Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are grateful to the National Science Foundation for a Presidential Young Investigator Award. This work made use of the SEM facilities of the Center for Electron Optics at Michigan State University.

Supplementary Material Available: Tables of atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all non-hydrogen atoms, bond distances and angles, and calculated and observed powder patterns for I and II (21 pages); listings of calculated and observed ($10F_o/10F_c$) structure factors for I and II (68 pages). Ordering information is given on any current masthead page.

Department of Chemistry and Center for Fundamental Materials Research
Michigan State University
East Lansing, Michigan 48824

Kang-Woo Kim
Mercouri G. Kanatzidis*

Received December 26, 1990

Volatile Copper and Barium–Copper Alkoxides. Crystal Structure of a Tricoordinate Copper(II) Complex, Ba{Cu[OCMe(CF$_3$)$_2$]$_3$}$_2$

The recent discovery of ceramic superconductors has prompted considerable research into the development of new copper and barium precursors for sol-gel and chemical vapor deposition (CVD) processes.[1] This research has resulted in recent reports of a number of new alkoxides, siloxides, organometallics, and acetylacetonates.[2] The Buhro group synthesized the most volatile copper alkoxide reported to date, $Cu[OCHMeCH_2NMe_2]_2$ (sublimed at 60 °C).[2d] The most volatile barium source in common use is $Ba(FOD)_2$, which transports at 170–200 °C,[1] although more volatile organometallics ($Cp^*{}_2Ba$ at 135 °C) are known.[2f] As bulky fluorinated ligands have allowed numerous volatile alkoxides of other metals to be synthesized,[3] we have recently been utilizing the hexafluoro-*tert*-butoxide [HFTB = $OCMe(CF_3)_2$] and perfluoro-*tert*-butoxide [PFTB = $OC(CF_3)_3$] ligands in our work. Thus we synthesized the structurally unique mixed alkoxide $Ba[Cu(HFTB)_3]_2$ (**1**), which is the first crystallographically characterized example of tricoordinate Cu(II). We have also prepared an extraordinarily volatile copper(II) perfluoro-*tert*-butoxide, tentatively identified as $Cu_4(PFTB)_7$ (**2**), and the corresponding Cu(I) complex,[4] $[Cu(PFTB)]_n$ (**3**). Compound **1** sublimed at 70–90 °C, **2** and its etherates transported under vacuum below room temperature, and **3** sublimed at 40–50 °C.[5a] We believe **1**–**3** to be the most volatile copper and barium alkoxides known today.

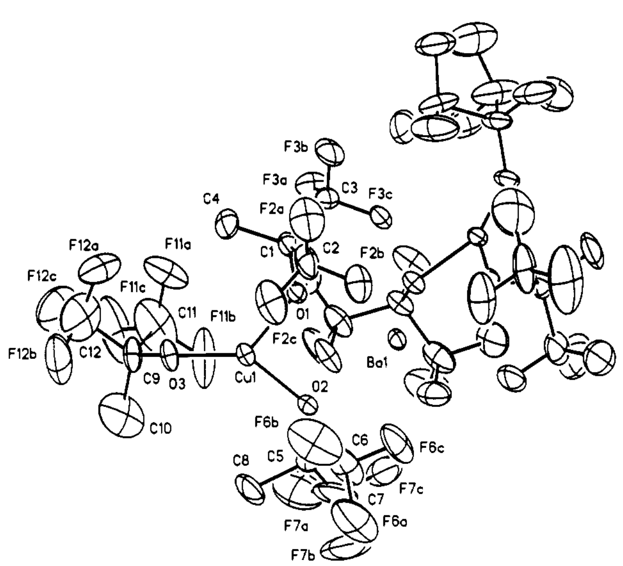

Figure 1. Plot of **1** drawn from experimental coordinates. Fluorines for the CF_3–CH_3 disorders at C(10) and all hydrogen atoms are not shown, and Ba coordination is omitted for clarity. Cu–O(1) = 1.889 (6) Å, Cu–O(2) = 1.878 (7) Å, Cu–O(3) = 1.781 (7) Å, ∠O(1)–Cu–O(2) = 88.4 (3)°, ∠O(2)–Cu–O(3) = 140.7 (3)°, and ∠O(1)–Cu–O(3) = 130.9 (3)°. Average C–C = 1.53 (2) Å, and average C–F = 1.33 (3) Å.

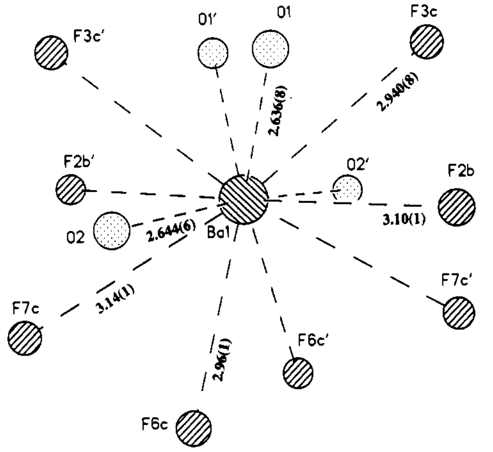

Figure 2. Environment of Ba, atoms labeled with a prime are related by the symmetry operation ($-x$, y, $^1/_2 - z$). Ba interacts with only two $Cu(OR)_3^-$ fragments. Ba--Cu = 3.612 (2) Å.

The new barium alkoxycuprate $Ba[Cu(HFTB)_3]_2$ (**1**) was synthesized from a reaction between $Ba(HFTB)_2$ and $CuCl_2$. When the reactants were combined in a 1:1 mole ratio,[6b] a very

---

(1) For example: (a) Rupich, M. W.; Lagos, B.; Hachey, J. P. *Appl. Phys. Lett.* **1989**, *55*, 2447. (b) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. (c) Mehrotra, R. C. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 81. (d) Zhao, J.; Dahmen, K.; Marcy, H. O.; Tonge, L. M.; Marks, T. J.; Wessels, B. W.; Kannewurf, C. R. *Appl. Phys. Lett.* **1988**, *53*, 1750.

(2) (a) McMullen, A. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1989**, *28*, 3772–4. (b) Goel, S. C.; Kramer, K. S.; Gibbons, P. C.; Buhro, W. E. *Inorg. Chem.* **1989**, *28*, 3619. (c) Horowitz, H. S.; McLain, S. J.; Sleight, A. W.; Druliner, J. D.; Gai P. L.; VanKavelaar, M. J.; Wagner, J. L.; Biggs, B. D.; Poon, S. J. *Science* **1989**, *243*, 66. (d) Goel, S. C.; Kramer, S. K.; Chaing, M. Y.; Buhro, W. E. *Polyhedron* **1990**, *9*, 611–613. (e) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345. (f) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31. (g) Sauer, N.; Garcia, E.; Salazar, K.; Ryan, R.; Martin, J. *J. Am. Chem. Soc.* **1990**, *112*, 1524. (h) Poncelet, O.; Hubert-Pfalzgraf, L. G.; Daran, J. C. *Inorg. Chem.* **1990**, *29*, 2883. (i) Purdy, A.; Berry, A. US Pat. 4982019, Jan 9, 1991.

(3) Willis, C. J. *Coord. Chem. Rev.* **1988**, *88*, 133–202.

(4) A mixture of MesCu (0.50 g, 2.74 mmol, Alfa Products), H(PFTB) (0.75 g, 3.18 mmol), and hexane (10 mL) was stirred at 60–70 °C for 1.5 h and then filtered to an orange solution and a brown residue. Solvent was removed at 0 °C; 0.39 g of sublimate was sublimed from the remaining solid at 60 °C, recrystallized from hexane, and dried in vacuo (0 °C), affording 0.19 g (23%) of the pale yellow **3**. Anal. Found (calcd) for C_4F_9OCu: C, 16.18 (16.09); H, 0 (0); F, 57.09 (57.27); Cu, 21.41 (21.28). Mp: 67–151 °C. NMR: ^{19}F δ −75.3.

(5) (a) Dynamic vacuum at $<10^{-5}$ Torr. (b) All manipulations were done under inert atmosphere. Proton and ^{19}F NMR were run at 300.13 and 282.4 MHz respectively. Electronic spectra were recorded from 1200 to 230 nm in hexane.

(6) (a) BaH_2 (1.13 g, 8.11 mmol) and H(HFTB) (2.5 mL) were stirred for 12 h in THF (5 mL) and filtered. $Ba(HFTB)_2$ (3.46 g, 85%) was isolated by solvent removal and drying at 100 °C in vacuo. Anal. Found (calcd): C, 19.22 (19.24); H, 1.29 (1.21); F, 45.43 (45.65). NMR (C_4D_8O): ^1H δ 1.35; ^{19}F δ −76.6. $Ba(PFTB)_2$ was prepared in a similar manner. (b) $Ba(HFTB)_2$ (0.67 g, 1.3 mmol), $CuCl_2$ (0.18 g, 1.3 mmol), and Et_2O (25 mL) were stirred at 70 °C for 1 day and filtered. After solvent removal from the filtrate at 0 °C, the residue was sublimed at 40–70 °C. Sublimation residue was recrystallized from C_6H_6/heptane affording **1** (0.16 g, 27%). A drop of unidentified orange liquid was distilled at room temperature from the heptane wash of the sublimate. (c) $Ba(HFTB)_2$ (0.502 g, 1.01 mmol), $CuCl_2$ (0.089 g, 0.66 mmol), and THF (8 mL) were stirred at 25 °C for 2 days and filtered, and solvent was removed from the filtrate to afford a solid (0.38 g. Anal. Found: C, 20.59; H, 1.23; Cu, 8.89; Ba, 13.21; Cl, 1.03; consistent with $Ba_2Cu_3(HFTB)_9Cl$). A 0.285-g sample of the latter was sublimed, affording **1** (0.14 g, 31%). A similar reaction in Et_2O (60–70 °C, 7 days), gave a 21% yield of **1**.

0020-1669/91/1330-1969$02.50/0

small quantity of an unidentified orange liquid was produced along with **1**. This liquid cosublimed with **1** at 40–70 °C, below the sublimation temperature of pure **1**. Combining the reactants in a 3:2 ratio[6c] (in ether or THF) produced a green-brown, ether-soluble solid from which **1** could be sublimed above 90 °C. The light green **1** melted at 124–126 °C and showed high thermal stability (dec pt >250 °C).[7] It was very soluble in ethereal solvents, and moderately soluble in hydrocarbons. While easily separated from Et_2O or THF, **1** could not be separated from coordinated tetraglyme or pyridine by sublimation.[5a] A strong bidentate ligand, $Me_2N(CH_2)_2NMe_2$ (TMEDA), reacted instantly with **1** to form a blue solid,[8] which was sublimed at 60–80 °C from the $Ba(HFTB)_2$ residue.

The X-ray analysis[9] of **1** shows (Figure 1) Ba to be located on a 2-fold axis so that only one of the $Cu(HFTB)_3^-$ anions is crystallographically unique. The $\{Cu^{II}O_3\}$ chromophore is three-coordinate, Y shaped, and planar (maximum deviation from a least-squares plane is 0.008 Å). Its dihedral angle with the $\{CuO_3\}$ plane related by the 2-fold axis is 56.8°, and with the O(1)–Ba–O(2) plane, it is 165.8°. While a three-coordinate planar geometry is common for $\{Cu^IX_3\}$,[10] the only other known compound[11] with a similar Cu(II) geometry is $[(PFTB)Cu_2(OCMe_3)_3]_2$. The Cu–O distances to the HFTB ligands that are also coordinated to Ba are short (1.889 (6) and 1.878 (7) Å), but similar to those in mononuclear copper(II) alkoxides[2d] (1.865–1.892 Å) and a monomeric copper(II) siloxide complex[2a] (1.835–1.861 Å). The Cu–O distance (1.781 (7) Å) to the unshared HFTB ligand is shorter. Comparable distances in $[(PFTB)Cu_2(OCMe_3)_3]_2$ are 1.865 (4), 1.867 (4), and 1.798 (5) Å. The Ba^{2+} cation is coordinated (Figure 2) to four oxygens (2.636–2.644 Å) and eight fluorines (2.94–3.14 Å). The monomeric structure of **1** (intermolecular Ba···F = 5.12 Å, Ba···O = 7.80 Å, and Cu···Cu = 8.77 Å) helps to explain its unusually low sublimation temperature.

The copper perfluoro-*tert*-butoxide **2** and its etherates [**2**·*n*OEt_2] were prepared from a reaction between $Ba(PFTB)_2$ and $CuCl_2$ (1:1 mole ratio).[13] The etherates with $n = 2$ to $n = 4$ were liquids, and the $n = 1$ etherate was a solid. The elemental analyses were consistent with the formulas $Cu_4(PFTB)_7$ and $Cu_4(PFTB)_7(OEt_2)_n$, implying a mixed-valence copper(I/II) alkoxide. Spontaneous reduction to Cu(I) is not unreasonable as it was previously observed in the reaction of $CuCl_2$ with salts of other bulky ligands such as $LiN(SiMe_3)_2$.[14] However, an X-ray powder pattern of the solids from the hydrolysis[15] of **2** shows no evidence for Cu_2O. While the mass spectrum of **2** shows no evidence for chloro or oxo ligands, the presence of a fluoro ligand or some other unusual arrangement, with all Cu atoms in the +2 oxidation state, cannot be ruled out.

Acknowledgment. We thank John Callahan (NRL) for assistance with the mass spectrum and ONR for financial support.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates (6 pages); a table of structure factors (11 pages). Ordering information is given on any current masthead page.

---

(7) Anal. Found (calcd) for $Ba[Cu(HFTB)_3]_2$: C, 21.26 (21.34); H, 1.05 (1.34); Cu 9.31 (9.41); Ba, 9.81 (10.17). NMR: ^1H (C_6D_6) δ −1.05 ($\upsilon_{1/2}$ = 370 Hz), −11.41 ($\upsilon_{1/2}$ = 780); ^{19}F ($CFCl_3$ ref) δ −51.0 ($\upsilon_{1/2} \approx$ 1800 Hz), −56.8, −60.2 ($\upsilon_{1/2} \approx$ 2500). ESR: (Et_2O) g = 2.21, 4.36; −196 °C, $g_\perp$ = 2.14, $g_\parallel$ = 2.51. UV/vis [λ, nm (ε)]: 270 (4300), 360 (7500), 755 (240), 875 (170), 980 (100).

(8) Anal. Found: C, 30.41; H, 3.75; F, 43.61; Cu, 11.98; consistent with $Cu(HFTB)_2(TMEDA)_{0.9}$ (TMEDA loss on sublimation?). Mp: 137–140 °C. Dec pt: 145–158 °C. NMR (C_6D_6): ^1H δ −5.45 ($\upsilon_{1/2}$ = 350 Hz); ^{19}F δ −45.6 ($\upsilon_{1/2}$ = 3400 Hz). ESR (C_6D_6, −196 °C); $g_\perp$ = 2.06, $g_\parallel$ = 2.33.

(9) **1** crystallizes in space group $C2/c$ with the following unit cell parameters: $a = 23.843$ (12) Å, $b = 18.324$ (8) Å, $c = 10.998$ (6) Å, $\beta = 116.97°$, $V = 4282$ (4) Å^3, $Z = 4$, $d_{calc} = 2.09$ g/cm^3, and $\mu = 20.8$ cm^{-1}. An irregular green translucent crystal was sealed in a glass capillary and a total of 3112 ($3.5 < 2\theta < 45°$, $0 \leq h \leq 25$, $0 \leq k \leq 19$, $-11 \leq l \leq 10$) data were collected (2825 unique, R_{int} = 1.02% for equivalents) on a computer-controlled diffractometer (four-circle Nicolet R3m/V with Mo Kα radiation, λ = 0.71073 Å, and incident beam monochromator) at −35 °C. Corrections were applied for Lorentz, polarization, and absorption effects. The structure was solved by direct methods with the aid of the program SHELXTL[12] and refined with a full-matrix least-squares refinements[12] with restraints on C–F and next-nearest-neighbor F–F distances. The fluorine atoms are not well-defined, and the HFTB ligand not coordinated to Ba was treated as a disorder with respect to methyl group position. Occupancy was refined to $^1/_5$, $^2/_5$, and $^2/_5$, and the corresponding CF_3 group occupancies were $^4/_5$, $^3/_5$, and $^3/_5$, respectively, for the three sites. Final R values for the 2355 data with $F_o > 3\sigma(|F_o|)$ were $R = 0.064$ and $R_w = 0.080$. The 341 parameters refined include the coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were placed in calculated positions.

(10) (a) Sorrel, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250. (b) Kappenstein, C.; Hugel, R. P. *Inorg. Chem.* **1977**, *16*, 250. (c) Sorrel, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883.

(11) George, C. F.; Purdy, A. P. Unpublished results.

(12) Sheldrick, G. M. SHELXTL80. *An integrated system for Solving, Refining, and Displaying Crystal Structures from Diffraction Data.* University of Gottingen, Federal Republic of Germany, 1980.

(13) A mixture of $Ba(PFTB)_2$[2i] (2.08 g, 3.42 mmol), $CuCl_2$ (0.471 g, 3.50 mmol), and Et_2O (25 mL) was stirred at 75 °C for 40 h, and the pale yellow mixture was filtered (residue 0.76 g). As the ether was vacuum evaporated at 0 °C, an off-white solid formed, which turned to a green liquid as more ether was removed. Repeated distillation with mild warming of the pot (heat gun) and the receiving flask at 0 °C allowed ether to be removed slowly,[5a] distilling green etherates (90% yield from first distillation) and ultimately a thermochromic orange crystalline material (**2**). Anal. Found (calcd) for $Cu_4(PFTB)_7(OEt_2)_4$: C, 24.04 (24.07); H, 1.44 (1.84); Cu, 11.12 (11.58); F, 54.11 (54.51). Found (calcd) for $Cu_4(PFTB)_7(OEt_2)$: C, 19.50 (19.48); H, 0.55 (0.51). Found (calcd) for $Cu_4(PFTB)_7$: C, 17.55 (17.71); H, 0 (0); Cu, 13.37 (13.38); F, 62.99 (63.02). $Cu_4(PFTB)_7(OEt_2)_2$ was identified by NMR integration ($C_6H_5CF_3$ internal standard). Data for **2** are as follows. Mp: 68–71 °C. NMR: ^{19}F δ −1.6 ($\upsilon_{1/2} \approx$ 2500 Hz), −51.7 (line width increased and intensity decreased with increased amount of Et_2O); ^1H (of etherates) CH_3 position variable, observed from δ 6 to 25. ESR: (C_6D_6) −196 °C, $g_\perp$ = 2.08, $g_\parallel$ = 2.63. UV/vis [λ, nm (ε)]: 360 (8400), 780 (230), 910 (180), 1050 (165). Test for chloride ($AgNO_3$) was negative. MS (of etherate): *m/e* 831 (12%), $Cu_2(PFTB)_3^+$; *m/e* 615 (16), $Cu_2(PFTB)_2F^+$; *m/e* 596 (29), $Cu_2(PFTB)_2^+$; *m/e* 380 (32), $Cu_2(PFTB)F^+$; *m/e* 361 (64), $Cu_2(PFTB)^+$; *m/e* 372 (70), $Cu(PFTB)(OEt_2)^+$; peaks from additional loss of CF_2 or CF_3. All attempts to solve the crystal structure were unsuccessful.

(14) Burger, H.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 1099.

(15) Dried at 140 °C under vacuum.

(16) Part of this work was performed while a NRC-NRL research associate.

SFA Inc.
1401 McCormick Drive
Landover, Maryland 20785
Andrew P. Purdy[16]

Naval Research Laboratory
Laboratory for the Structure of Matter
Code 6030
Washington, D.C. 20375-5000
Clifford F. George*

Received November 9, 1990

Synthesis and Structural Characterization of the Europium Sandwich $[1,1\text{-}(THF)_2\text{-}\mathit{commo}\text{-}1,1'\text{-}Eu(1,2,4\text{-}EuC_2B_{10}H_{12})_2]^{2-}$

Recent work from our laboratory has focused attention on the carborane complexes of the lanthanide elements, and we have recently reported representative dicarbollide complexes of Yb and Sm.[1,2] In this communication, we report the synthesis and

---

(1) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458.

(2) Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.*, in press.