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New Alkoxides of Copper and the Alkaline and Alkaline-Earth Metals. Crystal Structure of $Na_2Cu[OCH(CF_3)_2]_4$

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A variety of new alkoxides $Ba(OR)_2$ [R = CEt_3, $CMeEtPr^i$, $CH(CMe_3)_2$, 2-tetrahydrofurfuryl, and $CH(CF_3)_2$], $M[OC(CF_3)_3]_2$ (M = Ca, Sr, and Ba), $Cu(OCEt_3)_n$ (n = 1 and 2), $Na_2Cu(OR)_4$ [R = $CHMe_2$, $CH(CF_3)_2$, and 2-tetrahydrofurfuryl], $NaCu(OR)_3$ and $NaCu(OR)_2$ (R = CMe_3 and CEt_3), $Ba[Cu(OCMe_3)_n]_2$ (n = 2 and 3), and $BaCu[OCH(CF_3)_2]_4$ were prepared. The compounds were characterized by those methods compatible with their properties including mass, NMR, ESR, and electronic spectroscopy, elemental analysis, sublimation and melting points, molecular weight determinations, and solubility. The alkoxide $Na_2Cu[OCH(CF_3)_2]_4$ crystallizes in the space group $C2/c$; a = 15.965 (6) Å, b = 12.652 (5) Å, c = 11.837 (5) Å, β = 94.36 (3)°, Z = 4, and $R(F)$ = 6.07%. The $Cu(OR)_4^{2-}$ ions have a 22.4° dihedral angle between the two CuO_2 planes and Cu–O distances of 1.917 (5) and 1.968 (5) Å. The Na^+ ions are each coordinated to two O and five F atoms with Na–O distances of 2.281 (6) and 2.318 (6) Å and Na–F distances ranging from 2.481 (7) to 2.791 (7) Å, with the Na–Cu distances being 3.630 (4) and 3.821 (4) Å.

Introduction

As reported in several reviews, alkoxides can be excellent precursors for the chemical vapor deposition (CVD) or sol–gel production of various metal oxide products.[2] The discovery of cuprate superconductors has prompted interest in the alkoxides of Ba and Cu(II). The $Cu(OR)_2$ alkoxides where R = Me, Et, Pr, and Bu are both insoluble and nonvolatile, and the $Ba(OR)_2$ alkoxides where R = Me, Et, and Pr are nonvolatile and their solubility is limited.[3,4] One successful approach to reducing oligomerization and thus improving solubility and volatility has been to use multidentate alkoxy ligands. For example $Cu(OCH_2CH_2OCH_2CH_2OMe)_2$,[5a] $Cu(OCH_2CH_2OBu)_2$,[5b] and $Ba(OCH_2CH_2OBu)_2$[5c] are soluble in a range of organic solvents and $Cu(OCH_2CH_2NEt_2)_2$[5d] is one of the most volatile copper(II) alkoxides known, subliming at 60 °C under vacuum. Soluble fluorinated aminoalkoxides are also known.[6]

Another approach is to use heterometallic (or mixed) alkoxides $MM'(OR)_{x+y}$, which are often more soluble and volatile than their components $M(OR)_x$ and $M'(OR)_y$.[2,4] Heterometallic alkoxides containing Cu(II) or Ba are known. They include such compounds as $Cu(Al(OPr^i)_4)_2$,[7a] $Cu[Zr_2(OPr^i)_9]_2$,[7b] $Cu[Ta(OPr^i)_6]_2$,[7c] $ClCu[Ta(OPr^i)_6]$,[7d] $Ga(OPr^i)_4Cu[Zr_2(OPr^i)_9]$,[7d] $Ba[Al(OEt)(OPr^i)_3]_2$,[7e] $BaCu[OC_6H_4O]_2$,[7f] $Na_2Cu[O(Me)_2CC(Me)_2O]_2$,[7g] and $K_2Cu[O(F_3C)_2CC(CF_3)_2O]$.[7h] A mixed barium–copper alkoxide–acetylacetonate has been reported,[8a] and a soluble termetallic alkoxide $(CuO)_3Ba_2Y(OC_2H_4OMe)_7$ has been successfully used in the sol–gel synthesis of $YBa_2Cu_3O_7$.[8b]

Bulky and heavily fluorinated monodentate alkoxy ligands have been shown to enhance the solubility and/or volatility of alkoxides in many other metal systems including Be, Mg, Na, Mo, U, etc.[4,6,9] Aside from a bulky copper(II) siloxide[10] and barium *tert*-butoxide[11] there has been little reported on applying these methods to Cu(II) and barium. Our work was primarily concerned with synthesis and characterization of bulky, fluorinated, and heterometallic alkoxides.[12] The ligands used in this study include isopropoxy, *tert*-butoxy, *tert*-heptoxy, di-*tert*-butylmethoxy, hexafluoroisopropoxy ([HFIP] = $OCH(CF_3)_2$), and perfluoro-*tert*-butoxy ([PFTB] = $OC(CF_3)_3$) and one bidentate ligand, 2-tetrahydrofurfuroxy [THFFO].

Experimental Section

General Comments. All manipulations were performed under vacuum or inert atmosphere (He). All solvents were distilled from $NaOCPh_2$ prior to use. Material sources are as follows: Et_3COH, $MeEtPr^iCOH$, $(Me_3CO)_2$, and $BaBr_2$ (Aldrich); $(Me_3C)_2CHOH$, Ba, Sr, Ca, BaH_2, NaH, $CuCl_2$, $BaCl_2$, (Alfa); $(CF_3)_3COH$ and $(CF_3)_2CHOH$ (PCR); CuCl (Cerac). Alcohols were dried over 3-Å molecular sieves. Halides (except CuCl) were dried by heating to 250–300 °C under vacuum. Commercially obtained BaH_2 was determined to be only 70% active by hydrolysis and measurement of the resulting noncondensibles on the vacuum line. NMR spectra were obtained on either a JEOL FX-60Q or a Bruker MSL-300 instrument. Samples were in C_6D_6 solvent, and ^1H spectra were recorded at 300 MHZ unless specified otherwise. Residual hydrogens were used for ^1H reference; $CFCl_3$ (δ 0.0) was used for ^{19}F. X-band ESR spectra were recorded on a Bruker ER 200D instru-

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ment, and a Mn^{2+} reference was used. IR spectra (Nujol, KBr) were recorded on a PE 1430 ratio recording infrared spectrophotometer. Electronic spectra were recorded on a Cary 2390 spectrophotometer. Molecular weights (of compounds with sufficient solubility in C_6H_6) were measured in mercury-filled tensimeters, and the molecular weight of $NaCu(OCMe_3)_3$ was determined isopiestically at 41.85 °C, with benzophenone used as the standard. The tensimeters and the isopiestic apparatus were immersed in a stirred oil bath and read with a cathetometer. Elemental analyses were performed by E+R Microanalytical Laboratory Inc., Corona, NY. Some analyses of metals in impure products were done in our laboratory with a Perkin-Elmer PLASMA II ICP instrument.

Mass Spectral Studies. The electron-impact mass spectra of the volatile alkoxides were obtained on a Finnigan-MAT TSQ-70 spectrometer. Samples were contained in sealed capillary tubes, which were broken just prior to analysis. The samples were placed in a direct insertion probe, which was rapidly introduced into the vacuum lock of the spectrometer to minimize air exposure. Samples were analyzed by desorption electron-impact ionization. The electron energy was 70 eV, except where noted. The temperature of the probe was increased linearly from 100 to 350 °C at 313 °C/min (except where noted), and spectra were collected at 1–2-s intervals. Reported results represent an average of a minimum of 10 scans.

Mass spectra of the volatile byproducts from sublimation of **1** and **4** were obtained of a CVC MA-2 time-of-flight instrument at 70 eV.

Synthesis of Alkoxides. The known compounds[4,13] $NaOCMe_3$, Na[THFFO], and $NaOCEt_3$ were obtained from reaction between NaH and their respective alcohols in THF solution. $NaOCMe_3$ and $NaOCEt_3$ were purified by recrystallization from heptane. THF was removed by heating to ≈100 °C under vacuum. $Cu(OCMe_3)_2$ was obtained from $CuOCMe_3$ and $(Me_3CO)_2$.[14] All reactions were done under inert atmosphere (He) or vacuum in Pyrex bulbs containing a stir bar and sealed with a Kontes valve unless otherwise indicated. Filtrations were done in the Dri-lab unless an H-tube was used. Alcohol-containing mixtures were evaporated in vacuo and redissolved in THF before filtration in the Dri-lab. Reactions with copper(II) alkoxides were wrapped in Al foil to protect them from light. Data for $NaOCEt_3$: ^1H NMR (60 MHz) δ 0.88 (m, CH_3), 1.23 (q); ^{13}C NMR δ C 9.5 (CH_3), 35.9 (CH_2), 71.3 (C). Data for Na[THFFO]: ^{13}C NMR (15 MHz) δ 26.45, 27.18, 67.69, 71.99, 86.92.

$Ba(OCEt_3)_2$ (1) and $Ba(OCMeEtPr^i)_2$ (2). A mixture of Ba (1.05 g, 7.65 mmol), Et_3COH (5.0 mL), and THF (5 mL) was stirred for 7 days at 80 °C. Following evaporation in vacuo and addition of ≈40 mL THF, a fine suspension of the alkoxide was decanted from pieces of unreacted Ba. $Ba(OCEt_3)_2$ (2.10 g, 75%) was isolated by filtration and dried in vacuo at 90 °C for 1 day. Anal. Found (calcd) for $C_{14}H_{30}O_2Ba$: C, 45.67 (45.73); H, 7.89 (8.22); Ba, 37.66 (37.35). ^1H NMR: 0.81 (t) 1.37 (q).

A mixture of Ba (0.80 g, 5.8 mmol), $MeEtPr^iCOH$ (3 mL), and THF (15 mL) was stirred for 19 days at 75 °C, and $Ba(OCMeEtPr^i)_2$ (1.87 g, 87%) was isolated in a similar manner. Anal. Found (calcd) for $C_{14}H_{30}O_2Ba$: C, 45.72 (45.73); H, 8.02 (8.22); Ba, 37.30 (37.35).

$Ba(OCMe_3)_2$ (3). Stirring a mixture of Ba (1.01 g, 7.35 mmol), Me_3COH (8 g, 108 mmol), and THF (10 mL) in an H-tube at 60 °C initiated (heat then removed) a vigorous reaction, which resulted in a nearly homogeneous solution that exhibited the black color of finely divided barium. Filtration, solvent removal, and drying in vacuo at 95 °C for 1 day afforded 1.77 g (85%) of **3**. Anal. Found (calcd) for $C_8H_{18}O_2Ba$: C, 33.89 (33.76); H, 6.40 (6.57); Ba, 48.43 (48.38). ^1H NMR (C_4D_8O): δ (intensity) 1.20 (8), 1.27 (2), 1.39 (3), 1.45 (1).

A mixture of BaH_2 (2.25 g, 16.4 mmol) with Me_3COH (8 mL) in THF (10 mL) was stirred at 90 °C for 7 days (22.9 mmol H_2 evolved). Filtration (0.40 g residue), solvent removal, washing with heptane and benzene, and drying in vacuo (100 °C), afforded white solid **3′** (3.22 g). Anal. Found: C, 31.38; H, 6.20; Ba, 49.82. NMR: nearly identical with that of **3**, broader lines.

$Ba[OCH(CMe_3)_2]_2$ (4). A mixture of $(Me_3C)_2CHOH$ (1.31 g, 9.08 mmol) and Ba (0.30 g, 2.2 mmol) was stirred for 4 h at 80–95 °C. The noncondensable gas was measured (2.2 mmol), and 0.696 g of $(Me_3C)_2CHOH$ was recovered. The product was dissolved in hot THF, filtered twice, evaporated, and recrystallized from a THF/C_6H_6 mixture, affording the white **4**. Anal. Found (calcd) for $C_{18}H_{38}BaO_2$: C, 51.15 (51.01); H, 9.19 (9.04); Ba, 32.08 (32.40). ^1H NMR (60 MHz): δ 0.96 (Me), CH not positively identified, br.

Sublimation of 1–4. The sublimates were characterized by elemental analysis and the volatile products analyzed with NMR or mass spectroscopy.

Data for the sublimate of **1**. Anal. Found (for the sublimate): C, 42.60; H, 7.66; Ba, 39.59. Et_3COH and C_7H_{14} were identified by MS [*m/e* (%), M^+: 98 (5), C_7H_{14}; 88 (6), $C_5H_{12}O$; 87 (100), $C_5H_{11}O$; 83 (4); 70 (5); 69 (29); 57 (19); 56 (5); 55 (19); 53 (5); 45 (62); 43 (19); 41 (36); 39 (13). MS of parent alcohol had no M^+ or C_7H_{14}: *m/e* (%) 88 (6), 87 (100), 69 (17), 57 (19), 45 (64), 43 (17), 41 (22), 39 (7)].

Data for the sublimate of **2**. Anal. Found: C, 40.86; H, 7.20; Ba, 42.06; $MeEtPr^iCOH$ and $EtPr^iC{=}CH_2$ (with small amount of $MeEtC{=}CMe_2$ and $MePr^iC{=}CHMe$) were identified by ^1H NMR.

Data for the sublimate of **3**. Me_3COH and $Me_2C{=}CH_2$ were identified by ^1H and ^{13}C NMR.

Data for the sublimate of **3′**. Anal. Found: C, 28.80; H, 5.20; Ba, 53.53.

Data for the sublimate of **4**. Anal. Found: C, 47.38; H, 8.49; Ba, 35.97. $(Me_3C)_2C{=}O$ was identified by MS [*m/e* (%): 142 (2), 87 (4), 85 (2), 57 (35), 49 (16), 39 (7); no 144; MS of alcohol had M^+ at *m/e* 144].

Ba[HFIP]$_2$ (5). Dry $HOCH(CF_3)_2$ (1.5 mL, 13 mmol) was condensed onto BaH_2 (0.830 g, 6.0 mmol) in THF (20 mL) at −196 °C. Gas evolution was slow until the mixture approached 0 °C where the reaction became vigorous. The mixture was kept at 0 °C until completion, and then the solvent was removed in vacuo from the nearly homogeneous solution, leaving a white solid. The solid was redissolved in THF and filtered through dry talcum powder, the solvent was stripped off, and the resulting solid was heated to 95 °C for 12 h; 2.50 g (88%) white solid was isolated; Anal. Found (calcd) for $BaC_6H_2F_{12}O_2$: C, 15.10 (15.29); H, 0.60 (0.43); Ba, 28.90 (29.13). ^1H NMR: δ 5.00. ^{19}F NMR: δ −76.2 and −76.1 ($\upsilon_{1/2}$ = 200 Hz), −74.9 (5%).

Ca[PFTB]$_2$ (6). A mixture of H(PFTB) (2.11 g, 8.94 mmol) and Ca (0.08 g, 2.0 mmol) underwent a very slow reaction at room temperature. After the mixture was stirred for 12 h at 95 °C and for 7 days at 120–130 °C, hydrogen measurement (0.000 54 mol) indicated 27% completion. Addition of THF and 7 days of further heating brought the reaction to 66% completion. After removal of volatiles, the product was dissolved in ether, filtered, dried, and recrystallized from THF/heptane to yield 0.50 g of a yellow-white powder. Analysis indicated the presence of solvent, which was removable at 130 °C under vacuum. Sublimation (140–190 °C) afforded 0.22 g (21%) of white **6**. Anal. Found (calcd) for $C_8F_{18}CaO_2$: C, 19.06 (18.80); H, 0 (0); F, 66.65 (67.04). ^{19}F NMR: δ −75.6.

Sr[PFTB]$_2$ (7) and Ba[PFTB]$_2$ (8). $(CF_3)_3COH$ (7 mmol) was condensed onto Sr (0.1929 g, 2.202 mmol) in a tube. Little reaction occurred at ambient temperature or occurred when the tube was heated to 65–70 °C for $^1/_2$ h. The reaction proceeded slowly at 80 °C and was refluxed for 4 days at 93–94 °C until no further noncondensable gasses were produced. Removal of volatiles (0.6105 g) left a white solid (1.23 g, 100%) in the tube. A portion was crystallized from heptane/THF solution. Anal. Found (calcd) for $C_8F_{18}SrO_2$: C, 17.20 (17.41); H, 0 (0); F, 61.31 (61.10); Sr, 15.70 (15.66). ^{19}F NMR (60 MHz): δ −76.4.

In a similar manner $(CF_3)_3COH$ (0.8688 g, 3.681 mmol) and Ba (0.1073 g, 0.781 mmol) were heated to 95 °C for 3 days. A total of 2.122 mmol of H(PFTB) was recovered when the volatiles were removed. A portion of the white solid was removed and the remainder was dissolved in THF, filtered, and dried under vacuum for 3 days at 90 °C. Anal. Found (calcd) for $C_8F_{18}BaO_2$: C, 16.01 (15.82); H, 0 (0); F, 56.12 (56.3); Ba, 22.50 (22.6). ^{19}F NMR (60 MHz): δ −75.9.

The reaction of BaH_2 (0.590 g, 4.23 mmol) and $(CF_3)_3COH$ (1.4 mL, 9.74 mmol) in THF (10 mL) was more vigorous, taking only 30 min at ambient temperature, and purified like above, 2.16 g (84%) of **8** was isolated.

$Ba(OCH_2C_4H_7O)_2$ (9). Barium (0.50 g, 3.6 mmol) was dissolved in tetrahydrofurfuryl alcohol (1.95 g, 19.1 mmol) by stirring at 65 °C for 2 days. The alkoxide crystallized on cooling. Excess alcohol was removed by heating the product to 100–110 °C under vacuum (1.22 g, 100%). Anal. Found (calcd) for $C_{10}H_{18}O_4Ba$: C, 35.24 (35.37); H, 5.47 (5.34); Ba, 39.96 (40.44). ^1H NMR (C_4D_8O): δ 1.53 (br), 1.81 (br), 3.57, 3.89 (br).

$CuOCEt_3$ (10). A mixture of CuCl (3.00 g, 30.3 mmol), Et_3CONa (4.2 g, 30.4 mmol), and THF (25 mL) was stirred for 24 h and filtered. Evaporation of filtrate produced **10**, a light tan, rubbery liquid in >95% yield. Anal. Found (calcd) for $C_7H_{15}CuO$: C, 47.37 (47.04); H, 8.69 (8.46); Cu, 35.72 (35.55). ^1H NMR: δ 1.00 (^3J = 7.1 Hz, CH_3), 1.47 (CH_2). ^{13}C NMR: δ 8.7 (CH_3), 34.7 (CH_2), 77.2 (C). Molecular weight (32 °C, 0.1131 g/0.236 g of C_6H_6): 654.

Reaction of $NaOCEt_3$ with $CuCl_2$. $NaOCEt_3$ (1.00 g, 7.23 mmol) and $CuCl_2$ (0.49 g, 3.6 mmol), Et_3COH (3 mL), and C_6H_6 (3 mL) were stirred in an H-tube for 18 h and filtered. Evaporation of the filtrate in

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vacuo afforded an orange-brown liquid. Anal. Found (calcd) for $C_{14}H_{30}O_2Cu$: C, 53.91 (57.21); H, 9.79 (10.29); Cu, 23.73 (21.62); Cl, 0.0 (0). ^{1}H NMR (all lines broad): δ 5.85, 3.5–5.5 (m), 1.25, 1.0. ^{13}C{^{1}H} NMR (75.468 MHz): δ −10 (weak, unassigned), 1.0 (m) 2.5, 8.6 (CH_3), 28.36, 29.23, 34.76 (CH_2), 77.4 (C). UV/vis [nm (ϵ)] (THF): 240 (4300), 302 (1700), 460 (2400), 688 (100), 800 (60), 960 (50) [ϵ values assume $Cu(OCEt_3)_2$]. Reaction also forms the same product in THF, but only $NaCu(OCEt_3)_3$ forms in Et_2O.

An attempt was made to vacuum distill the orange-brown liquid. Evolution of volatile materials proceeded slowly at room temperature and increased as the temperature rose to 125 °C, where evolution was very rapid and was continued until complete. NMR (^{13}C) of liquid residue: Et_3COCu, with a small, unidentified peak at δ 27.9. The volatiles were vacuum fractionated. The −20 °C trap contained mostly Et_3COH, the primary product. The −45 °C contained Et_3COH and an unidentified C=O containing compound, probably a ketone (IR 1730–1740 cm^{-1}; ^{13}C NMR (15 MHz) δ 16.2, 26.7). The −196 °C trap contained ethylene and unidentified components (^{13}C NMR δ 7.86, 12.89, 23.12, 29.81, 35.05).

NaCu(OCMe$_3$)$_3$ (11). A mixture of $CuCl_2$ (4.7 g, 35.0 mmol), Me_3CONa (10 g, 104 mmol), and THF (90 mL) was stirred at 60–80 °C for 4 days and filtered cold; then **11** was sublimed from the solid in several portions at 110–120 °C, and 4.77 g (45%) was collected. Anal. Found (calcd) for $C_{12}H_{27}CuNaO_3$: C, 47.20 (47.12); H, 8.94 (8.90); Na, 7.24 (7.52); Cu, 20.83 (20.77). UV/vis [nm (ϵ)] (C_6H_{14}) 280 (1580), 347 (2980), 701 (225), 754 (220), 947 (36). ^{1}H NMR: δ ($\nu_{1/2}$) 11.09 (350 Hz), 6.24 (720 Hz). Molecular weight, 814; degree of association (n) = 2.66 vs 2.40 predicted from NMR data for a $0.0487/n$ M solution in C_6H_6 at 41.85 °C.

NaCu(OCEt$_3$)$_3$ (12). $NaOCEt_3$ (1.00 g, 7.23 mmol), $CuCl_2$ (0.32 g, 2.4 mmol), and THF were stirred for 2 days. Filtration and the evaporation of the filtrate afforded **12**, a green solid (0.75 g, 73%). Anal. Found (calcd) for $C_{21}H_{45}O_3NaCu$: C, 58.18 (58.37); H, 10.65 (10.50); Na, 5.21 (5.32); Cu, 15.02 (14.70). UV/vis [nm (ϵ)] (C_6H_{14}): 247 (1050), 363 (2850), 715 (225), 754 (220), 947 (36). ^{1}H NMR: δ ($\nu_{1/2}$) 10.3 (1500 Hz), 5.7 (600 Hz), 1.24 (110 Hz).

Na$_2$Cu(OCHMe$_2$)$_4$ (13). A mixture of $CuCl_2$ (0.125 g, 0.93 mmol), $NaOCHMe_2$ (0.305 g, 3.72 mmol), and THF (25 mL) was stirred for 12 h while protected from light. Heptane was added, the pink-purple mixture was filtered through dry talc, and the solvent was removed, affording a gray-green solid. Anal. Found (calcd) for $C_{12}H_{28}O_4Na_2Cu$: C, 41.76 (41.67); H, 7.92 (8.16); Na, 13.01 (13.29); Cu, 18.57 (18.37). The compound decomposes slowly at room temperature and must be kept cold. ^{1}H NMR (C_4D_8O): δ 11.76 ($\nu_{1/2}$ = 1400 Hz, Me). UV/vis [nm (ϵ)]: 270 (5370), 550 (60), 745 (17).

Na$_2$Cu[HFIP]$_4$ (14). $CuCl_2$ (0.5 g, 3.72 mmol), Na[HFIP] (2.12 g, 11.1 mmol), and THF (20 mL) were stirred in THF for 12 h at room temperature, 6 h at 60–80 °C and 2 days at 60 °C. The deep blue mixture was filtered through dry talc, evaporated to dryness, redissolved in a heptane–benzene mixture, filtered, and evaporated. After sublimation at 95–120 °C, it still contained some THF (THF adduct forms a blue goo) and was heated 75–80 °C under vacuum for 6 h affording light blue **14** (1.48 g, 68%). Anal. Found (calcd) for $C_{12}H_4F_{24}O_4Na_2Cu$: C, 17.95 (18.53); H, 0.54 (0.52); F, 58.76 (58.63); Na, 6.39 (5.91); Cu, 8.58 (8.17). ^{19}F NMR (C_4D_8O): δ −60.5 ($\nu_{1/2}$ = 3000 Hz). UV/vis [nm (ϵ)] (C_6H_{14} + small quantity of THF): 248 (2160), 707 (54).

Na$_2$Cu[THFFO]$_4$ (15). Sodium tetrahydrofurfuroxide (2.77 g, 22.3 mmol), $CuCl_2$ (1.00 g, 7.4 mmol), and THF (50 mL) were stirred for 1 day at 60 °C. The dark blue solution was filtered, and solids were washed with THF and benzene (2.13 g of solids). Removal of solvent from the combined filtrate afforded a blue, glassy material (1.35 g). Anal. Found (calcd) for $C_{20}H_{36}O_8CuNa_2$: C, 46.81 (46.73); H, 7.10 (7.06); Cu, 12.64 (12.36); Na, 8.60 (8.95). Molecular weight: 1060 (118.9 mg/195 mg of C_6H_6, 32.6 °C). UV/vis [nm (ϵ)] (THF): 256 (5120), ≈290 (≈3900), 642 (120) ^{1}H NMR: δ ($\nu_{1/2}$) 3.1 (500), 2.5 (300 Hz), 1.9 (300 Hz), 1.2 (30 Hz), 0.9 (20 Hz). Blue solids on frit (presumably NaCl and $Cu[THFFO]_2$) decompose at 160 °C.

BaCu[HFIP]$_4$ (16). $Ba[HFIP]_2$ (1.06 g, 2.24 mmol), $CuCl_2$ (0.153 g, 1.13 mmol), and 20 mL of THF were stirred for 1 day at room temperature and for 12 h at 60 °C, then filtered through dry talc, and dried in vacuo. An ether wash removed a small amount of a green material, and the residue was dissolved in hot THF. Addition of hexane precipitated most of the blue crystalline **16** (0.4567 g). The greenish mother liquor was combined with the ether wash and a second crop of **16** (0.1358 g) was isolated 2 days later. The product (0.59 g, 61%) was dried under vacuum. Anal. Found (calcd) for $C_{12}H_4F_{24}O_4BaCu$: C, 16.75 (16.59); H, 0.44 (0.46); F, 52.20 (52.47); Ba, 15.89 (15.80); Cu, 7.59 (7.31). ^{19}F NMR (C_4D_8O): δ −65.8 ($\nu_{1/2}$ = 4000 Hz). ^{13}C NMR: 44.09 (J_{CF} = 22 Hz), 118.46 (J_{CF} = 334 Hz). UV/vis [nm (ϵ)] (THF): 250 (3000), 642 (136).

$BaBr_2$ (0.20 g, 0.67 mmol), **14** (0.50 g, 0.64 mmol), and a C_6H_6/THF mixture (15 mL) were stirred for 4 days at 60 °C. Filtration and solvent removal afforded a blue solid containing green and purple portions, from which 0.22 g of **14** was sublimed.

Ba[Cu(OCMe$_3$)$_3$]$_2$ (17). A mixture of $BaBr_2$ (0.24 g, 0.81 mmol), $NaCu(OCMe_3)_3$ (0.5 g, 1.6 mmol), and THF (25 mL) was stirred at 67 °C for 4 days. Filtration and the evaporation of the filtrate afforded a yellow-green material (0.53 g; Anal. Found: Ba, 19.24; Cu, 17.82; Na, 0.29). An attempt to sublime 0.035 g at 133–160 °C resulted in 1.8 mg of sublimate (the rest decomposed); the sublimate contains Cu:Ba:Na = 5:2:1 by ICP. Recrystallization from heptane/benzene/THF yields 0.15 g (26%) of **17**. Anal. Found (calcd) for $C_{24}H_{54}BaCu_2O_6$: C, 41.10 (41.00); H, 7.84 (7.74); Ba, 19.73 (19.53); Cu, 17.99 (18.07); Na, <0.20 (0). UV/vis [nm (ϵ)] (C_6H_{14}): 233 (2510), 303 (3135), 405 (5035), 694 (275), 758 (210), 910 (110). ^{1}H NMR: δ ($\nu_{1/2}$) 13.81 (580) [25 °C: 0.0033 M, 37%; 0.0133 M, 43%; 0.03 M, 44%], 3.40 (1200), 2.33 (600).

A mixture of $Ba(OCMe_3)_2$ (0.0506 g, 0.178 mmol), $Cu(OCMe_3)_2$ (0.1115 g, 0.531 mmol), and THF (10 mL) was stirred for 14 days at room temperature. A residue of 0.0476 g (0.227 mmol) of $Cu(OCMe_3)_2$ remained after filtration.

Photolysis Reactions. Except as noted, photolysis reactions were conducted in an apparatus consisting of a 8 in. × 24 in. steel can with the insides lined with Al foil, containing three 15-W fluorescent tubes and cooled by a vertical flow of forced air.

(a) A saturated heptane/THF solution (≈20 mL) of **11** (0.62 g) was photolyzed under a fluorescent desklamp for several weeks until the green color disappeared. The mixture was filtered and the filtrate evaporated to yield a tan-brown solid. The solid was washed with a heptane/THF mixture, and dissolved in hot THF. Addition of heptane and reduction of volume afforded an off-white solid, $NaCu(OCMe_3)_2$ (**18**) (25 mg, 5%). Anal. Found (calcd) for $C_8H_{18}O_2NaCu$: C, 41.37 (41.28); H, 8.08 (7.80); Na, 10.03 (9.88); Cu, 27.60 (27.30). Other products were not identified. A photolysis of **11** (0.25 g) in heptane solution (20 mL) afforded a precipitate of **18** in 91% yield. ^{1}H NMR: (C_4D_8O): δ 1.19. NMR evidence for Me_3COH, **18**, and unidentified products was present in the photolysis of a C_6D_6 solution of **11** in an NMR tube.

A mixture of $NaOCMe_3$ (10.3 mg, 0.107 mmol), $CuOCMe_3$ (14.3 mg, 0.105 mmol), and C_4D_8O (0.49 mL) in an NMR tube dissolved completely. On mild heating with a heat-gun, a white precipitate formed. The NMR spectrum (of the remaining solution) was identical with that of **18**.

(b) Photolysis of a C_6D_6 solution of **12** produced a diamagnetic solution, which contained a dark brown residue, with NMR spectra showing the presence of Et_3COH and $NaCu(OCEt_3)_2$ (**19**) (43:57 mole ratio) and an unidentified peak at δ 5.27 in the ^{1}H NMR spectrum. Compound **19** was also prepared by combining $CuOCEt_3$ and $NaOCEt_3$ (4.07 mmol each) in hexane solution, reducing the volume, and recrystallizing (70% yield). ^{1}H NMR: δ 1.049 (t, J = 7.1 Hz), 1.126 (t, J = 7.2 Hz), 1.553 and 1.611 (q, J = 7.2 Hz). ^{13}C NMR: δ 9.22, 9.74, 35.28, 35.54, 74.03, 75.02. Molecular weight: 1241 (0.1534 g/0.867 g of C_6H_6).

(c) A solution of **17** (20 mg) in hexane (10 mL) was photolyzed for 2 days. The light tan precipitate was washed with hexane and dried affording $Ba[Cu(OCMe_3)_2]_2$ (**20**) (11.3 mg). Anal. Found (calcd) for $C_{16}H_{36}O_4Cu_2Ba$: C, 33.87 (34.51); H, 5.92 (6.52); Ba, 24.39 (24.66); Cu, 22.37 (22.82). ^{1}H NMR (C_4D_8O): δ 1.14.

(d) $Na_2Cu[HFIP]_4$ (0.100 g) was dissolved in 11.1 mL of C_6H_6 in a 6-in. tube and photolyzed for 60 days. The tube was coated with a coppery black deposit. Trap to trap distillation between −78 and −196 °C separated the benzene from volatile decomposition products. Hexafluoro-2-propanol was identified by ^{19}F, ^{13}C, and ^{1}H NMR spectroscopy; an unidentified product had a ^{19}F NMR signal at δ −62.3.

NMR Equilibrium Study of 11. Sealed NMR tubes containing three different concentrations of $[NaCu(OCMe_3)_3]_n$ (**11**) in C_6D_6 were prepared. The integral fractions [F for δ 11.09 (dimer), $1 - F$ for δ 6.24 (trimer)] of the two methyl peaks were determined at 23 °C [for δ 11.09, (nC, F): 0.0021 M, 0.68; 0.0227 M, 0.41; 0.0540 M, 0.36] (nC = concentration of monomeric unit). The identities of the dimer and trimer peaks were confirmed by the slope (1.53) of the plot of $\ln [(1 - F)nC]$ vs. $\ln (FnC)$ (slope = ratio of oligomerizations of the two species). The thermodynamic parameters were determined from a temperature dependent study of the $0.0227/n$ M sample (temperature, F: 45 °C, 0.63; 53 °C, 0.67; 62 °C, 0.72; 80 °C, 0.81] by using a Van Hoff plot [a plot of ln (mole fraction equilibrium constant) vs $1/T$].

Crystallographic Studies for Na$_2$Cu[HFIP]$_4$. Single crystals were obtained from a hot heptane solution with enough THF added to dissolve the material. A suitable 0.28 × 0.22 × 0.15 mm blue prism was mounted in a thin walled capillary under a He atmosphere. A Siemens R3m/V automated diffractometer with incident-beam graphite-monochromated Mo Kα radiation was used to obtain the intensity data. The unit cell parameters were determined from a least-squares treatment of 25 centered reflections for 2θ between 21 and 34°. Systematic absences fixed the space group as Cc or $C2/c$. The space group $C2/c$ was chosen based on E value statistics and the structure solution. Data were collected by the $\theta = 2\theta$ scan method to a $2\theta_{max} = 45°$ covering the range $0 \le h \le 17$, $0 \le k \le 13$, $-12 \le l \le 12$. Standards monitored every 100 reflections were used to scale the data for a 3.5% linear decay over data collection. The scan width was $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]°$ and the ω scan rate was a function of count rate with a minimum speed of 7.5°/min and maximum of 30.0°/min. There were 3442 reflections measured, of which there were 1590 unique ($R_{int} = 2.6\%$ from merging equivalents) and 1069 observed with $F_0 > 3\sigma(F_0)$. The data were corrected for Lorentz and polarization, but not for absorption effects.

The structure was solved with direct methods, and all atoms were located in Fourier difference maps. The full-matrix least-squares refinement[15] minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(|F_o + g(F_o)^2]$ and $g = 0.00023$. There were a total of 195 parameters refined. These include atom coordinates and anisotropic thermal parameters for all but the hydrogen atoms. These were placed in idealized positions and then allowed to ride on the carbons to which they were bonded. The coordinate shifts of the carbon was applied to the bonded hydrogen with C–H = 0.96 Å. Final difference Fourier excursions were = 0.49 and –0.48 e Å^{-3}, and the error in an observation of unit weight, S, was 1.27. Atomic scattering factors are from ref 16.

Results and Discussion

Synthesis and Reactivity. The alkaline-earth alkoxides **1**–**9** were synthesized by the standard method of allowing the metal or its hydride to react with the alcohol (eqs 1 and 2). While reaction of commercially obtained BaH_2 (70% pure) with the fluorinated alcohols was rapid and produced pure products, reaction with Me_3COH afforded a soluble oxide–alkoxide whose analysis corresponded to the empirical formula $Ba(OCMe_3)_{1.8}O_{0.1}$ (**3′**). A recent report described the formation of an oxo–alkoxide cluster $H_3Ba_6(O)(OCMe_3)_{11}(OCEt_2CH_2O)THF_3$ from the reaction of Me_3COH with Ba.[17] In our hands this reaction did not behave as described in ref 17, nor was any diol $HOCEt_2CH_2OH$ detected in the hydrolysis products of **3** even though the reaction conditions were almost identical. This puzzling result could be explicable by our use of different material sources or differences in experimental conditions (workup procedure was much different), and further work is necessary.

$$M + 2ROH \rightarrow M(OR)_2 + H_2 \qquad (1)$$

$$BaH_2 + 2ROH \rightarrow Ba(OR)_2 + 2H_2 \qquad (2)$$

$Ba(OCEt_3)_2$ (**1**) $Ba(OCMeEtPr^i)_2$ (**2**) $Ba(OCMe_3)_2$ (**3**)[11]
$Ba[OCH(CMe_3)_2]_2$ (**4**) $Ba[HFIP]_2$ (**5**) $Ca[PFTB]_2$ (**6**)
$Sr[PFTB]_2$ (**7**) $Ba[PFTB]_2$ (**8**) $Ba[THFFO]_2$ (**9**)

The elemental analyses of the sublimates of **1**–**4** were consistent with the oxide–alkoxides $[Ba(OR)_2]_x[BaO]_y$ and ranged from 13% to 33% BaO. The sublimates of **1** and **2** resublimed at the same temperature with some residue, but the sublimates of **3** and **3′** resublimed only slightly. Tertiary alkoxides **1**–**3** eliminated alkene and parent alcohol during sublimation, but the secondary alkoxide **4** emitted the ketone $(Me_3C)_2C{=}O$. The emission of alcohol and alkene and formation of oxides or oxide–alkoxides were observed in Bradley and Faktor's studies of the thermal decomposition of zirconium *tert*-butoxide. They showed that a chain hydrolysis mechanism operates.[18] In this mechanism, traces of water liberate alcohol, which subsequently cracks to alkene and water, thus continuing the chain reaction. A similar process probably occurs for **1**–**3** as they emit the same kind of volatile products.

Table I. Summary of Crystallographic Data for $Na_2Cu[HFIP]_4$

formula: $C_{12}H_4O_4F_{24}CuNa_2$	space group: $C2/c$
$a = 15.965\ (5)$ Å	$T = 295$ K
$b = 12.652\ (5)$ Å	$\lambda = 0.71073$ Å
$c = 11.837\ (5)$ Å	$\rho_{calc} = 2.167$ g cm^{-3}
$\beta = 94.36\ (3)°$	$\mu = 11.6$ cm^{-1}
$V = 2384.0\ (16)$ Å^3	transm coeff: 0.84_{max}; 0.72_{min}
$Z = 4$	fw = 777.7
$F(000) = 1500$	$R(F) = 6.07\%$
	$R_w(F) = 4.76\%$

The copper alkoxides were prepared by metathesis reactions between a sodium or barium compound and the appropriate halide (eqs 3–6).

$$NaOCEt_3 + CuCl \rightarrow \underset{\textbf{10}}{CuOCEt_3} + NaCl \qquad (3)$$

$$xNa(OR) + CuCl_2 \rightarrow Na_{x-2}Cu(OR)_x + 2NaCl \qquad (4)$$

$NaCu(OCMe_3)_3$ (**11**) $NaCu(OCEt_3)_3$ (**12**)

$Na_2Cu(OCHMe_2)_4$ (**13**) $Na_2Cu[HFIP]_4$ (**14**)

$Na_2Cu[THFFO]_4$ (**15**)

$$2Ba[HFIP]_2 + CuCl_2 \rightarrow \underset{\textbf{16}}{BaCu[HFIP]_4} + BaCl_2 \qquad (5)$$

$$2NaCu(OCMe_3)_3 + BaBr_2 \rightarrow \underset{\textbf{17}}{Ba[Cu(OCMe_3)_3]_2} + 2\ NaBr \qquad (6)$$

A 1:1 reaction between $NaOCEt_3$ and $CuCl_2$ afforded an orange-brown, paramagnetic, nonvolatile liquid product, whose NMR and elemental analysis were consistent with a mixture of **10** and $Cu(OCEt_3)_2$. This product was thermally unstable, even at room temperature, and decomposed to **10**, Et_3COH, C_2H_4, and other unidentified materials. The spontaneous reduction of Cu(II) to Cu(I) has also been observed in the reaction of $CuCl_2$ with $NaN(SiMe_3)_2$[19] and can be attributed to steric crowding between bulky ligands on the small Cu^{2+} ion.

Glycoxides with a CuO_4^{2-} unit similar to alkoxides **13**–**16** have been prepared before,[7g,h] but **11**, **12**, and **17** are, to the best of our knowledge, the first known examples of alkoxides of $M[Cu(OR)_3]_n$ stoichiometry. In no case did we observe the formation of both $NaCu(OR)_3$ and $Na_2Cu(OR)_4$ alkoxides for a given alkoxy ligand.

An attempt to synthesize **16** from a reaction between **14** and $BaBr_2$ failed as a substantial fraction of the **14** was recovered unchanged. It follows that the use of sodium alkoxycuprates as starting materials for their barium analogues is of limited utility. It is also noteworthy that up to 1.7 molar equiv of $Cu(OCMe_3)_2$ dissolved in a THF solution of $Ba(OCMe_3)_2$, indicating the formation of mixed alkoxides, but this reaction was not investigated further.

The three alkoxides of form $M[Cu(OR)_3]_n$ readily decomposed to Cu(I) alkoxides when irradiated with visible light (eq 7). Such susceptibility to photodecomposition is at least partially explained by the presence of strong (ϵ = 2500–5000) ligand-to-metal charge-transfer (LMCT) absorptions at 350–400 nm in **11**, **12**, and **17**. Both copper hexafluoroisopropoxides **14** and **16** had weak d–d absorptions, and their charge-transfer bands were well into the ultraviolet. As one would expect, solutions of **14** decomposed very slowly under visible light irradiation.

$$M[Cu(OR)_3]_n \xrightarrow{h\nu} M[Cu(OR)_2]_n,\ ROH,\text{ and unidentified products} \qquad (7)$$

$NaCu(OCMe_3)_2$ (**18**) $NaCu(OCEt_3)_2$ (**19**)

$Ba[Cu(OCMe_3)_2]_2$ (**20**)

Structure Study. X-ray quality crystals were obtained for one $M_n[Cu(OR)_4]$ complex, $Na_2Cu[HFIP]_4$ (**14**). Its structure is

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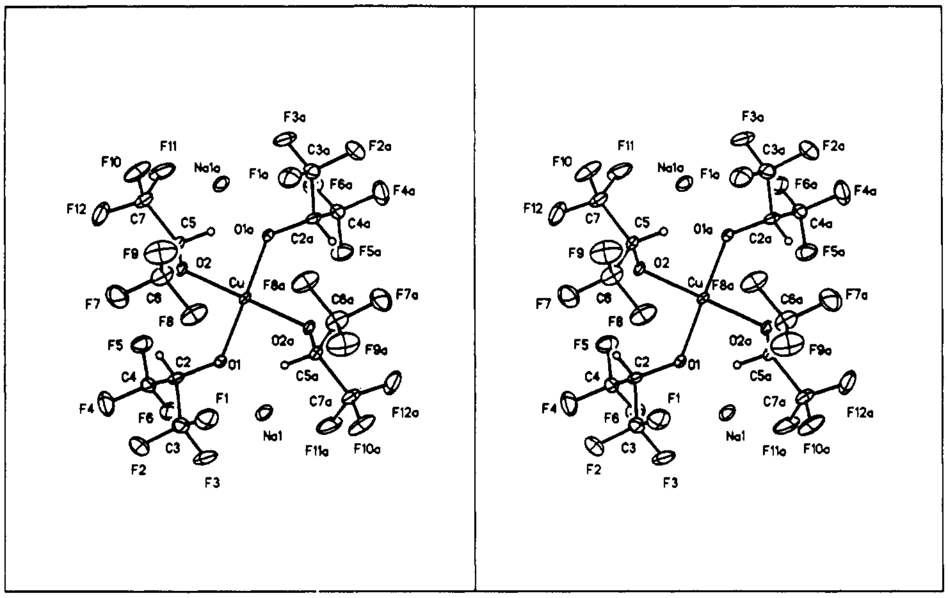

Figure 1. Thermal ellipsoid plot (stereoview) of $Na_2Cu[HFIP]_4$ drawn at the 20% probability level. Atom labels with the suffix a are related by $(-x, y, 0.5 - z)$.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)[a]
Cu	0	1081 (1)	2500	28 (1)
Na(1)	−1131 (2)	−26 (3)	4770 (3)	57 (1)
O(1)	−1068 (3)	856 (4)	3098 (4)	35 (2)
C(2)	−1838 (5)	1125 (7)	2584 (6)	34 (3)
C(3)	−2320 (7)	1784 (9)	3381 (8)	54 (4)
F(1)	−1901 (4)	2673 (5)	3664 (5)	78 (3)
F(2)	−3076 (3)	2062 (5)	2982 (5)	88 (3)
F(3)	−2406 (4)	1257 (5)	4357 (4)	81 (3)
C(4)	−2311 (6)	121 (9)	2238 (8)	51 (4)
F(4)	−3087 (4)	282 (6)	1786 (5)	93 (3)
F(5)	−1906 (4)	−400 (5)	1457 (4)	78 (3)
F(6)	−2375 (3)	−549 (5)	3085 (4)	70 (2)
O(2)	−465 (3)	1297 (4)	929 (4)	33 (2)
C(5)	−217 (6)	2239 (7)	484 (6)	37 (3)
C(6)	−804 (8)	3132 (9)	714 (9)	64 (5)
F(7)	−1585 (4)	2955 (5)	298 (5)	94 (3)
F(8)	−860 (4)	3217 (5)	1836 (5)	89 (3)
F(9)	−571 (5)	4062 (5)	359 (6)	106 (3)
C(7)	−143 (8)	2100 (10)	−785 (8)	57 (4)
F(10)	80 (5)	2985 (5)	−1283 (5)	96 (3)
F(11)	446 (5)	1391 (6)	−959 (5)	99 (3)
F(12)	−841 (4)	1748 (5)	−1318 (4)	87 (3)
H(2)	−1769	1542	1920	50
H(5)	319	2428	850	50

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Atom Spacings (Å), Bond Angles (deg), and Torsion Angles (deg)[a]

Cu–O(1)	1.916 (5)	Cu–O(2)	1.968 (5)
C–O(av)	1.373	C–F(av)	1.328
C–C(av)	1.516		
Na(1)- -O(1)	2.281 (6)	Cu- -Na(1)	3.630 (4)
Na(1)- -O(2)b	2.318 (6)	Cu- -Na(1)c	3.821 (4)
Na(1)- -F(11)a	2.481 (7)	Cu- -Cu c	6.520 (4)
Na(1)- -F(5)b	2.487 (7)	Na(1)- -Na(1)c	3.610 (4)
Na(1)- -F(12)b	2.590 (7)	Na(1)- -Na(1)a	6.697 (4)
Na(1)- -F(3)	2.621 (7)		
Na(1)- -F(6)	2.791 (7)		
O(1)–Cu–O(2)	95.0 (2)	O(2)–Cu–O(1)a	87.3 (2)
O(1)–Cu–O(1)a	162.9 (3)	O(2)–Cu–O(2)a	164.1 (3)
O(2)–Cu–O(1)–C(2)	−17.6	O(1a)–Cu–O(1)–C(2)	−114.9
O(2)a–Cu–O(1)–C(2)	146.6	C(5)a–O(2)a–Cu–O(1)	−72.0
C(5)a–O(2)a–Cu–O(2)	27.0	C(5)a–O(2)a–Cu–O(1)a	124.9

[a] Symmetry transformation indicated by suffix. a = $(-x, y, 0.5 - z)$ b = $(x, -y, 0.5 + z)$ c = $(-x, -y, 1.0 - z)$

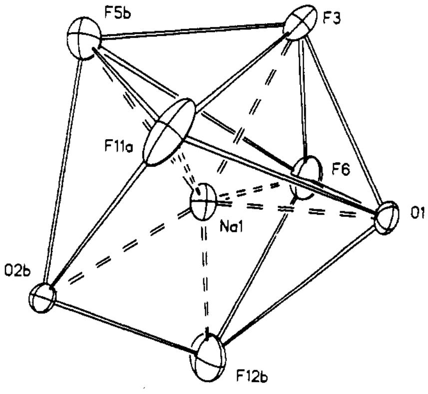

Figure 2. Coordination polyhedron about sodium in $Na_2Cu[HFIP]_4$.

shown in Figure 1, and the numbering of Tables I–III follows that indicated in this figure. The Cu atom is on a 2-fold axis, and the $Na_2Cu[HFIP]_4$ complex has C_2 molecular symmetry. The $\{CuO_4\}$ chromophore is four-coordinate and nearer to a rhombic coplanar than to a compressed tetrahedral configuration with a dihedral angle between O(1)–Cu–O(2) and the symmetry-related O(1a)–Cu–O(2a) of 22.4°. A twist nearly equal in magnitude has been observed[20] in [*N,N'*-ethylenebis(thioacetylacetone iminato)]copper(II). Bulky HFIP groups effectively block the axial Cu coordination positions, bonding to Cu in two different conformations; one pair with the O(1)–C(2) bond equatorial and the other pair with O(2)–C(5) axial to the approximate $\{CuO_4\}$ plane. For the axial pair all the CF_3 groups are to one side of the $\{CuO_4\}$ least-squares plane (maximum deviation from plane of 0.28 Å), and the Na ions lie on the opposite side along with a CF_3 group from each equatorial pair. The Cu–O bonds are significantly longer for the axial HFIP groups than those for the equatorial positions (1.968 (5) and 1.915 (5) Å), due in part to steric crowding.

The Na atoms are environed by five F atoms and two O atoms at distances ranging from 2.28 to 2.79 Å (Table III). The coordination polyhedron (Figure 2) about the sodium atom resembles a distorted monocapped trigonal prism, which is much like that observed in $Na_2Cu(C_2O_4)\cdot 2H_2O$.[21] The arrangement of the ions

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Table IV. Solubility and Sublimation Data and Decomposition Points (°C)[a]

compound				solubility[c]			compound				solubility[c]		
no.	formula	SP[b]	dec	H	B	T	no.	formula	SP[b]	dec	H	B	T
1	$Ba(OCEt_3)_2$	265	350	i	i	l	11	$NaCu(OCMe_3)_3$[d]	70*	170	s	s	s
2	$Ba(OCMeEtPr^i)_2$	240	325	i	i	l	12	$NaCu(OCEt_3)_3$	N	125	s	s	v
3	$Ba(OCMe_3)_2$[e]	270	320	i	i	s	13	$Na_2Cu(OCHMe_2)_4$	N	75		s	v
4	$Ba[OCH(CMe_3)_2]_2$	260	320	l	s	v	14	$Na_2Cu[HFIP]_4$[f]	90*	200	l	s	v
5	$Ba[HFIP]_2$	230	260	i	i	v	15	$Na_2Cu[THFFO]_4$	N	135	s	v	v
6	$Ca[PFTB]_2$	140	260	i	i	v	16	$BaCu[HFIP]_4$	220†	225	i	i	s
7	$Sr[PFTB]_2$	230*	320	i	i	v	17	$Ba[Cu(OCMe_3)_3]_2$	160†	170	s	s	v
8	$Ba[PFTB]_2$	280*	320	i	i	v	18	$NaCu(OCMe_3)_2$	180	240	i	i	s
9	$Ba[THFFO]_2$	N	215	i	i	l	19	$NaCu(OCEt_3)_2$	185	220	v	v	v
10	$Cu(OCEt_3)$	110	135	m	m	m	20	$Ba[Cu(OCMe_3)_2]_2$	N	240	i	i	l

[a] Temperatures for the beginning of sublimation (SP) (dynamic vacuum, $<10^{-5}$ Torr) are indicated. Appreciable rates of sublimation require 20–30 °C above SP for most compounds. The column "dec" indicates where decomposition becomes rapid. [b] An asterisk denotes rapid, almost complete sublimation, a dagger denotes very slight sublimation, N indicates no sublimation, and all others sublime with appreciable residue. [c] Key: H = saturated hydrocarbon; B = benzene; T = THF; i = insoluble; l = slightly soluble; s = soluble; v = very soluble; m = miscible in all proportions. [d] Mp: 170–175 °C. [e] Aging effects apparent as THF solubility decreases with time. [f] Mp: 140–146 °C.

Table V. Mass Spectral Data for $NaCu(OCMe_3)_3$ (**11**)

ion	*m/e*	rel intens 70 eV	rel intens 12 eV
	Cu_0		
$OCMe_3^+ - CH_2$	59	100	11
Na_2OR^+	119	73	
$Na_4(OR)_3^+$	311	17	3
$Na_7(OR)_4^+$	453	41	
	Cu_1		
$NaCuOR^+$	159	23	
$NaCu(OR)_2^+$-Me	217	18	0.2
$Na_2Cu(OR)_2^+$	255	94	0.5
$Na_2Cu(OR)_3^+$	328	87	12
$Na_3Cu(OR)_3^+$	351	17	0.2
$Na_3Cu(OR)_4^+$	424	33	4
$Na_7Cu(OR)_5^+$	589	5	
	Cu_2		
$Na_2Cu_2(OR)_3^+$	391	35	0.7
$Na_2Cu_2(OR)_4^+$	464	49	11
$Na_3Cu_2(OR)_4^+$	487	6	0.1
$Na_2Cu_2(OR)_5^+$	537	76	100
$Na_3Cu_2(OR)_5^+$	560	7	1
$Na_3Cu_2(OR)_6^+$	633	9	0.6
$Na_4Cu_2(OR)_6^+$	656	3	1
$Na_4Cu_2(OR)_7^+$	729	32	0.1
	Cu_3–Cu_6		
$Na_3Cu_3(OR)_7^+$	769	5	0.04
$Na_4Cu_3(OR)_7^+$	792		0.04
$Na_3Cu_3(OR)_8^+$	842	0.2	
$Na_4Cu_3(OR)_8^+$	865	0.3	
$Na_8Cu_4(OR)_5^+$	801	0.05	
$Na_4Cu_6(OR)_2^+$	616	2	2
$Na_6Cu_6(OR)_4^+$	808	0.1	0.03

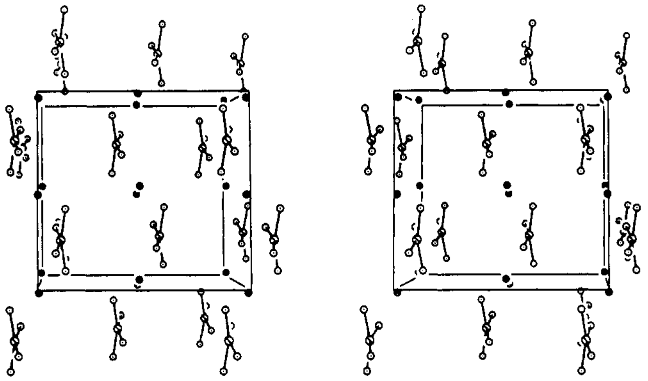

Figure 3. Stereoview packing diagram of $Na_2Cu[HFIP]_4$ viewed down the *a* axis. Only copper, sodium, and oxygen atoms are shown.

in the unit cell is shown in Figure 3. The sodium ions are aligned along the *c* axis in planar sheets spaced half a cell apart in *b*. These are sandwiched by opposing facing layers of the $Cu[HFIP]_4^{2-}$ ions.

Crystals of sufficient quality for structural studies were not obtained for any of the $M[Cu(OR)_3]_n$ type compounds. A low quality crystal of **17** was determined to be orthorhombic with unit cell dimensions 10.12 (1), 29.54 (4), and 33.16 (4) Å.

Properties and Characterization. The physical properties of all compounds with relevance to sol–gel and CVD processes, namely solubility, volatility, and thermal stability, are listed in Table IV.

Information on the molecularity or degree of association of these alkoxides were obtained from a number of sources. Mass spectroscopy revealed volatile **11** (Table V) to be predominantly dimeric in the vapor phase. Peaks corresponding to $Na_2Cu_2(OR)_5^+$ (dimer − alkoxy group) increased in relative intensity as the ionization voltage was reduced. Reducing the electron energy from 15 to 12 eV caused the relative intensity of the other major fragments (*m/e* 59, 328, and 464) to drop from approximately 40% to about 10%. Some peaks corresponding to aggregates of

Table VI. ESR Data for Copper(II) Alkoxides

	C_6H_6		THF		
	solution	frozen	solution	frozen	
	g_{iso} (*A*, G)	g (*A*, G)	g_{iso} (*A*, G)	$g_\perp$ (*A*, G)	$g_\parallel$ (*A*, G)
$Na_2Cu[HFIP]_4$	2.164 (60)	2.086 ⊥ 2.331 ∥ (150)	2.162 (61)[i]	2.067 (43)[i]	2.302 (164)[i]
$Na_2Cu[THFFO]_4$	2.162 (42)	2.136	2.159 (43)	2.043 (23)[a]	
$Na_2Cu(OCHMe_2)_4$	...	...	2.112 (43)	2.042 (23)[a]	2.291 (94)
$NaCu(OCMe_3)_3$	2.183	2.191	2.190[b]	2.051[c]	2.493 (20)
$NaCu(OCEt_3)_3$	2.174	2.14[d]	2.195	2.050	2.492 (16)
$Cu(OCEt_3)_2$[h]	2.179	2.057 ⊥ 2.522 ∥[g]	...	2.052	2.5
$Ba[Cu(OCMe_3)_3]_2$	2.166	2.143	2.243[e]	2.12, 2.07[f]	
$BaCu[HFIP]_4$	...	...	2.150 (73)	2.054 (31)	2.310 (164)

[a] Septet. [b] In C_6H_6 + a quantity of small qty THF, 2.12, 2.44; frozen, 2.06, 2.10, 2.39. [c] Broad multiplet 2.08–2.44, see Figure 4b. [d] Main peak, broad hump 2.03–2.50. [e] C_6H_6 + small quantity of THF 2.184. [f] Numerous unresolved peaks 1.85–2.35. [g] Also broad ∥ peak 2.23. [h] Mixed with **10** (see text). Broad resonance ≈5 in C_6H_6 solution and frozen THF; g = 5.71 in frozen C_6H_6. [i] THF added to benzene solution.

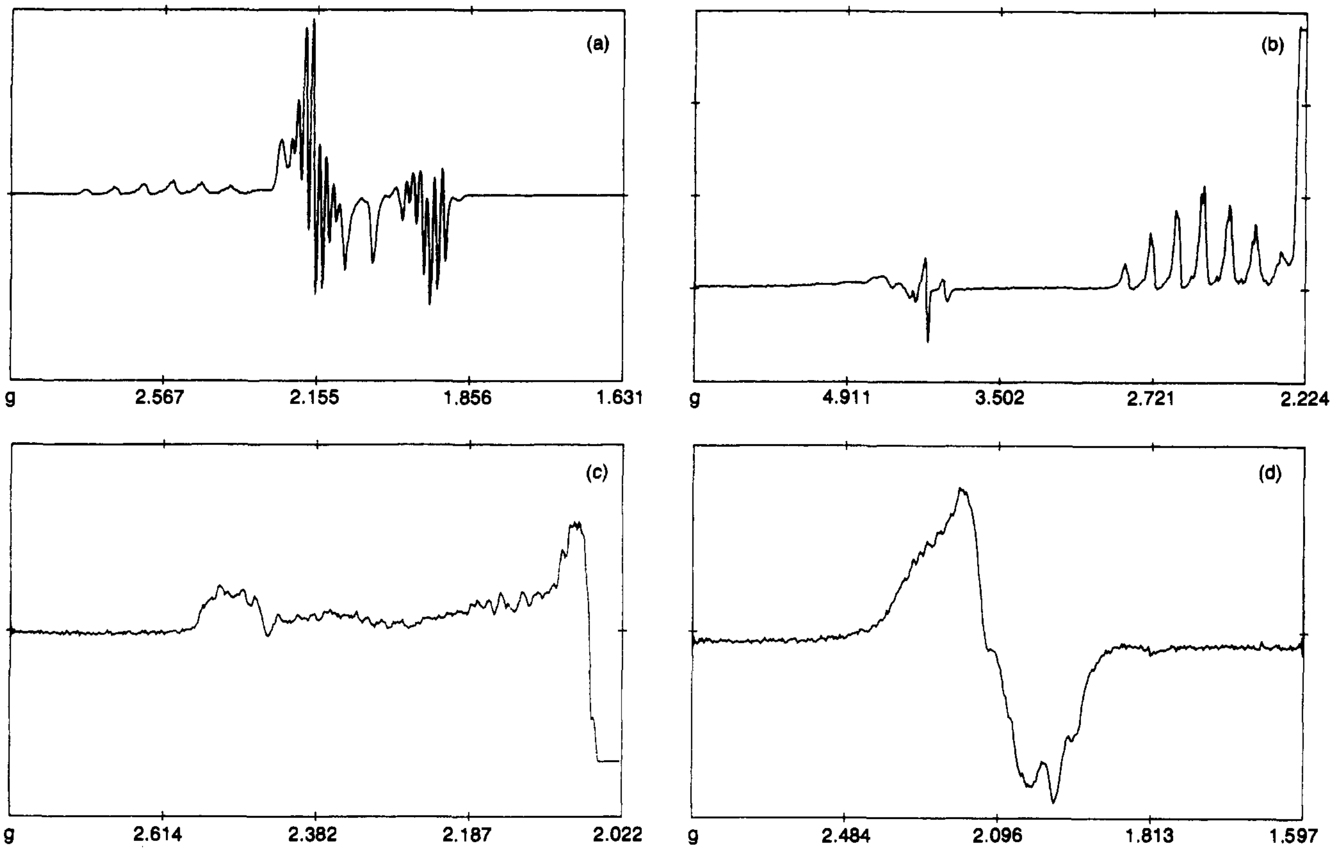

Figure 4. Selected ESR spectra of frozen THF solutions: (a) $Na_2Cu(OCHMe_2)_4$ (**13**); (b) $Na_2Cu(OCHMe_2)_4$, half-field region; (c) $NaCu(OCMe_3)_3$ (**11**); (d) $Ba[Cu(OCMe_3)_3]_2$ (**17**).

three or more Cu or Na atoms were observed even at low voltage, but with the exception of $Na_4Cu_6(OR)_2^+$ (*m/e* 616), the intensities were substantially reduced. Either ion–molecule reactions or the presence of a small fraction of higher oligomers could account for the high-mass peaks. Information on the vapor-phase oligomerization of the other complexes was, however, less conclusive, and mass spectral data on other complexes is provided only as supplementary material.

Tensimetric molecular weight measurements (C_6H_6) indicated a degree of association of 3.7 for $CuOCEt_3$ (**10**) and 3.9 for $NaCu(OCEt_3)_2$ (**19**). While the proton NMR spectrum of **10** had broad lines indicative of chemical exchange between multiple species, **19** showed evidence for only one species (tetramer).

The proton NMR spectra of the $M[Cu(OR)_3]_n$ compounds all contained paramagnetically broadened and shifted peaks in two (Na) or three (Ba) different environments. The relative areas of the peaks in **11** were strongly concentration and temperature dependent. An analysis of spectra from several concentrations indicated the presence of a dimer-trimer equilibrium (eq 8). This was consistent with the isopiestic molecular weight in C_6H_6 solution. The results of concentration dependent studies on **12** were

$$\underset{\delta\ 11.09}{3[NaCu(OCMe_3)_3]_2} \rightleftarrows \underset{\delta\ 6.24}{2[NaCu(OCMe_3)_3]_3} \qquad (8)$$

$$\Delta H = -15.5 \pm 0.9 \text{ kcal/mol} \qquad \Delta S = -37 \pm 3 \text{ cal/mol K}$$

inconclusive. With $Ba[Cu(OCMe_3)_3]_2$ (**17**), the relative area of the peak at 14 ppm increased slightly with increasing concentration but was decreased substantially in a solution with a 1:1 $Ba(OCMe_3)_2$:$Cu(OCMe_3)_2$ ratio. Only one environment was observed in the proton spectrum of **13** and the ^{19}F spectra of the $M_n[Cu(HFIP)_4]$ compounds **14** and **16**.

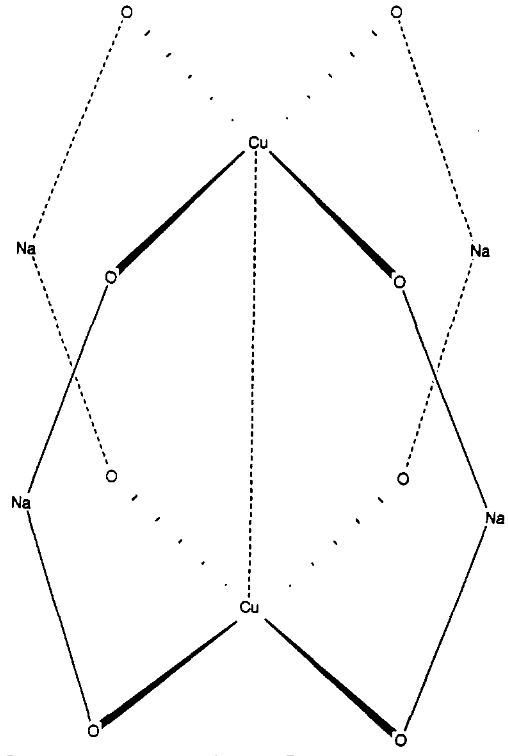

Figure 5. Proposed structure for $Na_2Cu(OCHMe_2)_4$ (**13**).

The X-band ESR spectra (Table VI) of frozen THF solutions of **14** and **16** were well resolved, clearly showing both $g_\parallel$ and $g_\perp$, each with the four hyperfine lines indicative of mononuclear copper. This is consistent with an axially symmetric monomeric species. The crystallographic structure of **14** is not axially symmetric, but THF complexation of the Na^+ ions could increase the molecular symmetry. The ESR spectra of the unfluorinated isopropoxide **13** (Figure 4a, b) were also well resolved, clearly showing the seven-line hyperfine pattern of axially symmetric, binuclear copper for both $g_\parallel$ and $g_\perp$ and for g_{iso} in solution.

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Half-field lines were further evidence for binuclearity. According to Bleany and Bowers,[22] a dimeric $S = {}^1/_2$ system with axial symmetry has four allowed transitions in the solid state, two for $g_\parallel$ separated by $2D$ and two for $g_\perp$ separated by $3E + D$. Thus, the zero-field splitting parameters D and E are 0.0299 ± 0.0009 cm^{-1} and 0.0004 ± 0.0003 cm^{-1} respectively. The internuclear Cu–Cu distance was estimated to be 4.85 Å from the equation of Chasteen and Belford.[23]

$$R = (0.650 g_\parallel{}^2/D)^{1/3} \tag{9}$$

This distance is consistent with a Na-bridged structure such as that illustrated in Figure 5. The tetrahydrofurfuroxide **15** also exhibited a seven-line hyperfine pattern in frozen THF solution ($3E + D = 0.0363$ cm^{-1}) indicating a structure similar to **13**. However, the copper centers must be further apart at room temperature since the spectra displayed a poorly resolved four-line pattern despite solution molecular weight measurements indicating a dimer.

Benzene solutions of $M[Cu(OR)_3]_n$ complexes **11**, **12**, and **17** had broad ESR lines with no resolution of $g_\perp$, $g_\parallel$, or hyperfine splitting. Broad lines could be caused by a number of things: molecular asymmetry, small unresolved hyperfine couplings, spin–spin relaxation, and the presence of multiple chemical species. All may be acting here. Both g values and a poorly resolved $A_\parallel$ (quartet) were identifiable for the frozen THF solutions of **11** and **12**; these peaks were assigned to a mononuclear THF adduct. Frozen solutions of **11** also had an extremely broad, barely discernible half-field resonance around $g = 4.5$ and a broad multiplet (see Figure 4c) that were attributable to dimers and/or higher oligomers. Frozen THF solutions of **17** had complex ESR spectra, which were not assigned (Figure 4d).

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Supplementary Material Available: Tables of crystal data, anisotropic displacement coefficients, and complete bond lengths and angles for $Na_2Cu[HFIP]_4$, the log/log and van't Hoff plots for **11**, and tables of mass spectral data for **1–8**, **14**, **16**, and **17** (12 pages); a table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Notes

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Role of Solvent in Photoredox Reactions of Cobalt(III) Am(m)ine Complexes

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Charge-transfer (CT) excited states of transition-metal complexes arise from the radial movement of electron density between metal and ligands (or solvent), and this redistribution of charge should be inherently sensitive to changes in solvent medium. The commonly observed solvatochromism of CT absorption and luminescence bands, for example, results from dielectric (e.g. dipole–dipole, dipole–induced dipole, dispersion) and/or hydrogen-bonding interactions between the complex and solvent molecules.[1] Solvent viscosity also can influence CT luminescence through its effect upon the rate of solvent reorientation about the excited complex.[2]

A fundamental consideration in discussions of CT photochemical behavior is the role played by the environment. Does solvent participate chemically in the reactions of CT excited states, or is its influence confined to medium effects of the type noted above? This issue was addressed for ligand-to-metal charge-transfer (LMCT) states several years ago by Endicott et al. in their comprehensive studies of the $Co(NH_3)_5X^{2+}$ family (X is a uninegative ligand such as Cl$^-$ or Br$^-$).[3] It was concluded that the environmental influence on the photoredox chemistry of these complexes is appreciable. In particular, whether a LMCT state is bound or dissociative appeared to depend upon the solvent. Moreover, it was suggested that photooxidation of the solvent via a solvent-to-metal charge-transfer process is reasonably general for deep ultraviolet excitations of metal complexes.

Our interest in base-generating photoinitiators for microlithographic applications led us to examine the ultraviolet spectroscopy and photochemistry of several $Co(NH_2R)_5X^{2+}$ complexes (R is methyl, ethyl, or *n*-propyl) in different solvents.[4] Unlike the results obtained previously for the $Co(NH_3)_5X^{2+}$ family, we find that the LMCT excited states of these alkylamine complexes undergo redox reactions with no discernible chemical involvement of solvent. This disparity suggests the need to revisit the issue of solvent influence on the reactivity of LMCT excited states. Reported below are spectral and photochemical data that facilitate some meaningful discussion along this line.

Experimental Section

Analytically pure samples of $[Co(NH_3)_5Br](ClO_4)_2$[5] and $[Co(NH_2CH_3)_5Br](ClO_4)_2$[6] were synthesized according to published procedures. Distilled water and commercially available acetonitrile (Burdick and Jackson spectral grade), methanol (Baker HPLC grade), and glycerol (Baker reagent grade) were used as solvents. Solutions of the complexes were acidified to pH ~3 with perchloric acid and maintained at 10.0 ± 0.5 °C in thermostated 1-cm quartz cells. Electronic absorption spectra were measured on a Varian DMS 300 spectrophotometer. Photolyses at selected wavelengths above 254 nm were conducted with a high-pressure mercury lamp in conjunction with a monochromator, while low-pressure mercury, cadmium, and zinc lamps were employed for 254-, 229-, and 214-nm excitations, respectively. Incident light intensities at wavelengths ≥254 nm were determined with a ferrioxalate actinometer,[7] while the redox decomposition of $Co(NH_3)_5Cl^{2+}$ was employed as an actinometer at shorter wavelengths.[3c] Photolyzed solutions were analyzed for Co^{2+}[8] and formaldehyde[9] by standard methods.

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