Syntheses, Structures, and Thermal Properties of Heterometallic Copper(II)−Alkaline-Earth Metal Complexes with 1,3-Bis(dimethylamino)-2-propanolato (bdmap) and Trifluoroacetato as Ligands: $CaCu(bdmap)_2(O_2CCF_3)_2(H_2O)$, $Sr_2Cu_2(bdmap)_4(O_2CCF_3)_4$, and $Sr_2Cu(bdmap)_6(O_2CCF_3)_4(\mu_3\text{-}OH)_2$

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Three new heterometallic copper(II)−alkaline-earth metal complexes have been synthesized by using 1,3-bis(dimethylamino)-2-propanolato (bdmap) and trifluoroacetato as ligands. These three compounds have been formulated as $CaCu(bdmap)_2(O_2CCF_3)_2(H_2O)$ (**1**), $Sr_2Cu_2(bdmap)_4(O_2CCF_3)_4$ (**2**), and $Sr_2Cu_4(bdmap)_6(O_2CCF_3)_4(\mu_3\text{-}OH)_2$ (**3**), respectively. Their structures have been determined by single-crystal X-ray diffraction analyses. Compound **1** is a dinuclear complex and dimerizes in the solid state through intermolecular hydrogen bonds. Compound **2** is a tetranuclear complex, while compound **3** is a hexanuclear complex, where metal ions are linked together through the bridging ligands. The thermal properties of these compounds have been investigated by thermogravimetric analysis. These compounds decompose to either the corresponding oxide or a mixture of metal fluoride and oxides at temperatures below 400 °C. Crystal data: **1**, $C_{18}H_{36}CuCaF_6O_7N_4$, monoclinic, $P2_1/n$, $a = 13.234(4)$ Å, $b = 15.401(3)$ Å, $c = 14.445(2)$ Å, $\beta = 94.79(2)°$, $V = 2934(1)$ Å^3, $Z = 4$, $d_{calc} = 1.445$ g cm^{-3}; **2**, $C_{36}H_{68}Sr_2Cu_2F_{12}O_{12}N_8$, monoclinic, $P2_1/c$, $a = 13.291(3)$ Å, $b = 11.238(5)$ Å, $c = 18.472(7)$ Å, $\beta = 91.51(2)$, $V = 2758(1)$ Å^3, $Z = 2$, $d_{calc} = 1.608$ g cm^{-3}; **3**, $C_{50}H_{104}Sr_2Cu_4F_{12}O_{16}N_{12}\cdot 2C_4H_8O$, monoclinic, $P2_1/n$, $a = 16.112(9)$ Å, $b = 19.634(8)$ Å, $c = 16.85(1)$ Å, $\beta = 111.63(5)°$, $V = 4954(5)$ Å^3, $Z = 2$, $d_{calc} = 1.29$ g cm^{-3}.

Introduction

We have reported recently a percursor system for the $YBa_2Cu_3O_{7-x}$ superconductor where 1,3-bis(dimethylamino)-2-propanol (bdmapH) and acetic acid were employed as the cross-linking reagents.[1] While several heterometallic species such as $LaCu_2$ and Y_2Cu_6 related to this precursor system have been characterized,[1] heterometallic complexes involving barium and copper with bdmap and acetate ligands are still unknown. Prompted by the need to further understand the role of the multidentate bdmap ligand and the carboxylate ligand in our multicomponent precursor system, and the recent discovery of the simple binary Sr(Ca)−Cu−O superconductors,[2] we carried out the syntheses of Sr−Cu and Ca−Cu complexes with bdmap and trifluoroacetate as ligands. Three new Sr−Cu and Ca−Cu complexes with novel structural features and thermal properties have been obtained. The details are described herein.

Experimental Section

All reactions were carried out under an dry nitrogen atmosphere. Solvents were distilled prior to use. Copper methoxide, strontium metal, calcium hydride, and trifluoroacetic acid were purchased from Aldrich Chemical Co. 1,3-Bis(dimethylamino)-2-propanol was obtained from Janssen Chemical Co. Strontium trifluoroacetate and calcium trifluoroacetate were prepared through the reaction of strontium metal or calcium hydride with 2 equiv of trifluoroacetic acid in THF. Elemental analyses were performed by Desert Analytics, Tucson, AZ (C, H, N), and by Galbraith Laboratories, Inc, Knoxville, TN (F). X-ray powder diffraction experiments were performed on a Rigaku X-ray powder diffractometer. IR spectra were recorded on a Nicolet FTIR spectrometer. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 analyzer.

Synthesis of $CaCu(O_2CCF_3)_2(bdmap)_2(H_2O)$ (1). $Cu(OCH_3)_2$ (100 mg, 0.80 mmol), $Ca(O_2CCF_3)_2$ (212 mg, 0.80 mmol), and bdmapH (233 mg, 1.59 mmol) were mixed in 15 mL of THF. The mixture was stirred for 20 h at 23 °C. The solution was filtered. The filtrate was concentrated to approximately 7 mL, and 2 mL of hexane was added to crystallize the product. A 97 mg amount of dark blue crystals of **1** was obtained (0.15 mmol, 19% yield). Anal. Calcd for $C_{18}H_{36}CuCaF_6O_7N_4$: C, 33.84; H, 5.64; N, 8.78. Found: C, 33.69; H, 5.97; N, 8.69. IR (KBr, cm^{-1}): 1673 s, 1468 m, 1434 w (C=O), 1206 s, 1184 m, 1131 s (C−O, C−F). Compound **1** is stable in solution and in the solid state.

Synthesis of $Sr_2Cu_2(bdmap)_4(O_2CCF_3)_4$ (2). $Cu(OCH_3)_2$ (100 mg, 0.80 mmol), $Sr(O_2CCF_3)_2$ (250 mg, 0.80 mmol), and bdmapH (233 mg, 1.59 mmol) were mixed in 15 mL of THF. The mixture was stirred for 20 h at 23 °C. The solution was then filtered. The filtrate was concentrated to about 7 mL, and 2 mL of hexane was added to crystallize the product. Dark blue crystals of **2** (76 mg, 0.057 mmol, 14%) were obtained. Anal. Calcd for $C_{36}H_{68}Sr_2Cu_2F_{12}O_{12}N_8$: C, 32.35; H, 5.09; N, 8.38. Found: C, 32.04; H, 5.12; N, 8.21. IR (KBr, cm^{-1}): 1695 s, 1672 s, 1465 m (C=O), 1209 s, 1183 s, 1131 s (C−O, C−F). Compound **2** is stable in solution and in the solid state.

The microcrystalline form of **2** can be obtained readily by concentrating the THF solution to the minimum volume, from which the solid of **2** precipitated in nearly quantitative yield. The results of elemental analysis for this solid are consistent with the composition of **2**: C, 31.82; H, 5.10; N, 7.99.

Synthesis of $Sr_2Cu_4(bdmap)_6(O_2CCF_3)_4(\mu_3\text{-}OH)_2(THF)_2$ (3). $Cu(OCH_3)_2$ (100 mg, 0.80 mmol), $Sr(O_2CCF_3)_2$ (125 mg, 0.40 mmol), and bdmapH (233 mg, 1.59 mmol) were mixed in 15 mL of THF. The mixture was stirred for 20 h at 23 °C. The solution was then filtered, and the filtrate was concentrated to about 7 mL. A 2 mL volume of hexane was added to crystallize the product. Dark blue crystals of **3** (153 mg, 0.079 mmol, 40%) were obtained. Anal. Calcd for the dried sample $C_{50}H_{104}Sr_2Cu_4F_{12}O_{16}N_{12}$: C, 33.61; H, 5.87; N, 9.41. Found: C, 33.65; H, 5.90; N, 9.29. IR (KBr, cm^{-1}): 1682 s, 1466 m, 1420 w (C=O), 1204 s, 1177 s, 1129 s (C−O, C−F). Compound **3** is stable in solution and in the solid state.

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(1) (a) Wang, S.; Smith, K. D. L.; Pang, Z.; Wagner, M. J. *J. Chem. Soc., Chem. Commun* **1992**, 1595. (b) Wang, S.; Pang, Z.; Smith, K. D. L.; Wagner, M. J. *J. Chem. Soc., Dalton Trans.* **1994**, 955.

(2) (a) Azuma, M.; Hiroi, Z.; Takano, M.; Bando, Y.; Takeda, Y. *Nature* **1992**, *356*, 775. (b) Hiroi, Z.; Takano, M.; Azuma, M.; Takeda, Y. *Nature* **1993**, *364*, 315.

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Pyrolysis of $Sr_2Cu_2(bdmap)_4(O_2CCF_3)_4$ (2). The powder of **2** was placed in a crucible which was then placed inside a quartz tube. The quartz tube was subsequently placed in a Lindberg tube furnace and purged with oxygen gas. The temperature of the furnace was raised to 525 °C over a time period of approximately 3 h while the quartz tube was kept under 1 atm of oxygen. The furnace was then allowed to cool down to the room temperature over about 3 h. The resulting oxide powder was then ground to a fine powder and pressed into a pellet under a 20 000 psi pressure, which was then sintered under 1 atm of oxygen at 750 °C for 3 h. No C–O stretching vibration bands due to the carbonate group were observed in the IR spectrum of this material. The X-ray powder diffraction pattern of this sample revealed the presence of SrF_2 and CuO phases. The pattern of the remaining peaks does not match any of the previously reported Sr–O, Cu–O, or Sr–Cu–O phases.

Single-Crystal X-ray Diffraction Analysis. Dark blue crystals of compounds **1**–**3**, obtained from the THF/hexane solution by slow diffusion of the solvents, were mounted on glass fibers and sealed with epoxy glues. Data were collected over the range of $2 < 2\theta < 50°$ for **1**, $2 < 2\theta < 47°$ for **2**, and $2 < 2\theta < 50°$ for **3** on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation operating at 50 kV and 35 mA. The orientation matrix for **1** was obtained from 14 reflections in the range of $40 < 2\theta < 45°$; for **2**, from 16 reflections in the range of $12 < 2\theta < 16°$; and for **3**, from 20 reflections in the range of $6 < 2\theta < 15°$. Three standard reflections were measured every 147 reflections. Data were processed on a Silicon Graphics computer using the TEXSAN crystallographic package (version 5.0) and corrected for Lorentz–polarization effects. Empirical absorption corrections were applied for all crystals. Compounds **1** and **2** did not show any significant decay, while compound **3** decayed by about 15% at the end of data collection due to the loss of solvent molecules. A decay correction was therefore applied for **3**.

The crystals of **1**–**3** belong to the monoclinic crystal system with the space group being $P2_1/n$, $P2_1/c$, and $P2_1/n$, respectively. The positions of metal atoms were determined by direct methods. Other non-hydrogen atoms were located by subsequent difference Fourier syntheses. The fluorine atoms in **1** and **3** displayed a C_2 disorder. Two sets of fluorine atoms for each CF_3 group in **1** and **3** were located and refined with a 50% occupancy factor. A disordered THF molecule was located in the lattice of **3** (2 THF/molecule of **3**). The disorder of this solvent molecule could not be modeled. The high *R* factor for the structure of **3** is attributed to the disorder of THF and the CF_3 groups. Due to the limitation of the number of reflections, only metal atoms and some of the fluorine and oxygen atoms in **1** and **2** were refined anisotropically. All non-hydrogen atoms except the disordered fluorine atoms and the THF solvent molecule in **3** were refined anisotropically. The positions of hydrogen atoms in all structures were calculated, and their contributions in structural factor calculations were included. The data of the crystallographic analysis are given in Table 1. The details can be found in the supplementary material.

Table 1. Crystallographic Data

	compd		
	1	**2**	**3**
formula	$C_{18}H_{36}Cu$-$CaF_6O_7N_4$	$C_{36}H_{68}Sr_2$-$Cu_2F_{12}O_{12}N_8$	$C_{50}H_{104}Sr_2Cu$-$_4F_{12}O_{16}N_{12}\cdot 2C_4H_8O$
fw	638.12	1335.30	1931.06
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	13.234(4)	13.291(3)	16.112(9)
b, Å	15.401(3)	11.238(5)	19.634(8)
c, Å	14.445(2)	18.472(7)	16.85(1)
α, deg	90	90	90
β, deg	94.79(2)	91.51(2)	111.63(5)
γ, deg	90	90	90
V, $Å^3$	2934(1)	2758(1)	4954(5)
Z	4	2	2
d_{calcd}, g cm^{-3}	1.445	1.608	1.294
μ, cm^{-1}	9.96	27.80	19.89
λ(Mo Kα), Å		0.710 69	
T, °C		23	
R^a	0.068	0.082	0.103
$R_w{}^b$	0.048	0.064	0.085

[a] $R = \sum_{i=1}^{n}(|F_o|_i - |F_c|_i)/\sum_{i=1}^{n}|F_o|_i$. [b] $R_w = (\sum_{i=1}^{n}W_i(|F_o|_i - |F_c|_i)^2/\sum_{i=1}^{n}W_i|F_o|_i^2)^{1/2}$; $W = 1/\sigma^2(F_o)$.

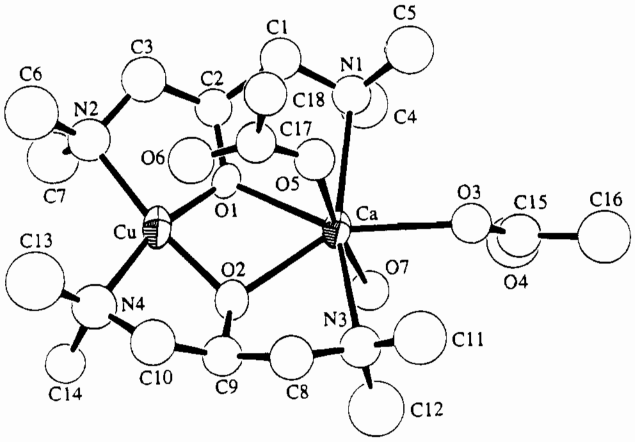

Figure 1. ORTEP diagram showing the molecular structure of compound **1** with labeling scheme and 50% thermal ellipsoids. The fluorine atoms were omitted for clarity.

Results and Discussion

Synthesis and Structure of $CaCu(bdmap)_2(O_2CCF_3)_2(H_2O)$ (1). We have reported recently that the bdmap ligand can bring two very different metal centers such as copper(II) and lanthanides(III) together through both the amino and the alkoxo sites.[1,3,9c] Since alkaline-earth metal ions behave quite similarly to the lanthanides due to their highly electropositive nature, the bdmap ligand was also anticipated to be a useful ligand for the synthesis of mixed-metal complexes involving alkaline-earth metals and the copper(II) ion. Indeed, several such mixed-metal complexes have been obtained readily by using the bdmap ligand. Compound **1** was obtained from the reaction of $Ca(O_2CCF_3)_2$ and $Cu(OCH_3)_2$ with 2 equiv of the bdmapH ligand in THF at 23 °C. Elemental and single-crystal X-ray diffraction analyses established compound **1**'s composition as $CaCu(bdmap)_2(O_2CCF_3)_2(H_2O)$. The adventitious water molecule in this product was very likely from the bdmapH reagent or the THF solvent.[4,12] Compound **1** is stable under air in the solid state. The structure of this compound is shown in Figure 1. Positional and thermal parameters are given in Table 2a. Selected bond lengths and angles are listed in Table 3a. Compound **1** contains a Cu(II) ion and a Ca(II) ion bridged by two bdmap ligands with the Cu–Ca separation distance of 3.262(2) Å. The copper center is coordinated by two nitrogen atoms and two oxygen atoms in an approximate square-planar fashion with typical Cu–O and Cu–N bond distances. The O(6) atom of the carboxylate occupies the fifth position of the copper center with a long Cu–O(6) bond distance of 2.397(8) Å. The geometry of the copper center can be, therefore, described as a square-pyramid. The calcium center is surrounded by two nitrogen and five oxygen atoms in an approximate pentagonal bipyramidal geometry with O(5) and O(7) occupying the axial positions (O(5)–Ca–O(7) = 173.9(3)°). The Ca–O distances range from 2.321(7) to 2.415(7) Å, while the Ca–N(1) and Ca–N(3) distances of 2.695(9) and 2.642(9) Å are much longer, attributable to the poor affinity of the neutral amino group toward the calcium cation in comparison with the negatively charged oxygen centers. A similar bonding pattern has been observed in a dinuclear YCu complex, where the

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(3) Wang, S.; Pang, Z.; Smith, K. D. L., *Inorg. Chem.*, **1993**, *32*, 4993.

(4) Wang, S.; Trepanier, S. J.; Zheng, J. C.; Pang, Z.; Wagner, M. *J. Inorg. Chem.*, **1992**, *31*, 2118.

Table 2. Positional and Thermal Parameters (Å^2)

atom	*x*	*y*	*z*	*B*(eq)[a]	atom	*x*	*y*	*z*	*B*(eq)[a]
(a) Compound **1**									
Cu	0.1165(1)	0.1605(1)	−0.15749(8)	3.69(7)	N(1)	0.2904(7)	−0.0222(6)	0.0371(6)	4.0(2)
Ca	0.1655(2)	0.1126(1)	0.0617(1)	3.2(1)	N(2)	0.1778(7)	0.0974(6)	−0.2669(6)	4.6(2)
F(1)	0.224(2)	0.136(2)	0.404(1)	6.6(6)	N(3)	0.0869(7)	0.2543(6)	0.1296(6)	4.5(2)
F(2)	0.146(1)	0.067(3)	0.430(1)	14(2)	N(4)	0.0372(7)	0.2704(6)	−0.2065(6)	5.2(2)
F(3)	0.199(3)	0.012(2)	0.442(2)	9.3(7)	C(1)	0.3192(9)	−0.0080(7)	−0.0592(8)	4.8(3)
F(4)	0.271(4)	−0.005(2)	0.430(2)	15(2)	C(2)	0.2256(9)	0.0049(7)	−0.1285(7)	3.8(2)
F(5)	0.337(2)	0.032(2)	0.382(1)	8(1)	C(3)	0.259(1)	0.0468(8)	−0.2171(8)	5.5(3)
F(6)	0.289(3)	0.123(3)	0.401(1)	14(2)	C(4)	0.238(1)	−0.1033(8)	0.0461(8)	6.5(3)
F(7)	0.419(3)	0.355(2)	0.004(3)	13(3)	C(5)	0.383(1)	−0.0183(8)	0.0972(8)	6.3(3)
F(8)	0.454(4)	0.315(4)	0.034(2)	9(3)	C(6)	0.222(1)	0.1484(9)	−0.3382(9)	7.7(4)
F(9)	0.501(4)	0.237(4)	−0.007(4)	12(3)	C(7)	0.103(7)	0.0365(9)	−0.3119(9)	7.2(4)
F(10)	0.492(3)	0.231(3)	−0.058(5)	13(3)	C(8)	0.0757(8)	0.3149(7)	0.0526(8)	5.2(3)
F(11)	0.449(3)	0.314(4)	−0.124(2)	14(2)	C(9)	0.0229(8)	0.2722(8)	−0.0373(7)	4.3(3)
F(12)	0.431(3)	0.345(2)	−0.100(2)	9(2)	C(10)	0.0430(9)	0.3267(8)	−0.1209(8)	5.5(3)
O(1)	0.1540(5)	0.0549(4)	−0.0917(4)	3.2(3)	C(11)	0.150(1)	0.2982(8)	0.2058(8)	7.0(4)
O(2)	0.0598(5)	0.1892(4)	−0.0455(4)	3.6(4)	C(12)	−0.009(1)	0.232(1)	0.162(1)	8.6(4)
O(3)	0.2216(5)	0.0923(5)	0.2236(5)	4.3(2)	C(13)	0.076(1)	0.322(1)	−0.281(1)	9.0(4)
O(4)	0.1458(7)	−0.0271(6)	0.2693(6)	7.3(2)	C(14)	−0.070(1)	0.2473(8)	−0.2308(8)	4.0(3)
O(5)	0.3051(5)	0.1990(4)	0.0257(5)	4.5(2)	C(15)	0.195(1)	0.0388(8)	0.2798(8)	4.8(3)
O(6)	0.2715(6)	0.2389(5)	−0.1233(5)	5.5(2)	C(16)	0.239(2)	0.059(1)	0.385(1)	7.3(4)
O(7)	0.0375(5)	0.0163(4)	0.1075(5)	4.3(2)	C(17)	0.3238(9)	0.2356(7)	−0.0478(8)	4.3(3)
C(18)	0.425(1)	0.285(1)	−0.043(1)	4.9(3)					
(b) Compound **2**									
Sr	0.8196(1)	0.1008(2)	0.0503(1)	3.2(1)	C(1)	0.722(1)	0.328(2)	−0.059(1)	3.5(4)
Cu	0.5769(2)	0.1591(2)	0.0900(1)	2.9(1)	C(2)	0.629(1)	0.254(2)	−0.045(1)	1.9(3)
F(1)	0.805(1)	−0.229(2)	−0.144(1)	12(1)	C(3)	0.545(1)	0.326(2)	−0.019(1)	4.3(5)
F(2)	0.954(1)	−0.290(2)	−0.129(1)	19(2)	C(4)	0.902(2)	0.343(2)	−0.073(1)	6.3(6)
F(3)	0.846(1)	−0.333(2)	−0.056(1)	14(2)	C(5)	0.806(1)	0.194(2)	−0.135(1)	6.0(6)
F(4)	0.853(1)	0.520(1)	0.125(1)	12(1)	C(6)	0.413(2)	0.347(2)	0.071(1)	7.5(7)
F(5)	0.705(1)	0.563(1)	0.136(1)	10(1)	C(7)	0.416(2)	0.186(2)	−0.018(1)	6.1(6)
F(6)	0.786(1)	0.506(2)	0.223(1)	11(1)	C(8)	0.596(1)	0.074(2)	0.229(1)	3.8(5)
O(1)	0.6523(8)	0.164(1)	0.0030(7)	3.3(6)	C(9)	0.671(1)	0.009(2)	0.191(1)	3.6(4)
O(2)	0.6693(8)	0.042(1)	0.1192(7)	3.4(7)	C(10)	0.773(2)	0.012(2)	0.224(1)	5.0(5)
O(3)	0.8329(9)	−0.087(1)	−0.0315(7)	4.6(8)	C(11)	0.456(1)	0.209(2)	0.225(1)	5.8(6)
O(4)	0.996(1)	−0.122(1)	−0.045(1)	7(1)	C(12)	0.441(1)	0.017(2)	0.177(1)	6.0(6)
O(5)	0.8077(9)	0.286(1)	0.1251(9)	5(1)	C(13)	0.845(2)	−0.161(2)	0.162(1)	6.8(6)
O(6)	0.648(1)	0.336(1)	0.1482(8)	4.6(8)	C(14)	0.950(2)	0.000(2)	0.213(1)	6.8(6)
N(1)	0.814(1)	0.263(2)	−0.069(1)	4.1(4)	C(15)	0.907(1)	−0.139(2)	−0.054(1)	3.1(4)
N(2)	0.476(1)	0.259(1)	0.0303(9)	3.7(4)	C(16)	0.872(2)	−0.246(3)	−0.101(2)	5.4(6)
N(3)	0.508(1)	0.111(1)	0.1886(8)	3.4(3)	C(17)	0.740(1)	0.354(2)	0.141(1)	2.9(4)
N(4)	0.854(1)	−0.026(2)	0.177(1)	4.5(4)	C(18)	0.770(2)	0.492(2)	0.152(1)	5.1(6)
(c) Compound **3**									
Sr(1)	0.6897(2)	0.1269(1)	0.0822(2)	4.24(7)	C(5)	0.658(2)	0.314(2)	0.107(2)	10(1)
Cu(1)	0.5492(2)	−0.0039(2)	0.0901(2)	3.85(8)	C(6)	0.871(2)	0.188(2)	−0.174(2)	11(1)
Cu(2)	0.7692(2)	0.1011(2)	−0.0800(2)	4.73(10)	C(7)	0.707(3)	0.171(2)	−0.244(2)	12(1)
O(1)	0.6917(10)	0.1642(8)	−0.0600(9)	4.4(4)	C(8)	0.716(2)	0.083(2)	0.295(2)	5.7(7)
O(2)	0.661(1)	0.0298(8)	0.1585(9)	5.0(5)	C(9)	0.687(2)	0.019(1)	0.245(2)	5.8(7)
O(3)	0.7393(9)	0.0428(9)	−0.009(1)	5.2(5)	C(10)	0.612(2)	−0.014(1)	0.268(2)	5.3(6)
O(4)	0.5625(9)	0.0420(8)	−0.0081(8)	3.6(4)	C(11)	0.800(3)	0.193(3)	0.312(2)	11(1)
O(5)	0.857(1)	0.1680(10)	0.124(1)	6.8(6)	C(12)	0.868(3)	0.084(2)	0.294(2)	10(1)
O(6)	0.913(1)	0.137(1)	0.031(1)	7.7(7)	C(13)	0.472(2)	−0.070(2)	0.209(2)	8(1)
O(7)	0.560(1)	0.1672(10)	0.130(1)	6.3(6)	C(14)	0.602(2)	−0.124(2)	0.189(2)	8(1)
O(8)	0.466(1)	0.086(1)	0.123(1)	5.6(6)	C(15)	0.854(2)	−0.027(2)	−0.041(2)	9(1)
N(1)	0.645(2)	0.268(1)	0.031(1)	7.5(8)	C(16)	0.784(2)	−0.024(1)	0.001(2)	4.2(6)
N(2)	0.785(2)	0.180(1)	−0.159(2)	7.3(9)	C(17)	0.797(2)	−0.058(2)	0.079(2)	9.6(10)
N(3)	0.779(2)	0.124(2)	0.271(2)	8.7(10)	C(18)	0.910(4)	0.027(2)	−0.124(2)	14(1)
N(4)	0.558(2)	−0.061(1)	0.194(1)	6.3(8)	C(19)	0.759(3)	−0.024(4)	−0.184(3)	25(2)
N(5)	0.824(2)	0.015(1)	−0.112(2)	7.7(9)	C(20)	0.806(4)	−0.161(3)	0.082(4)	16(2)
N(6)	0.866(3)	−0.112(2)	0.110(4)	12(1)	C(21)	0.907(3)	−0.120(3)	0.193(4)	17(2)
C(1)	0.715(2)	0.280(2)	−0.010(2)	7.1(8)	C(22)	0.915(2)	0.162(2)	0.093(2)	6(1)
C(2)	0.693(2)	0.230(2)	−0.085(2)	4.8(6)	C(23)	1.009(2)	0.204(2)	0.160(2)	8.0(9)
C(3)	0.775(2)	0.243(2)	−0.113(2)	9.1(10)	C(24)	0.494(2)	0.139(2)	0.134(2)	5(1)
C(4)	0.556(2)	0.279(2)	−0.021(2)	11(1)	C(25)	0.427(3)	0.207(2)	0.156(3)	11(1)

[a] $B(\mathrm{eq}) = {}^{8}/_{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

bdmap ligand bridges the copper(II) ion and the highly electropositive yttrium ion.[3] In the solid state, compound **1** dimerizes through two intermolecular hydrogen bonds as shown in Figure 2. The O(7) atom of the water molecule forms an intramolecular hydrogen bond[5] with the O(4) atom of the trifluoroacetate ligand and an intermolecular hydrogen bond with the O(1) atom of the bdmap ligand, as evidenced by the O(1′)−O(7) and O(4)−O(7) distances of 2.754(9) and 2.72(1) Å, which are significantly shorter than the sum of van der Waals radii[6] of oxygen and nitrogen atoms. The Cu−O(2) and Ca−O(2) distances of 1.891(6) and 2.321(7) Å are substantially shorter than the corresponding Cu−O(1) and Ca−O(1) distances of

Table 3. Selected Bond Lengths (Å) and Angles (deg)

(a) Compound **1**

Distances

Cu−O(1)	1.927(6)	Cu−O(2)	1.891(6)	N(1)−C(5)	1.45(1)	N(2)−C(3)	1.47(1)
Cu−N(2)	2.078(9)	Cu−N(4)	2.084(9)	N(2)−C(6)	1.45(1)	N(2)−C(7)	1.47(1)
Ca−O(1)	2.380(6)	Ca−O(2)	2.321(7)	N(3)−C(8)	1.45(1)	N(3)−C(11)	1.49(1)
Ca−O(3)	2.415(7)	Ca−O(5)	2.370(8)	N(3)−C(12)	1.44(1)	N(4)−C(10)	1.51(1)
Ca−O(7)	2.386(7)	Ca−N(1)	2.695(9)	N(4)−C(13)	1.46(1)	N(4)−C(14)	1.47(1)
Ca−N(3)	2.642(9)	O(2)−C(9)	1.38(1)	C(1)−C(2)	1.54(1)	C(2)−C(3)	1.53(1)
O(3)−C(15)	1.23(1)	O(4)−C(15)	1.21(1)	C(8)−C(9)	1.57(1)	C(9)−C(10)	1.51(1)
O(5)−C(17)	1.25(1)	O(6)−C(17)	1.24(1)	C(15)−C(16)	1.62(2)	C(17)−C(18)	1.54(1)
N(1)−C(1)	1.49(1)	N(1)−C(4)	1.44(1)				

Angles

O(1)−Cu−O(2)	83.1(3)	N(1)−Ca−N(3)	161.8(3)	C(8)−N(3)−C(11)	106.8(9)	C(8)−N(3)−C(12)	111.4(9)
O(1)−Cu−N(2)	83.1(3)	O(1)−Cu−N(4)	162.6(3)	C(11)−N(3)−C(12)	109(1)	Cu−O(1)−Ca	97.9(3)
O(2)−Cu−N(2)	165.5(3)	O(2)−Cu−N(4)	82.9(3)	Cu−O(2)−Ca	101.1(3)	C(10)−N(4)−C(13)	107(1)
N(2)−Cu−N(4)	109.8(4)	O(1)−Ca−O(2)	65.2(2)	C(10)−N(4)−C(14)	108.5(9)	C(13)−N(4)−C(14)	111(1)
O(1)−Ca−O(3)	147.6(2)	O(1)−Ca−O(5)	89.8(2)	N(1)−C(1)−C(2)	111.8(9)	O(1)−C(2)−C(1)	111.6(9)
O(1)−Ca−O(7)	92.0(2)	O(1)−Ca−N(1)	65.3(2)	O(1)−C(2)−C(3)	110.4(9)	C(1)−C(2)−C(3)	109(1)
O(1)−Ca−N(3)	131.1(3)	O(2)−Ca−O(3)	146.3(2)	N(2)−C(3)−C(2)	112(1)	C(1)−N(1)−C(4)	112.0(9)
O(2)−Ca−O(5)	90.3(2)	O(2)−Ca−O(7)	95.7(2)	N(3)−C(8)−C(9)	112(1)	C(1)−N(1)−C(5)	106.5(9)
O(2)−Ca−N(1)	130.2(2)	O(2)−Ca−N(3)	66.0(3)	O(2)−C(9)−C(8)	109.0(9)	C(4)−N(1)−C(5)	112.0(9)
O(3)−Ca−O(5)	95.9(3)	O(3)−Ca−O(7)	79.6(2)	O(2)−C(9)−C(10)	111.0(9)	C(8)−C(9)−C(10)	109(1)
O(3)−Ca−N(1)	83.5(2)	O(3)−Ca−N(3)	81.1(3)	N(4)−C(10)−C(9)	110(1)	O(5)−C(17)−C(18)	115(1)
O(5)−Ca−O(7)	173.9.(3)	O(5)−Ca−N(1)	84.6(3)	O(3)−C(15)−O(4)	131(1)	O(6)−C(17)−C(18)	116(1)
O(5)−Ca−N(3)	87.5(3)	O(7)−Ca−N(1)	90.9(3)	O(3)−C(15)−C(16)	113(1)	O(4)−C(15)−C(16)	116(1)
O(7)−Ca−N(3)	95.7(3)	C(3)−N(2)−C(6)	108(1)	O(5)−C(17)−O(6)	129(1)		
C(3)−N(2)−C(7)	108(1)	C(6)−N(2)−C(7)	109(1)				

(b) Compound **2**

Distances

Sr−Cu	3.390(3)	O(4)−C(15)	1.21(2)	Cu−O(2)	1.87(1)	N(3)−C(8)	1.43(2)
Sr−O(1)	2.47(1)	O(5)−C(17)	1.23(2)	Cu−N(2)	2.04(2)	N(3)−C(11)	1.47(2)
Sr−O(2)	2.49(1)	O(6)−C(17)	1.25(2)	Cu−N(3)	2.13(1)	N(3)−C(12)	1.40(2)
Sr−O(3)	2.60(1)	N(1)−C(1)	1.44(2)	N(4)−C(10)	1.46(2)	N(4)−C(13)	1.55(3)
Sr−O(4′)	2.47(1)	N(1)−C(4)	1.48(2)	N(4)−C(14)	1.45(2)	C(1)−C(2)	1.52(2)
Sr−O(5)	2.51(2)	N(1)−C(5)	1.45(3)	C(2)−C(3)	1.48(2)	C(8)−C(9)	1.44(2)
Sr−N(1)	2.86(2)	N(2)−C(3)	1.50(2)	O(1)−C(2)	1.38(2)	C(9)−C(10)	1.46(2)
Sr−N(4)	2.77(2)	N(2)−C(6)	1.51(3)	O(2)−C(9)	1.39(2)	C(15)−C(16)	1.56(3)
Cu−O(1)	1.92(1)	N(2)−C(7)	1.44(3)	O(3)−C(15)	1.22(2)	C(17)−C(18)	1.60(3)

Angles

N(1)−Sr−N(4)	168.5(5)	O(1)−Cu−O(2)	84.7(5)	O(4′)−Sr−O(5)	90.9(5)	O(4′)−Sr−N(1)	85.0(5)
O(1)−Sr−O(2)	61.9(4)	O(1)−Cu−N(2)	83.2(6)	O(4′)−Sr−N(4)	86.7(5)	C(1)−N(1)−C(4)	112(2)
O(5)−Sr−N(4)	88.4(5)	O(5)−Sr−N(1)	83.7(5)	C(1)−N(1)−C(5)	110(2)	C(4)−N(1)−C(5)	108(2)
O(1)−Sr−O(3)	95.8(4)	O(1)−Cu−N(3)	165.9(6)	O(2)−C(9)−C(10)	113(2)	O(3)−C(15)−O(4)	132(2)
O(1)−Sr−O(4′)	147.5(5)	O(2)−Cu−N(2)	163.0(6)	C(3)−N(2)−C(6)	108(2)	O(3)−C(15)−C(16)	110(2)
O(1)−Sr−O(5)	83.5(4)	O(2)−Cu−N(3)	82.4(6)	C(3)−N(2)−C(7)	104(2)	O(4)−C(15)−C(16)	118(2)
O(1)−Sr−N(1)	62.6(4)	N(2)−Cu−N(3)	108.1(6)	C(6)−N(2)−C(7)	112(2)	C(8)−N(3)−C(11)	111(2)
O(1)−Sr−N(4)	124.9(4)	Sr−O(1)−Cu	100.4(5)	C(8)−N(3)−C(12)	112(2)	C(11)−N(3)−C(12)	109(2)
O(2)−Sr−O(3)	98.6(4)	O(2)−Sr−O(4′)	149.2(5)	O(5)−C(17)−O(6)	130(2)	O(5)−C(17)−C(18)	117(2)
O(2)−Sr−O(5)	82.9(4)	Sr−O(2)−Cu	101.3(5)	O(6)−C(17)−C(18)	113(2)	C(10)−N(4)−C(13)	110(2)
O(2)−Sr−N(1)	124.0(4)	O(2)−Sr−N(4)	63.0(4)	C(10)−N(4)−C(14)	109(2)	C(13)−N(4)−C(14)	110(2)
O(3)−Sr−O(4′)	88.5(5)	O(3)−Sr−O(5)	177.9(5)	O(1)−C(2)−C(1)	110(1)	O(1)−C(2)−C(3)	111(1)
O(3)−Sr−N(1)	94.1(5)	O(3)−Sr−N(4)	93.6(5)	O(2)−C(9)−C(8)	109(2)		

(c) Compound **3**

Distances

Sr(1)−O(1)	2.52(2)	Cu(1)−Cu(1′)	2.865(5)	Cu(1)−N(4)	2.04(2)	N(5)−C(15)	1.37(5)
Sr(1)−O(2)	2.44(2)	N(1)−C(1)	1.53(5)	Cu(2)−O(1)	1.88(2)	N(5)−C(18)	1.50(7)
Sr(1)−O(3)	2.57(2)	N(1)−C(4)	1.39(4)	Cu(2)−O(3)	1.85(2)	N(5)−C(19)	1.46(6)
Sr(1)−O(4)	2.64(1)	N(1)−C(5)	1.52(5)	Cu(2)−N(2)	2.11(3)	N(6)−C(17)	1.51(6)
Sr(1)−O(5)	2.65(2)	N(2)−C(3)	1.50(5)	Cu(2)−N(5)	2.08(3)	N(6)−C(20)	1.32(7)
Sr(1)−O(7)	2.62(2)	N(2)−C(6)	1.51(5)	O(1)−C(2)	1.35(3)	N(6)−C(21)	1.34(8)
Sr(1)−N(1)	2.91(3)	N(2)−C(7)	1.53(4)	O(2)−C(9)	1.38(3)	C(1)−C(2)	1.53(4)
Sr(1)−N(3)	2.97(2)	N(3)−C(8)	1.47(5)	O(3)−C(16)	1.47(3)	C(2)−C(3)	1.57(5)
N(3)−C(11)	1.46(6)	O(8)−C(24)	1.13(4)	O(5)−C(22)	1.23(5)	C(8)−C(9)	1.47(4)
Cu(1)−O(2)	1.87(1)	N(3)−C(12)	1.57(5)	O(6)−C(22)	1.14(4)	C(9)−C(10)	1.53(4)
Cu(1)−O(4)	1.96(2)	N(4)−C(10)	1.53(3)	O(7)−C(24)	1.22(4)	C(15)−C(16)	1.54(6)
Cu(1)−O(4′)	1.97(1)	N(4)−C(13)	1.49(5)	C(16)−C(17)	1.42(5)	C(22)−C(23)	1.74(4)
Cu(1)−O(8)	2.40(2)	N(4)−C(14)	1.44(5)				

Table III (Continued)

Angles							
O(2)−Sr(1)−O(5)	118.0(5)	O(2)−Sr(1)−O(7)	75.4(6)	O(1)−Cu(2)−O(3)	86.9(8)	C(1)−N(1)−C(5)	113(2)
O(2)−Sr(1)−N(1)	145.9(7)	O(2)−Sr(1)−N(3)	61.7(7)	O(1)−Cu(2)−N(2)	82(1)	C(4)−N(1)−C(5)	103(3)
O(3)−Sr(1)−O(4)	66.3(5)	O(3)−Sr(1)−O(5)	81.0(5)	O(1)−Cu(2)−N(5)	164.3(9)	O(3)−Cu(2)−N(2)	169(1)
O(3)−Sr(1)−O(7)	146.4(5)	O(3)−Sr(1)−N(1)	122.0(7)	O(3)−Cu(2)−N(5)	84(1)	N(2)−Cu(2)−N(5)	106(1)
O(3)−Sr(1)−N(3)	119.4(7)	O(4)−Sr(1)−O(5)	147.2(6)	C(3)−N(2)−C(6)	107(3)	Sr(1)−O(1)−Cu(2)	102.6(6)
O(4)−Sr(1)−O(7)	80.1(5)	O(4)−Sr(1)−N(1)	111.9(5)	C(3)−N(2)−C(7)	112(3)	C(6)−N(2)−C(7)	110(3)
O(4)−Sr(1)−N(3)	124.5(7)	O(5)−Sr(1)−O(7)	132.6(6)	N(3)−C(8)−C(9)	115(3)	O(2)−C(9)−C(8)	112(2)
O(5)−Sr(1)−N(1)	84.5(7)	O(5)−Sr(1)−N(3)	71.5(8)	O(2)−C(9)−C(10)	112(2)	C(8)−N(3)−C(11)	116(3)
O(7)−Sr(1)−N(1)	70.7(7)	O(1)−Sr(1)−O(2)	143.3(5)	C(8)−C(9)−C(10)	109(3)	C(8)−N(3)−C(12)	109(3)
O(7)−Sr(1)−N(3)	78.6(8)	O(1)−Sr(1)−O(3)	60.4(5)	N(4)−C(10)−C(9)	109(2)	C(11)−N(3)−C(12)	109(3)
N(1)−Sr(1)−N(3)	108.1(8)	O(1)−Sr(1)−O(4)	85.1(5)	N(5)−C(15)−C(16)	107(3)	O(3)−C(16)−C(15)	113(2)
O(1)−Sr(1)−O(5)	78.1(5)	O(1)−Sr(1)−O(7)	119.6(5)	O(3)−C(16)−C(17)	114(3)	C(15)−C(16)−C(17)	122(3)
O(1)−Sr(1)−N(1)	61.7(7)	O(1)−Sr(1)−N(3)	149.0(7)	C(10)−N(4)−C(13)	104(2)	N(6)−C(17)−C(16)	118(4)
O(2)−Sr(1)−O(3)	88.4(6)	O(2)−Sr(1)−O(4)	63.5(4)	C(10)−N(4)−C(14)	114(2)	O(5)−C(22)−O(6)	132(3)
Sr(1)−O(2)−Cu(1)	106.1(6)	O(2)−Cu(1)−O(4)	88.6(6)	C(13)−N(4)−C(14)	114(3)	O(5)−C(22)−C(23)	107(3)
Sr(1)−O(3)−Cu(2)	101.5(8)	O(2)−Cu(1)−O(4′)	173.2(7)	O(6)−C(22)−C(23)	121(3)	C(15)−N(5)−C(18)	99(3)
O(2)−Cu(1)−O(8)	95.1(7)	O(2)−Cu(1)−N(4)	85.3(8)	C(15)−N(5)−C(19)	113(4)	C(18)−N(5)−C(19)	111(4)
Sr(1)−O(4)−Cu(1)	96.2(5)	O(4)−Cu(1)−O(4′)	86.5(7)	C(17)−N(6)−C(20)	92(4)	C(17)−N(6)−C(21)	116(5)
Sr(1)−O(4)−Cu(1′)	163.3(7)	O(4)−Cu(1)−O(8)	95.8(7)	C(20)−N(6)−C(21)	107(5)	N(1)−C(1)−C(2)	107(2)
Cu(1)−O(4)−Cu(1′)	93.5(7)	O(4)−Cu(1)−N(4)	168.9(9)	O(1)−C(2)−C(1)	112(2)	O(1)−C(2)−C(3)	110(2)
O(4)−Cu(1)−O(8)	90.1(6)	O(4′)−Cu(1)−N(4)	98.7(8)	C(1)−C(2)−C(3)	100(2)	N(2)−C(3)−C(2)	107(3)
O(8)−Cu(1)−N(4)	94(1)	C(1)−N(1)−C(4)	117(3)	O(7)−C(24)−O(8)	134(4)		

1.927(6) and 2.380(6) Å, attributable to the hydrogen-bond formation of the O(1) atom. Several CaCu complexes have been reported previously where bifunctional ligands such as carboxylates and formate were used as the bridging ligands.[7]

Synthesis and Structure of $Sr_2Cu_2(bdmap)_4(O_2CCF_3)_4$ (2). Compound 2 was obtained from the reaction of $Sr(O_2CCF_3)_2$ and $Cu(OCH_3)_2$ with 2 equiv of bdmapH in a similar manner as that in the synthesis of compound 1. However, unlike 1, compound 2 does not contain any H_2O ligand, as established by elemental and X-ray diffraction analysis. The molecular structure of compound 2 is shown in Figure 3. Positional and thermal parameters are given in Table 2b. Selected bond lengths and angles are listed in Table 3b. In the solid state, the molecule of 2 contains two dinuclear $SrCu(bdmap)_2(O_2CCF_3)_2$ units, related by an inversion center. The structure of the dinuclear unit resembles that of compound 1. The Sr−Cu separation distance is 3.390(3) Å. The copper(II) ion is coordinated by two oxygen and two nitrogen atoms with normal bond lengths and an approximate square planar geometry. The fifth position of the copper atom is again occupied by an oxygen atom O(6) of the trifluoroacetate ligand with the Cu−O(6) bond length of 2.43(1) Å, slightly longer than that found in 1. The strontium ion was surrounded by five oxygen and two nitrogen atoms in an approximate pentagonal bipyramidal geometry with two oxygen atoms occupying the axial positions, O(3)−Sr−O(5) = 177.95(5)°. The Sr−O and Sr−N bonds show a bond length variation similar to that observed in 1. In contrast to the structure of compound 1 where the two dinuclear units are linked together through intermolecular hydrogen bonds, forming a face to face dimer, the two dinuclear units in 2 are linked together through two trifluoroacetate bridges and Sr−O bonds, forming a linear chain structure. Strontium is an important ingredient in the Bi−Sr−Ca−Cu−O and the Sr(Ca)−Cu−O superconductor series.[8] However, few heteronuclear metal complexes involving strontium and copper have been reported previously. To our knowledge, compound 1 is the first example of a tetranuclear SrCu linear chain compound. A few examples of heterometallic complexes involving other alkaline-earth metal ions and the copper(II) ion with bifunctional ligands have been reported previously.[9]

Synthesis of $Sr_2Cu_4(bdmap)_6(O_2CCF_3)_4(\mu_3\text{-}OH)_2(THF)_2$ (3). Compound 3 was isolated as the major product from the reaction of $Sr(O_2CCF_3)_2$ and $Cu(O_2CCF_3)_2$ with bdmapH in a 1:2:4 ratio in THF. In contrast to compounds 1 and 2 where no hydroxo groups are present, there are two hydroxo ligands in 3. The formation of hydroxo or oxo ligands in reactions involving metal alkoxides has been frequently observed.[10] The adventitious H_2O from the bdmapH reagent or the THF solvent is again believed to be the source of the hydroxo ligand. The structure of compound 3 is shown in Figure 4. Positional and thermal parameters exclusive of the fluorine atoms and the THF molecule are given in Table 2c. Selected bond lengths and angles are listed in Table 3c. Compound 3 consists of two SrCu units and one Cu_2 unit with a crystallographically imposed inversion center symmetry. In the SrCu unit, the Sr(1) and Cu(2) ions are bridged together (Sr(1)−Cu(2) = 3.456(4) Å) by two bdmap ligands in a fashion similar to that in 2, except that one of the amino groups (N(6)) of the bdmap ligand is not coordinated. The lone pair of the N(6) atom is oriented away from the molecule, and there is no indication of hydrogen-bond formation involving the N(6) atom according to the structural data. A similar situation involving a dangling, non-hydrogen-bonded amino group has been observed in the $BaCu_4(bdmap)_4(PyO)_4(O_2CCF_3)_2$ complex.[9c] The Cu(2) atom again has a square-pyramidal geometry with the O(6) atom of the trifluoroacetate ligand occupying the fifth position (Cu(2)−O(6) = 2.49(2) Å). The Sr(1) atom is surrounded by two nitrogen atoms and six oxygen atoms with an approximate square antiprism geometry (Figure 5). The Sr−N distances are again

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(5) (a) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solid*; W. A. Benjamin, Inc.: New York, 1968. (b) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: New York, 1971.

(6) Emsley, J. *The Elements*; Clarendon Press: Oxford, U.K., 1991.

(7) (a) Smith, G.; O'Reilly, E. J.; Kennard, C. H. L.; White, A. H. *J. Chem. Soc., Dalton Trans.*, **1985**, 243. (b) Sanchis, M. J.; Gómez-Romero, P.; Folgado, J. V.; Sapiña, F.; Ibáñez, R.; Beltràn, A.; García, J.; Beltràn, D. *Inorg. Chem.* **1992**, *31*, 2915. (c) Sanchis, M. J.; Sapiña, F.; Ibáñez, R.; Beltrán, A.; Beltrán, D. *Mater. Lett.* **1992**, *12*, 409.

(8) (a) Poole, C. P., Jr.; Data, T.; Farach, H. A. *Copper Oxide Superconductors*; John Wiley & Sons: New york, 1988. (b) *Chemistry of Advanced Materials*; Rao, C. N. R., Ed.; Blackwell Scientific publications: Oxford, U.K., 1993.

(9) (a) Fenton, D. E. *J. Chem. Soc., Chem. Commun.* **1979**, *39*. (b) Love, C. P.; Torardi, C. C.; Page, C. J. *Inorg. Chem.* **1992**, *31*, 1784. (c) Wang, S.; Trepanier, S. J.; Wagner, M. J. *Inorg. Chem.* **1993**, *32*, 833.

(10) (a) Wang, S. *Inorg. Chem.* **1990**, *30*, 2252. (b) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969. (c) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, *93*, 1205.

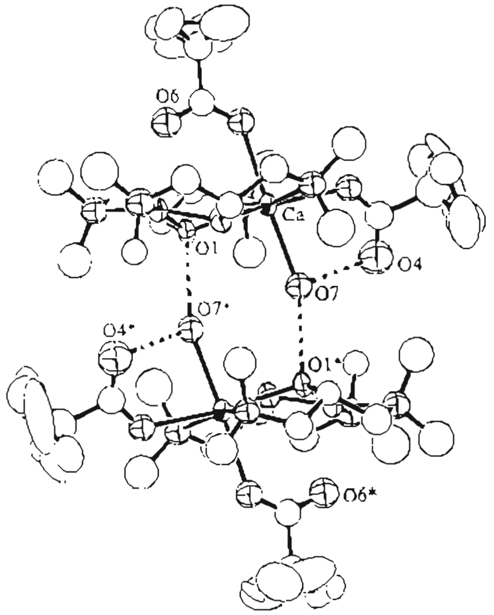

Figure 2. ORTEP diagram showing the intra- and intermolecular hydrogen bonds in compound 1.

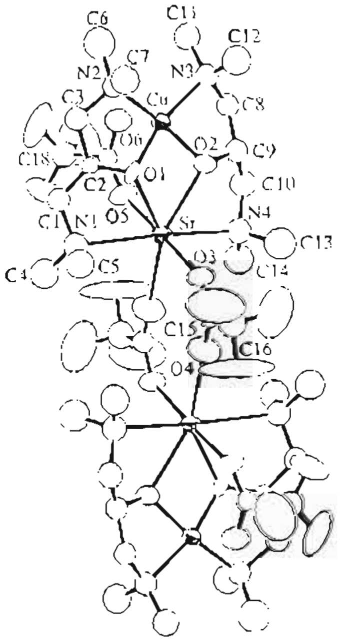

Figure 3. ORTEP diagram showing the molecular structure of compound 2 with labeling scheme and 50% thermal ellipsoids.

significantly longer than the Sr—O distances as found in 2. Most interestingly, this SrCu unit is linked to a Cu_2 unit by a hydroxo group and a bdmap ligand, producing a zigzag SrCu—Cu_2—SrCu chain. The Sr(1)—Cu(1) distance of 3.457(4) Å is nearly identical to that of Sr(1)—Cu(2). The two copper atoms in the Cu_2 unit are bridged by two hydroxo ligands with the Cu(1)—Cu(1′) separation of 2.865(5) Å. Each copper atom in the Cu_2 unit is also coordinated by a nitrogen atom and an oxygen atom of the bdmap ligand. The $Cu_2O_4N_2$ portion of this unit is essentially planar. The Cu(1) atom's fifth position is occupied by the O(8) atom of the trifluoroacetate ligand (Cu(1)—O(8) = 2.40(2) Å). The geometry of Cu(1) is therefore also a square pyramid. The OH group appears to form a hydrogen bond with the O(3) atom of the bdmap ligand, as evidenced by the O(3)⋯O(4) distance of 2.85(2) Å. The O(4) atom of the OH ligand has an unusual planar geometry, in contrast to the frequently observed pyramidal geometry for a μ_3-OH group.

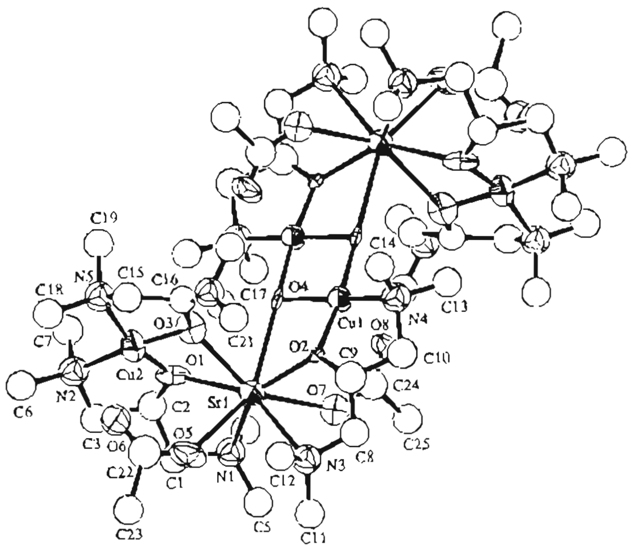

Figure 4. ORTEP diagram showing the molecular structure of compound 3 with labeling scheme and 50% thermal ellipsoids. The fluorine atoms were omitted for clarity.

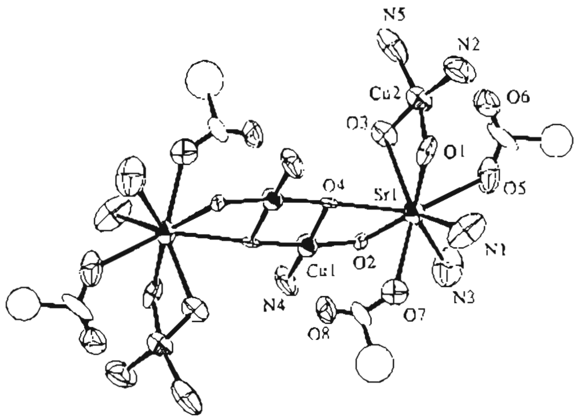

Figure 5. ORTEP diagram showing the connectivity and coordination geometries of the metal ions in compound 3.

The Cu(1)—O(4)—Cu(1′) angle of 93.5(7)° is unusually small, perhaps the smallest among the known μ_2-dihydroxo-bridged dinuclear Cu(II) complexes.[11] Such a small Cu—O—Cu angle could lead to interesting magnetic exchanges between the two Cu(II) centers[11] which are currently under investigation in our group. Several complexes with a planar μ_4-O ligand have been reported previously;[12] however, to our knowledge, there are no previous examples of metal complexes with a planar μ_3-OH ligand. The connectivity and coordination geometries of the metal centers in 3 are shown in Figure 5.

The common features in all three structures are that the alkaline-earth metal ion and the copper ion are linked together through the negatively charged oxygen center of the bdmap ligand, and the carboxylate ligands are coordinated predominately to the alkaline-earth metal ion. The preference of the Ca(II) and Sr(II) ions for the negatively charged oxygen centers is apparently due to their highly electropositive nature. The structures of compounds 1—3 demonstrate again the capability

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(11) Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985; pp 555—602.

(12) (a) Rambo, J. A.; Huffman, J. C.; Christou, G.; Eisenstein, O. *J. Am. Chem. Soc.* **1989**, *111*, 8027. (b) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc* **1990**, *112*, 1584. (c) Samuel, J. A.; Vaartstra, B. A.; Huffman, J. C.; Trojan, K. L.; Hatfield, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 9623.

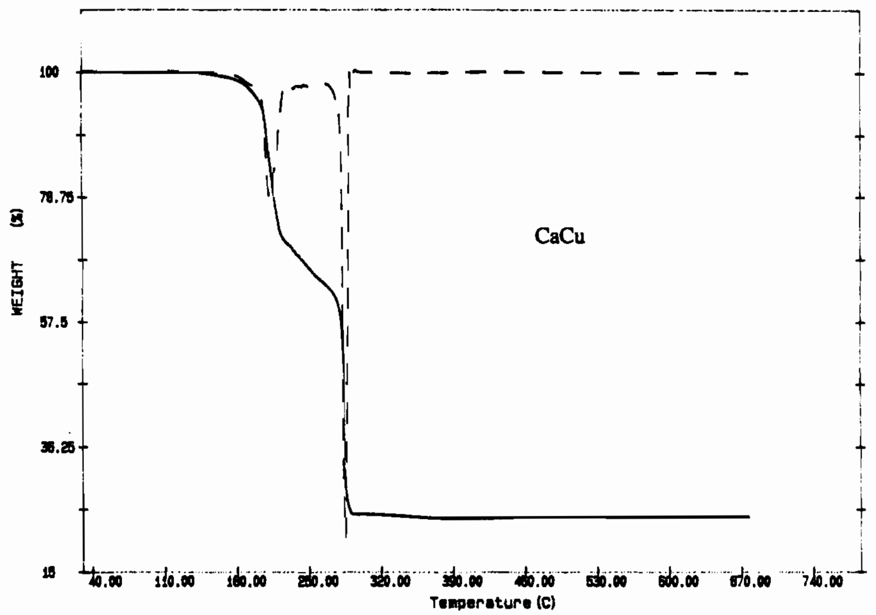

Figure 6. TGA diagram for compound **1**: Solid line; percentage of weight; dashed line, first derivative of the percentage of weight.

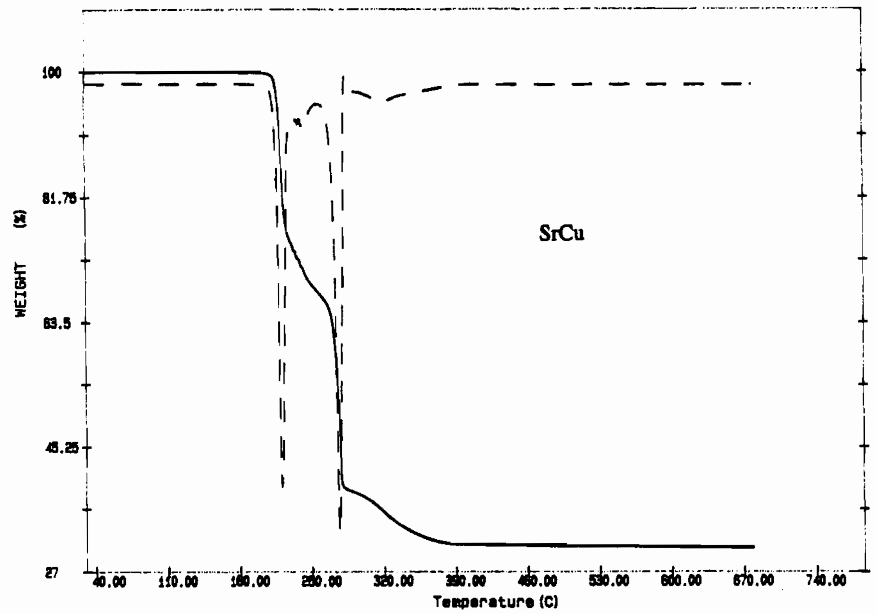

Figure 7. TGA diagram for compound **2**: Solid line, percentage of weight; dashed line, first derivative of the percentage of weight.

of the bdmap ligand to incorporate both a highly electropositive metal ion and the copper(II) ion. Although the analogous barium–copper complex was neither isolable from the precursor solution of the $YBa_2Cu_3O_{7-x}$ superconductor[1] nor obtainable by independent syntheses, it is very likely that the bdmap and the acetate ligand link the Ba(II) ion and the Cu(II) ion together in the precursor solution in a manner similar to that observed in compounds **1**–**3**. The adventitious H_2O molecule appears to play an important role in the formation of the mixed-metal complexes **1**–**3**. In compound **2**, the absence of the H_2O ligand makes the formation of the tetranuclear chain structure possible. In compound **3**, the metal centers were hydrolyzed and two hydroxo ligands were produced, which link the copper centers and the strontium ion together to form the hexanuclear complex. The different degrees of hydration and hydrolysis of these complexes could be a result of different susceptibilities of **1**–**3** toward hydrolysis. Despite the fact that we are unable to control the amount of the adventitious H_2O and the hydrolysis in this system, the syntheses of all three compounds are reproducible. If the extent of the hydrolysis in this system could be manipulated in a somewhat controlled fashion, new heteronuclear species involving copper(II) ion and other electropositive metal ions might be obtained.

Thermal Decomposition of Compounds 1-3. The thermal behavior of compounds **1**–**3** has been examined by thermogravimetric analyses, performed under 1 atm of oxygen. The TGA diagrams of these three compounds obtained with a scanning rate of 10.0 °C/min are shown in Figure 6–8, respectively. Compound **1** undergoes two major stages of weight loss upon heating. The first stage of weight loss occurs at 180–220 °C, while the second major weight loss occurs at about 280 °C. The residual weight (23.8%), becoming steady at a temperature above 300 °C, is significantly higher than the expected composition of $CaCuO_2$ (21.3%) but close to the $CaCuF_2O$ composition (24.7%), implying the possible fluorine contamination. Compound **2** undergoes a similar thermal decomposition involving two major stages of weight loss at 200–250 °C and 260–300 °C. The residual weight (30.5%),

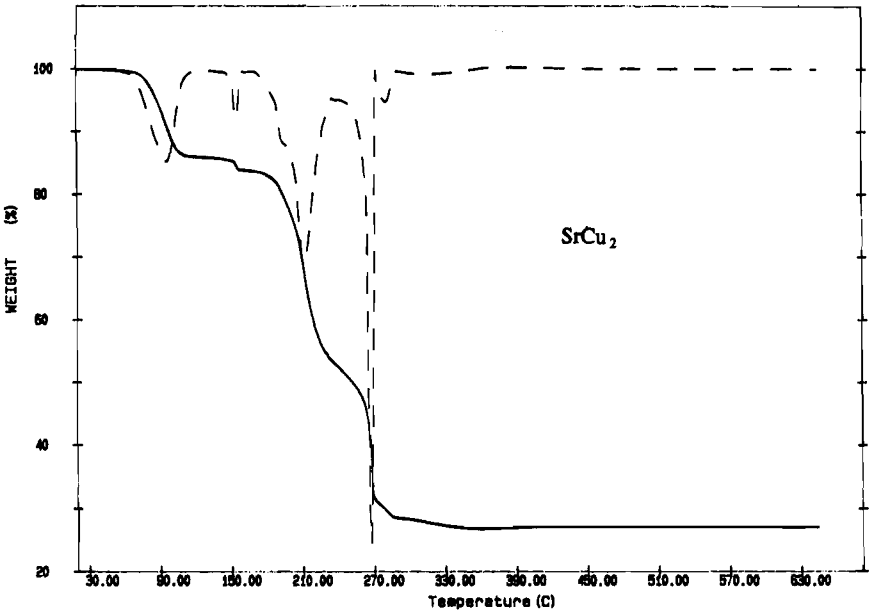

Figure 8. TGA diagram for compound **3**: solid line, percentage of weight; dashed line, first derivative of the percentage of weight.

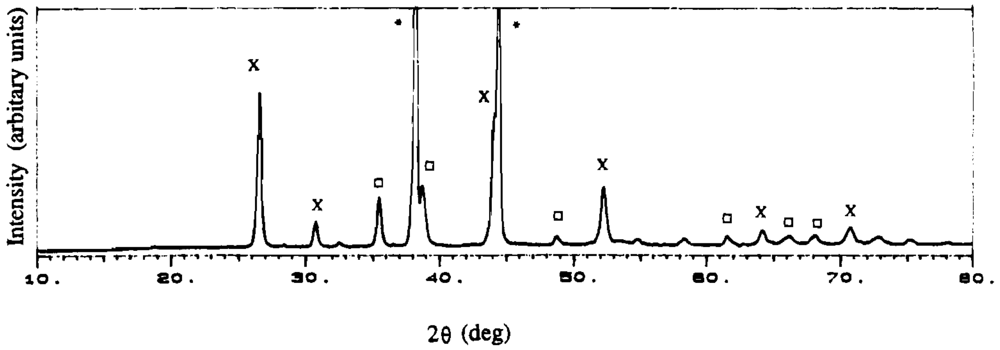

Figure 9. X-ray powder diffraction diagram for the pyrolyzed product of compound **2**. The peaks marked with X's belong to the SrF_2 phase, while the peaks due to the CuO phases are marked with squares. The peaks marked with asterisks are unidentified phases.

becoming steady after 390 °C, does not correspond to the composition of $SrCuO_2$ (25.5%) but to that of $SrCuF_2O$ (30.8%). The X-ray powder diffraction diagram for the bulk sample obtained through the pyrolysis procedure described in the Experimental Section revealed the presence of substantial amounts of SrF_2 and CuO phases (Figure 9). The unidentified phases in this diagram do not match any of the previously reported oxide phases involving strontium and copper. The presence of fluorine in the sample was further confirmed by elemental analysis which indicated that the fluorine content is about 2.4%. The fluorine contamination has been observed in other alkaline-earth metal systems, where fluorinated ligands are employed.[13] Magnetic susceptibility measurements over the range 4–300 K indicated that this sample is an antiferromagnetically coupled system (Figure 10). The rise of the susceptibility at low temperature implies the presence of paramagnetic species. The Sr–Cu–O phases can be superconducting when treated under high oxygen pressure to achieve oxygen doping.[2b] Due to the lack of appropriate high-pressure equipment, high-pressure thermal decomposition was not attempted in our laboratory. Compound **3** undergoes several stages of weight loss. The first stage appears to occur at about 70–100 °C, attributable to the loss of THF molecules. The sample mass becomes constant after about 330 °C, and the residual weight (27.5%) is consistent with the $SrCu_2O_3$ composition (27.2%). There is no evidence of fluorine contamination in this sample. The presence of the hydroxy ligands in compound **3** perhaps inhibited the formation of fluoride. Further examination of the effects of hydroxy and oxo ligands on the thermal behavior of mixed-metal complexes is in progress in our laboratory. The IR spectra of all three thermally decomposed compounds do not show any C–O stretching vibration bands, indicative of the absence of carbonates.

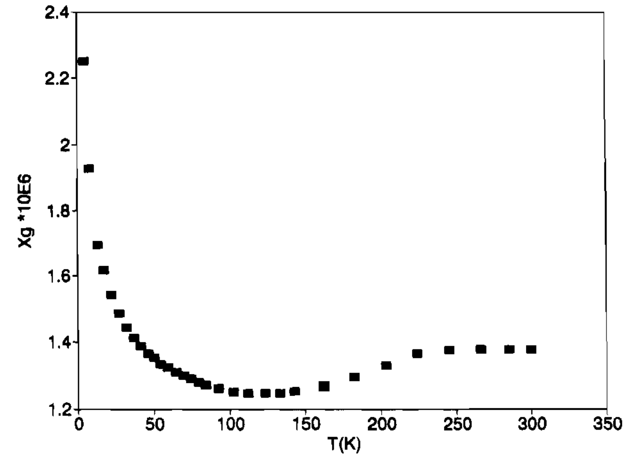

Figure 10. Diagram showing the gram susceptibility (χ_g) of the pyrolyzed product of compound **2** versus temperature (K).

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[13] Labrize, F.; Hubert-Pfalzgraf, L. G.; Daran, Jean-Claude; Halut, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1556.

Conclusion. Mixed-metal complexes involving alkaline-earth metal and copper ions can be obtained readily by using the 1,3-bis(dimethylamino)-2-propanolato ligand and the trifluoroacetato ligand. The structures and compositions of these complexes appear to be dependent on the behavior of the adventitious water present in the reaction media. These mixed-metal complexes can be decomposed thermally and converted either to oxides or a mixture of oxide and fluoride at mild temperatures.

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Supplementary Material Available: Tables of crystallographic analysis data, complete positional and thermal parameters, and bond lengths and angles (37 pages). Ordering information is given on any current masthead page.