.; George, C. F. *Inorg. Chem.* **1991**, *30*, 1969.

[16] Borup, B.; Folting, K.; Caulton, K. G. *Chem. Mater.* **1997**, *9*, 1021.

[17] Borup, B.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1997**, *536*, 109.

Table 4. Mass Spectral Data for [$(THF)_2Ba_2Cu_2(HFTB)_6$]

fragment ion	*m*/*e*	rel intens	fragment ion	*m*/*e*	rel intens
[$Ba_2Cu_3(HFTB)_7]^+$	1733	5	[$Ba_2Cu_2(HFTB)_5]^+$	1305	34
[$Ba_2Cu_3(HFTB)_6]^+$	1548	5	[$Ba_2Cu(HFTB)_4]^+$	1062	100
[$Ba_2Cu_2(HFTB)_6]^+$	1485	29	[$BaCu(HFTB)_3]^+$	738	11

twinning in all of the crystals grown so far. Mass spectral analysis of both the sublimed compound and [$(THF)_2Ba_2Cu_2(HFTB)_6$] are identical and display peaks which have both barium and copper (Table 4), but do not contain the solvent THF, indicating that it is very labile. Observation of a Ba_2Cu_3 species in the mass spectrum is probably due to the formation of large aggregates upon loss of THF.

Thermolysis of **1** proceeds by initial loss of THF, after which only two more mass losses are observed. The initial loss of THF is at about 40 °C, during which the mass loss (3.3%) is much less than would be expected if all of the THF were lost. A second mass loss is observed at 160 °C and a third mass loss at 270 °C, to leave a residue of 19.9%. Sublimation of some of the compound must occur during the last step because the final mass is smaller (19.9%) than that expected (at least 28.8%, depending on barium product) for the final products BaO, BaF_2, and copper metal. Formation of $BaCO_3$, which we have found previously as a decomposition product for the nonfluorinated analogue [$(Me_3NO)_2Ba_2Cu_4(O^tBu)_8$] (**3**), is not observed during the thermolysis. Analysis of a sample thermolyzed to 450 °C only showed BaF_2 and Cu by X-ray powder diffraction.

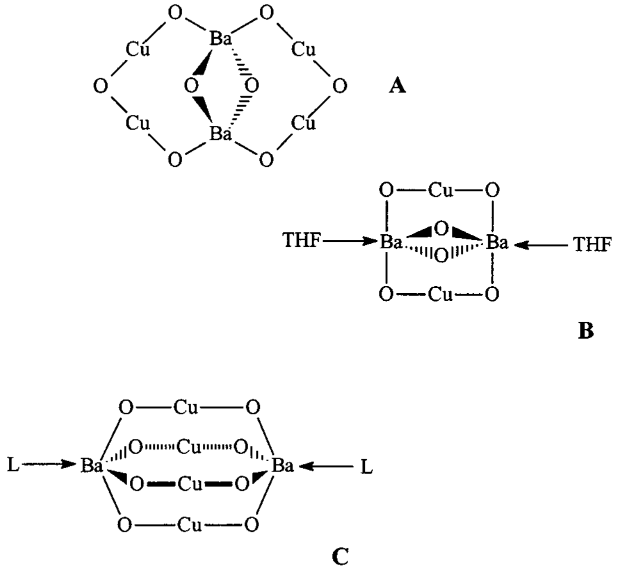
Thermolysis of [$(Me_3NO)_2Ba_2Cu_4(TFTB)_8$] (2). Thermolysis proceeds in two distinct steps. At 90 °C, about 20% of the mass of the compound is lost and, thereafter, at 230 °C, another 40% is lost to give the final mass of 39.3%, which is lower than would be expected for the products BaO, BaF_2, and copper metal. This is an indication of partial sublimation of the compound during decomposition. Here again, $BaCO_3$, the formation of which we have observed for the nonfluorinated analogue [$(Me_3NO)_2Ba_2Cu_4(O^tBu)_8$] (**3**), is not formed here. Analysis of a sample thermolyzed to 450 °C showed only BaF_2 and Cu by X-ray powder diffraction.

Discussion

Among the five reported barium copper(I) alkoxides, three distinct structural forms (**A**−**C**) are found (Chart 1): [$Ba_2Cu_4(OCEt_3)_8$][8] (**5**) (**A**), [$(THF)_2Ba_2Cu_2(HFTB)_6$] (**1**) (**B**), [$(Me_3NO)_2Ba_2Cu_4(O^tBu)_8$][16] (**3**), [$(Et_3PO)_2Ba_2Cu_4(O^tBu)_8$][17](**4**), and [$(Me_3NO)_2Ba_2Cu_4(TFTB)_8$] (**2**) (**C**). The building blocks that comprise each of the structures are similar, but in each structure, they are assembled in a different fashion. Copper is always in a linear environment, whereas barium is either four- or five-coordinate (with the fifth coordination site always being occupied by a neutral donor). The alkoxide ligand is always found in a μ_2-bridging mode.

A comparison of the three structural motifs shows how they can be derived from one another. Removal of two Cu(OR) groups from **C** and exchange of the amine or phosphine oxides for THF result in **B**. This has no effect on the coordination number of barium and only distorts the geometry around barium from square-pyramidal to trigonal-bipyramidal. In addition, the Ba−Ba distance decreases from 5.41 Å (for OR = TFTB) and 5.29 Å (for OR = O^{t}Bu) to 4.27 Å in **B**. Insertion of two Cu(OR) groups into each of the two Ba−(OR)−Cu bonds and removal of the THF convert **B** into **A**. This has the effect of lengthening the two Ba−(OR)−Cu−(OR)−Ba "bridges" and compensating for the loss of THF by creating a tetrahedral barium coordination geometry. This again shortens the Ba−Ba distance from 4.27 to 3.96 Å. In turn, **A** can be converted into **C** by removing one of the Cu(OR) groups from each Ba−(OR)−Cu−(OR)−Cu(OR)−Ba bridge and inserting it into the Ba−(OR)−Ba bridge, followed by addition of a neutral ligand to the barium center. In effect, the barium coordination number increases and the loss of tetrahedral coordination environment around barium is compensated by the addition of a neutral ligand.

Chart 1. Core Structures of [$Ba_2Cu_4(OCEt)_8$] (**5**) (**A**), [$(THF)_2Ba_2Cu_2(HFTB)_6$] (**1**) (**B**), and [$L_2Ba_2Cu_4(OR)_8$] (L = $ONMe_3$ (**2**), $OPEt_3$ (**3**), R = O^{t}Bu; L = $ONMe_3$ (**4**), R = TFTB (**C**))[a]



[a] All alkyl groups have been omitted from the alkoxide ligands for simplicity.

Recognizing that **B** and **C** are related is facile, whereas actual experimental interconversion is more difficult. For instance, the addition to **B** of $^1/_2$ equiv of [$Cu(O^tBu)]_4$ or [$Cu(HFTB)]_4$[18] does not result in a compound of structure **C** but rather results in a mixture of compounds, as evidenced by a large number of peaks in the ^{1}H NMR spectrum. Two of the peaks could be identified as the starting materials.

Thermolysis of the fluorinated alkoxides **1** and **2** proceeds to form BaF_2 and copper metal. This is different from the thermolysis of nonfluorinated analogues **3** and **4** and must happen in lieu of carbonate formation. We propose that the Ba−F contacts present in the solid facilitate the C−F bond activation that occurs during thermolysis. Formation of fluorides from CVD of fluorinated alkoxide or *β*-diketonate precursors has been observed before.[19] However, the absence of carbonate formation suggests that the CF_3 groups present in the ligand hinder the mechanism of carbonate formation.

The *tert*-butoxide and the trifluoro-*tert*-butoxide analogs, [$BaCu_2(O^tBu)_4$][17] and [$BaCu_2(TFTB)_4]_x$, are insoluble in donor solvents such as THF, DME, and pyridine. Also, the addition of Et_3P or pyridine *N*-oxide to a suspension of [$BaCu_2(O^tBu)_4$][17] or [$BaCu_2(TFTB)_4]_x$ in THF did not result in a soluble product. It is only upon addition of a Lewis basic ligand such as Me_3NO that these two compounds react to form soluble compounds. The barium apparently requires a very hard Lewis basic oxygen which, in the absence of a neutral ligand, is another alkoxide

---

(18) Borup, B.; Minear, C.; Baxter, D. V.; Caulton, K. G. *Chem. Mater.*, submitted for publication.

(19) (a) Ling, L. J.; Berry, A. D.; Purdy, A. P.; Ewing, K. J. *Thin Solid Films* **1992**, *209*, 9. (b) Samuels, J. A.; Chiang, W.-C.; Yu, C.-P.; Apen, E.; Smith, D. C.; Baxter, D. V.; Caulton, K. G. *Chem. Mater.* **1994**, *6*, 1684. (c) Gilland, D. G.; Hitchman, M. L.; Thompson, S. C.; Cole-Hamilton, D. J. *J. Phys. III* **1992**, *2*, 1381.

from a neighboring molecule, leading to polymerization. On the other hand, $[Ba_2Cu_2(HFTB)_6]_x$ is soluble in THF, yielding $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (**1**), whereas $[Ba_2Cu_4(OCEt_3)_8]$ (**5**) is soluble in pentane in the absence of any additional donor ligand;[20] this is attributable to the great steric bulk of the $OCEt_3$ ligand.

Comparing all of these structures, one is struck by the number of different barium coordination geometries (ranging from tetrahedral to trigonal-bipyramidal to square-pyramidal), the difference in neutral donor (or absence thereof) needed to prevent polymerization, and the change in stoichiometry (from 1:1 to 1:2 Ba:Cu) encountered. Several factors are involved in explaining this variety. First, the steric requirements of the ligands are different and increase with increasing fluorination, and $OCEt_3$ is much bulkier than O^tBu. This explains well the observation that $[Ba_2Cu_4(OCEt_3)_8]$ (**5**)[20] does not need an additional ligand at the barium to yield a soluble product, whereas $[(Me_3NO)_2Ba_2Cu_4(O^tBu)_8]$ (**3**)[16] does. In this case, it is probable that $[Ba_2Cu_4(OCEt_3)_8]$, (**5**) is soluble in pentane without an additional ligand because the bulky $OCEt_3$ ligand prevents alkoxide bridging to a neighboring molecule. Bulkiness of the ligand does not explain the change in the Ba:Cu ratio observed with increasing fluorination. The steric requirement of $OCEt_3$ is similar to that of HFTB, but the resulting compounds have different structures and stoichiometries. This is attributed to barium−fluorine contacts, which increase the coordination number around that metal, changing the preferred structure. With increasing fluorination, the ligands can be arranged more easily to maximize these interactions and fewer $CuOR_F$ units are needed to provide the necessary fluorine donors. Also, an increasing number of Ba−F contacts shields the metal center sufficiently, preventing polymerization and thereby eliminating the need to add a neutral ligand with a very Lewis basic oxygen (such as Me_3NO). THF is sufficient for $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (**1**) to solubilize the compound. The third important influence is the electronegativity of the fluorine and its influence on the σ-donating ability of the alkoxide oxygen. With increasing fluorination, the σ-donating ability of the alkoxide oxygen diminishes and makes the O−Cu bond less favorable. The oxygen−barium bond is more ionic in character; thus σ-bonding has less influence on the stability of the system. It suffices that there is a negative charge on the oxygen. The small increase in electrophilic character of the barium can be compensated by additional Ba−F interactions. We can thus understand the increase in Ba:Cu ratio on going from the TFTB to the HFTB ligand, as this decreases the number of Cu−O bonds in the structure.

In all of the alkoxides described above, the sum of the angles around the alkoxide oxygens is greater than 356°. This is true even for the alkoxides that solely bridge the barium atoms. While this might imply that the alkoxides are π-bonding to both the barium and the copper metal, this is not necessarily true. In the case of $[Cu(O^tBu)]_4$, the oxygen atoms are distinctly pyramidal, with bond angle sums ranging from 337 to 344°, even though the central Cu_4O_4 core is planar[21] and copper has an empty orbital. Another compound with a central Cu_4O_4 core is $[Cu(OSiPh_3)]_4$,[22] where two of the oxygens are planar (oxygen bond angle sum of 360°) and two are pyramidal (oxygen bond angle of 324°). In contrast to these two molecules, all of the alkoxide oxygens in the Ba/Cu systems are planar. This must be due to the influence of the very electropositive barium metal center.

A direct comparison can be made between $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (**1**) and both of the $[Cu (OR)]_4$ compounds, since both have an almost square central M_4O_4 structure. In both of the $[Cu(OR)]_4$ compounds, the Cu−O−Cu average bond angles are 94°, whereas in the Ba_2Cu_2 compound, it is 99°. On the other hand, all the Ba_2Cu_4 structures display larger Ba−O−Cu angles of 104−111°.[23] This implies that either the decrease in bond angle on going from the Ba_2Cu_4 compounds to Ba_2Cu_2 does not lead to a significant amount of strain or this strain is compensated for by the larger number of Ba−F interactions.

Conclusions

Heterometallic barium copper(I) alkoxides display a large variety of structures which accommodate the different steric requirements of the ligands. The common feature of these very different structures is that each of the metals attains its desired coordination number and (for copper) geometry; barium appears to be very flexible in the geometry it will accept.

Barium−fluorine contacts increase the coordination number around the barium center and decrease the tendency of the barium alkoxides to polymerize and form insoluble products. With increasing coordination number (due to the fluorine interactions with the barium center), the need for a very Lewis basic neutral ligand decreases, making it possible for $[(THF)_2Ba_2Cu_2(HFTB)_6]$ (**1**) to be a molecular compound in the absence of Me_3NO.

Stoichiometry of the compounds is affected by the σ-donating ability of the alkoxide oxygen. A decrease in the σ-donating ability of the oxygen decreases the stability of the copper−oxygen bond and thus the number of O−Cu bonds are decreased in the molecule in favor of more barium−oxygen bonds.

Acknowledgment. This work was supported by the Department of Energy.

Supporting Information Available: Listings of X-ray experimental details, atomic coordinates, and thermal parameters (8 pages). Ordering information is given on any current masthead page.

IC970234S

---

[20] Purdy, A. P.; George, C. F. *Polyhedron* **1995**, *14*, 761.

[21] Greiser, Th.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142.

[22] McGeary, M. J.; Wedlich, R. C.; Coan, P. S.; Folting, K.; Caulton, K. G. *Polyhedron* **1992**, *11*, 2459.

[23] This is closer to the 120° angle expected for sp^2 hybridization.