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Molecular Copper-Barium Compounds. Syntheses, Crystal Structures, and Magnetic Properties of Two Sandwich Copper-Barium Complexes: $BaCu_4(bdmap)_4(PyO)_4(O_2CCF_3)_2 \cdot 0.5THF$ and $BaCu_4(deae)_4(PyO)_4(O_2CCF_3)_2$ (bdmap = 1,3-Bis(dimethylamino)-2-propanolato, PyO = Deprotonated 2-Hydroxypyridine, deae = 2-(Diethylamino)ethanolato)

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Two pentanuclear copper-barium complexes of formulas $BaCu_4(bdmap)_4(PyO)_4(O_2CCF_3)_2$ (**1**) and $BaCu_4(deae)_4(PyO)_4(O_2CCF_3)_2$ (**2**) have been synthesized by the reactions of $Cu(OCH_3)_2$ with $Ba(O_2CCF_3)_2$, 2-hydroxypyridine, and 1,3-bis(dimethylamino)-2-propanol (bdmapH) or 2-(diethylamino)ethanol (deaeH). Both compounds were characterized structurally. The barium ion is sandwiched between two dicopper anions, $[Cu_2L_2(PyO)_2(O_2CCF_3)]^-$ (L = bdmap or deae) and coordinated by eight oxygen atoms. The oxygen atoms on the PyO^- ligands coordinate exclusively to the barium ion. Crystal data: **1**, $C_{52}H_{84}BaCu_4F_6O_{12}N_{12} \cdot 0.5THF$, monoclinic crystal system, space group $C2$, $a = 25.75(2)$ Å, $b = 13.631(3)$ Å, $c = 23.57(2)$ Å, $\beta = 115.58(7)°$, $V = 7461(10)$ Å^3, $Z = 4$; **2**, $C_{48}H_{72}BaCu_4F_6O_{12}N_8 \cdot x THF$, monoclinic crystal system, space group $P2_1/c$, $a = 15.919(6)$ Å, $b = 15.903(6)$ Å, $c = 30.31(2)$ Å, $\beta = 95.16(5)°$, $V = 7641(7)$ Å^3, $Z = 4$. Both compounds have an antiferromagnetic ground state.

Introduction

The recent discovery of high-temperature superconductors has stimulated the intense research in molecular complexes developed as precursors for high T_c superconductors by chemical processes.[1-4] While most of the complexes previously reported have been homonuclear species,[2] we have been interested in multi-component molecular complexes containing barium, yttrium and copper with structures resembling those of high-temperature superconductors. Such molecular complexes might not only find direct use as precursors but may also serve as molecular models for the study of chemical and physical properties of superconductors. A few interesting Ba-Cu complexes such as $Ba_2Cu_2(OR)_4(acac)_4 \cdot 2HOR$ ($R = CH_2CH_2OCH_3$), isolated from the precursor solution of a $YBa_2Cu_3O_7$ thin film,[3a] $BaCu_2[OCMe(CF_3)_2]_6$, a very volatile compound,[3b] and a $BaCu(C_2H_6O_2)_n(C_2H_4O_2)_2$ (n = 3, 6) compound[3c] related to a precursor solution of the $YBa_2Cu_3O_{7-x}$ superconductor have been reported recently. We have recently discovered that an excellent precursor system for the $YBa_2Cu_3O_{7-x}$ superconductor can be obtained readily by using metal acetates or trifluoroacetates as the starting material and the 1,3-bis(dimethylamino)-2-propanol (bdmapH) ligand as an additive.[4c] This prompted us to investigate the synthesis of bimetallic Ba-Cu and Y-Cu complexes and trimetallic Ba-Y-Cu complexes involving acetate or trifluoroacetate and bdmap ligands. We report here the syntheses and characterization of two new pentanuclear copper-barium complexes with trifluoroacetate, bdmapH or 2-(diethylamino)ethanol, and 2-hydroxypyridine ligands.

Experimental Section

All reactions were carried out under nitrogen atmosphere. Solvents were distilled prior to use. Copper methoxide and 2-(diethylamino)ethanol were purchased from Aldrich Chemical Co. 1,3-Bis(dimethylamino)-2-propanol was purchased from Janssen Chimica and used without further purification. The $Ba(O_2CCF_3)_2$ compound was synthesized by the reaction of $Ba(OH)_2$ with HO_2CCF_3 in THF. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada, and Desert Analytics, Tucson, AZ.

Preparation of $BaCu_4(PyO)_4(bdmap)_4(O_2CCF_3)_2$ (1). $Cu(OCH_3)_2$ (100 mg, 0.80 mmol) was added to a flask containing 30 mL of THF. 1,3-Bis(dimethylamino)-2-propanol (117 mg, 0.80 mmol) was added to this solution. A blue solution was obtained. After 10 min $Ba(O_2CCF_3)_2$ (72 mg, 0.20 mmol) was added. The mixture was stirred for about 10 min. PyOH (76 mg, 0.80 mmol) was then added. The solution color became dark green immediately. After being stirred for 4.5 h, the solution was filtered and concentrated to about 2 mL by vacuum. Excess diethyl ether was added to crystallize the product. After standing at 23 °C for a few days dark blue-green crystals of **1** formed (98 mg, 0.070 mmol, 35% yield). The crystals decompose at 205 °C. Anal. Calc for $C_{52}H_{84}BaCu_4F_6O_{12}N_{12} \cdot 0.5C_4H_8O$: C, 40.27; H, 5.47; N, 10.44. Found: C, 40.07; H, 5.76; N, 10.83.

Preparation of $BaCu_4(PyO)_4(deae)_4(O_2CCF_3)_2$ (2). $Cu(OCH_3)_2$ (100 mg, 0.80 mmol) and 2-(diethylamino)ethanol (93 mg, 0.80 mmol) were added to a flask containing 30 mL of THF. The mixture was stirred for 30 min. $Ba(O_2CCF_3)_2$ (72 mg, 0.20 mmol) and 2-hydroxypyridine (76 mg, 0.80 mmol) were added to this solution. The blue solution changed color rapidly to dark green. After being stirred for 3 h, the solution was filtered and concentrated to about 3 mL by vacuum. Excess diethyl ether was added. After standing at 23 °C for several days, dark green

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Table I. Crystallographic Data

compd	1	2
formula	$C_{52}H_{84}BaCu_4F_6O_{12}N_{12}{\cdot}0.5C_4H_8O$	$C_{48}H_{72}BaCu_4F_6O_{12}N_8{\cdot}x$THF
fw	1610.1	1458.07 (without THF)
space group	$C2$	$P2_1/c$
a, Å	25.75(2)	15.919(6)
b, Å	13.631(3)	15.903(6)
c, Å	23.57(2)	30.31(2)
β, deg	115.58(7)	95.16(5)
V, Å^3	7461(10)	7641(7)
Z	4	4
d_{calc}, g cm^{-3}	1.44	1.27
μ(Mo Kα), cm^{-1}	17.16	16.67
$R(F_o^2)^a$	0.093	0.127
$R_w(F_o^2)^b$	0.099	0.144

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

rectangular crystals of **2** were obtained (dry weight 155 mg, 0.11 mmol, 53% yield). M.p: 198 °C. Anal. Calc for $C_{48}H_{72}BaCu_4F_6O_{12}N_8$: C, 39.52; H, 4.98; N, 7.69. Found: C, 39.60; H, 4.94; N, 7.40.

X-ray Diffraction Analysis. Dark blue-green single-crystals of **1** and dark green single-crystals of **2** with rectangular shapes were obtained from concentrated THF solutions at 23 °C. The crystals with the dimensions of 0.30 × 0.50 × 0.50 mm^3 were mounted on glass fibers and sealed with epoxy glue. Data were collected over the range $2 < 2\theta < 50°$ for **1** and $2 < 2\theta < 45°$ for **2** on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo Kα radiation operated at 50 kV and 35 mA. The initial orientation matrix for **1** was obtained from 15 reflections ($10 < 2\theta < 14°$) located by the SEARCH routine. The initial orientation matrix for **2** was obtained from 20 reflections ($11 < 2\theta < 16°$). The refinements of high-angle cells were not successful due to too few available strong reflections. Three standard reflections were measured every 147 reflections. Data were processed on a VAX workstation 3520 using the TEXSAN crystallographic package (version 5.0). Data were corrected for Lorentz–polarization effects. Empirical absorption corrections were applied for both crystals.

1 crystallizes in the monoclinic crystal system. The systematic absences agree with three possible space groups: $C2$, Cm and $C2/m$. The acentric space group $C2$ was chosen. The correctness of this choice was confirmed by the successful solution and refinement of the structure. **2** crystallizes in the monoclinic crystal system. The space group $P2_1/c$ was uniquely determined by the systematic absences. The positions of metal atoms were determined by the direct method (MITHRIL). Other non-hydrogen atoms were located by subsequent difference Fourier syntheses. The molecule of **1** has an approximate C_2 symmetry. Both CF_3 groups are disordered. The CF_3 group bonded to C51 was refined as a rigid body with the fixed C–F bond length of 1.31 Å and F–C–F angle of 109°. The disorder of this group could not be modeled. The three fluorine atoms bonded to C50 displayed a typical C_2 disorder with respect to the C50–C49 bond. Two F_3 sets of atoms were located from the difference Fourier map and refined with 50% occupancy, respectively. Due to the disorder, the fluorine atoms were not refined anisotropically. A disordered THF solvent molecule (0.5 THF molecule/per molecule of **1**) was located in the lattice. The oxygen atom of the THF molecule is disordered over the 2-fold axis with 50% occupancy for each site. This solvent molecule was refined successfully. The pyridine rings in **1** were refined as rigid bodies with the idealized C–C (C–N) bond length of 1.40 Å and C–C–C (C–N–C, C–C–N) angle of 120°. Metal atoms and some of the oxygen and nitrogen atoms were refined anisotropically. The positions of hydrogen atoms except those bonded to the disordered THF molecule were calculated. Their temperature factors were tied to the temperature factor of the carbon atoms to which they are bonded (multiplied by 1.10). Their contribution in structural factor calculations was included. The largest peak in the final difference Fourier map is 2.629 e Å^{-3}, 1.05 Å from the Ba1 atom. The high R factor could be attributed to the disorder of the molecule and the imperfect absorption correction.

The compound **2** crystallizes with the THF solvent molecule. Upon isolation of the crystals from the solution the crystals lose solvent molecules rapidly. Before the crystal was sealed by the epoxy glue, it already decomposed partially. At the end of the data collection, additional 20% intensity decay was observed. As a result, the intensity of the reflections and the positions of atoms have a poor accuracy. The ethyl groups of the deae ligand show varied degrees of disorder. Their positions were only partially determined. Both of the CF_3 groups showed a C_2 disorder with respect to the C–C bonds. Two sets of fluorine atoms of the CF_3 group bonded to the C–O1–O6 acetate group were located and refined successfully with 50% occupancy for each set. Only one set of fluorine atoms of the CF_3 group bonded to the C–O3–O5 acetate group were located from the difference Fourier map. This group could be refined only as a rigid CF_3 group with a group thermal parameter. Although there was an apparent disorder of this group, we were unable to determine the pattern of the disorder. The pyridine rings in **2** were refined as rigid bodies. Due to the decomposition and disorder, the position of THF solvent molecules could not be determined. The high R factor of this structure can be attributed to these disorders, the partially resolved structure, and the poor quality of the data. Only metal atoms in **2** were refined anisotropically. The largest peak in the final difference Fourier map is 1.645 e Å^{-3}, 1.21 Å away from the barium ion. The data for the X-ray diffraction analysis are given in Table I.

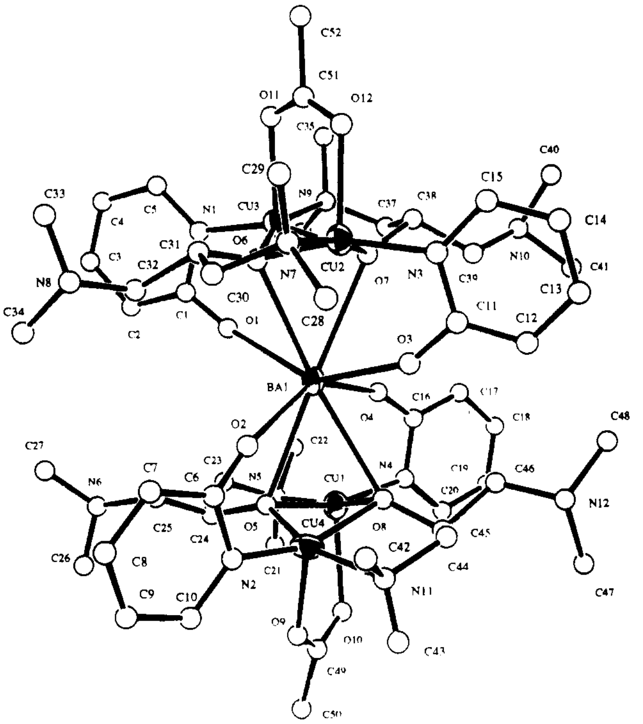

Figure 1. ORTEP diagram of **1** with labeling scheme. The disordered fluorine atoms and THF solvent molecule are omitted for clarity.

Magnetic Susceptibility Measurement. Magnetic susceptibilities for compounds **1** and **2** were measured on a SQUID device (SHF variable-temperature susceptometer) at Michigan State University. The samples were loaded in a nitrogen-filled glovebag and run in an Al–Si alloy bucket. The samples were quenched to 5 K at zero applied field. The field was cycled to minimize residual field.

Results and Discussion

Synthesis and Crystal Structure of $BaCu_4(bdmap)_4(PyO)_4(O_2CCF_3)_2$ (1). In order to understand the role of the bdmapH ligand in the acetate or trifluoroacetate precursor systems, we investigated the reaction of $Ba(O_2CCH_3)_2$ and $Cu(O_2CCH_3)_2$ with the bdmapH ligand (eq 1) and the reaction of $Ba(O_2CCF_3)_2$ and $Cu(O_2CCF_3)_2$ with the bdmapH ligand (eq 2). From reaction 1 a two-dimensional polymeric copper(II) complex linked by hydrogen bonds and the bdmap ligand was isolated.[4c] No bimetallic Ba–Cu complexes were obtained. We believed that the poor solubility of the $Ba(O_2CCH_3)_2$ compound in organic solvents may have prevented it from reacting with the bdmapH ligand. From reaction 2 only blue oily material was obtained. We have not been able to characterize this material unambiguously. Although we have not succeeded in isolating any bimetallic Ba–Cu complexes from these reactions, we have found that bimetallic Ba–Cu complexes can be obtained readily by the

Table II. Positional and Thermal Parameters for **1**

atom	x	y	z	B_{eq},[a] Å^2
Ba1	0.49481(8)	0.5340	0.2489(1)	2.54(7)
Cu1	0.3596(2)	0.5144(4)	0.2446(2)	3.5(2)
Cu2	0.6259(2)	0.6217(3)	0.2656(2)	3.4(2)
Cu3	0.6324(2)	0.4705(3)	0.3564(2)	3.3(2)
Cu4	0.3615(1)	0.5394(5)	0.1225(2)	3.9(2)
F1	0.150(2)	0.546(5)	0.047(2)	7(1)
F2	0.159(2)	0.457(4)	0.131(3)	7(1)
F3	0.161(3)	0.422(6)	0.054(4)	9(2)
F4	0.183(2)	0.373(4)	0.096(3)	8(1)
F5	0.143(3)	0.513(5)	0.100(3)	10(2)
F6	0.155(2)	0.464(5)	0.014(3)	9(2)
O1	0.536(1)	0.367(2)	0.317(1)	5(1)
O2	0.465(1)	0.493(2)	0.127(1)	6(1)
O3	0.5190(9)	0.710(2)	0.214(1)	4(1)
O4	0.458(1)	0.575(2)	0.339(1)	5(1)
O5	0.383(1)	0.445(2)	0.183(1)	3.3(5)
O6	0.612(1)	0.492(2)	0.261(1)	5(1)
O7	0.601(1)	0.615(2)	0.338(1)	4(1)
O8	0.3826(7)	0.624(1)	0.2033(9)	1.5(4)
O9	0.273(1)	0.500(2)	0.095(1)	7(2)
O10	0.262(1)	0.524(3)	0.174(1)	8(2)
O11	0.730(1)	0.493(2)	0.381(1)	8(2)
O12	0.720(1)	0.631(2)	0.326(1)	6(1)
O13	0.021(3)	0.316(5)	0.012(4)	10(2)
C1	0.5714(9)	0.298(2)	0.336(1)	3.8(8)
C2	0.5596(9)	0.198(2)	0.331(1)	7(1)
C3	0.605(1)	0.131(1)	0.356(1)	7(1)
C4	0.661(1)	0.163(2)	0.386(1)	8(1)
C5	0.6732(7)	0.264(2)	0.391(1)	5(1)
N1	0.628(1)	0.331(1)	0.366(1)	5.7(8)
C6	0.4317(8)	0.459(2)	0.077(1)	4.0(8)
C7	0.4497(8)	0.401(2)	0.040(1)	6(1)
C8	0.409(1)	0.352(2)	−0.012(1)	8(1)
C9	0.351(1)	0.361(2)	−0.028(1)	7(1)
C10	0.3327(7)	0.418(2)	0.009(1)	3.9(8)
N2	0.373(1)	0.467(2)	0.062(1)	4.6(7)
C11	0.5534(8)	0.786(2)	0.226(1)	4.0(8)
C12	0.5346(7)	0.883(2)	0.218(1)	4.8(9)
C13	0.575(1)	0.959(1)	0.235(1)	7(1)
C14	0.633(1)	0.938(2)	0.262(1)	4.9(9)
C15	0.6522(7)	0.841(2)	0.271(1)	5(1)
N3	0.612(1)	0.765(1)	0.253(1)	3.9(6)
C16	0.4236(9)	0.616(2)	0.355(1)	3.7(7)
C17	0.4381(8)	0.677(2)	0.407(1)	6(1)
C18	0.395(1)	0.722(2)	0.419(1)	6(1)
C19	0.337(1)	0.705(2)	0.379(1)	6(1)
C20	0.3226(7)	0.644(2)	0.327(1)	5(1)
N4	0.366(1)	0.599(2)	0.315(1)	5.4(8)
C52	0.8132(8)	0.569(2)	0.397(1)	24(4)
N5	0.353(1)	0.385(3)	0.284(1)	5(2)
N6	0.387(2)	0.172(2)	0.163(2)	8(2)
N7	0.637(1)	0.598(2)	0.186(1)	4(1)
N8	0.614(2)	0.274(3)	0.165(1)	5(2)
N9	0.642(1)	0.502(2)	0.450(1)	3(1)
N10	0.605(1)	0.813(2)	0.441(1)	5(1)
N11	0.351(1)	0.678(2)	0.074(1)	5(1)
N12	0.377(2)	0.897(2)	0.223(2)	7(2)
C21	0.299(2)	0.362(4)	0.273(2)	8(1)
C22	0.389(2)	0.387(4)	0.359(3)	10(2)
C23	0.382(2)	0.321(4)	0.257(2)	7(1)
C24	0.369(1)	0.343(3)	0.187(2)	4(1)
C25	0.398(2)	0.282(3)	0.162(2)	4.9(9)
C26	0.336(2)	0.153(3)	0.120(2)	7(1)
C27	0.430(2)	0.113(4)	0.157(2)	7(1)
C28	0.597(2)	0.668(3)	0.128(2)	7(1)
C29	0.692(2)	0.610(3)	0.189(2)	7(1)
C30	0.616(1)	0.493(3)	0.163(2)	3.4(8)
C31	0.627(1)	0.436(3)	0.221(2)	3.3(8)
C32	0.598(2)	0.334(4)	0.204(2)	7(1)
C33	0.670(2)	0.247(4)	0.192(3)	8(1)
C34	0.574(2)	0.195(4)	0.141(2)	7(1)
C35	0.702(2)	0.495(4)	0.501(2)	9(1)
C36	0.609(2)	0.436(3)	0.467(2)	6(1)
C37	0.614(2)	0.600(3)	0.436(2)	6(1)
C38	0.625(1)	0.667(2)	0.397(1)	2.3(6)
C39	0.591(1)	0.759(3)	0.382(2)	4.8(9)
C40	0.653(3)	0.873(5)	0.455(3)	13(2)
C41	0.564(2)	0.890(4)	0.434(2)	8(1)
C42	0.386(2)	0.683(4)	0.040(2)	8(1)
C43	0.300(2)	0.697(4)	0.039(3)	9(1)
C44	0.372(1)	0.753(3)	0.128(2)	3.8(8)
C45	0.357(2)	0.718(3)	0.182(2)	4(1)
C46	0.390(2)	0.789(3)	0.237(2)	5(1)
C47	0.312(2)	0.915(4)	0.208(3)	10(2)
C48	0.421(2)	0.956(4)	0.278(3)	9(1)
C49	0.245(2)	0.507(3)	0.117(2)	5(1)
C50	0.180(2)	0.466(5)	0.094(3)	8(1)
C51	0.745(2)	0.562(3)	0.364(2)	4(1)
C53	0.001(3)	0.478(5)	0.035(3)	11(2)
C54	−0.006(3)	0.394(5)	0.043(3)	13(2)
F7	0.837(1)	0.482(2)	0.406(2)	13(1)
F8	0.835(2)	0.623(2)	0.366(1)	15(1)
F9	0.824(2)	0.610(2)	0.451(2)	17(1)

[a] $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j$.

addition of 2-hydroxypyridine ligand and the replacement of the $Cu(O_2CCF_3)_2$ with $Cu(OCH_3)_2$ in reaction 2, as shown in eq 3.

$$Ba(O_2CCH_3)_2 + Cu_2(O_2CCH_3)_4(H_2O)_2 + \text{bdmaph} \rightarrow \{[Cu_4(O_2CCH_3)_6(\text{dmap})_2](H_2O)_6\}_n \quad (1)$$

$$Ba(O_2CCF_3)_2 + Cu_2(O_2CCF_3)_4 + \text{bdmapH} \rightarrow \text{blue oil} \quad (2)$$

$$Ba(O_2CCF_3)_2 + 4Cu(OCH_3)_2 + 4\text{PyOH} + 4\text{bdmapH} \rightarrow \underset{\mathbf{1}}{BaCu_4(\text{bdmap})_4(\text{PyO})_4(O_2CCF_3)_2} \quad (3)$$

The reaction of $Cu(OCH_3)_2$ with bdmapH, PyOH and $Ba(O_2CCF_3)_2$ in tetrahydrofuran at 23 °C yielded a dark blue-green solution. After the solution was filtered and concentrated to about 3 mL, dark blue-green crystals of compound **1** with rectangular shape were obtained. Compound **1** was characterized as $BaCu_4(\text{bdamp})_4(\text{PyO})_4(O_2CCF_3)_2\cdot 0.5THF$ by means of elemental and single-crystal X-ray diffraction analyses.

The molecular structure of **1** is shown in Figure 1. Positional and thermal parameters are given in Table II. Selected bond distances and angles are listed in Table III. The molecule consists of two anionic dicopper units with the formula of $[Cu_2(\text{PyO})_2(\mu\text{-dmap})_2(O_2CCF_3)]^-$ and a barium cation. In the dicopper anion, the two copper(II) ions are bridged by two oxygen atoms from the two bdmap ligands with normal Cu–O bond distances, except that the Cu2–O6 distance (1.80(2) Å) and Cu4–O5 distance (1.83(2) Å) are quite short compared with the known Cu–O bonds involving the dmap ligand.[5] The Cu–Cu separations in the dicopper units, Cu1–Cu4 = 2.919(7) Å, Cu2–Cu3 = 2.921(7) Å, are comparable to those of previously reported dinuclear copper complexes.[6] The two Cu_2O_2 units are buckled with a dihedral angle of 38.8° between Cu1–O5–O8 and Cu4–O5–O8 planes and a dihedral angle of 38.7° between Cu2–O6–O7 and Cu3–O6–O7 planes. Each copper atom is coordinated by two nitrogen atoms, one from a dmap ligand and one from a PyO^- ligand. The Cu–N distances vary considerably from 1.87(3) Å of Cu4–N2 to 2.17(3) Å of Cu4–N11. The averaged Cu–N (PyO) distance, 1.93 Å, is significantly shorter than the averaged Cu–N (bdmap) distance, 2.10 Å, indicating that the nitrogen atom of the PyO^- ligand is a better electron donor than that of

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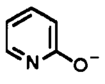
Table III. Selected Bond Distances (Å) and Angles (deg) for Compound **1**[a]

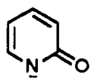
			Distances				
Ba1–O1	2.72(2)	Cu4–O5	1.83(2)	O6–C31	1.38(5)	N9–C37	1.49(5)
Ba1–O2	2.70(3)	Cu4–O8	2.09(2)	O7–C38	1.44(4)	N10–C39	1.47(5)
Ba1–O3	2.70(2)	Cu4–O9	2.15(3)	O8–C45	1.44(4)	N10–C40	1.41(8)
Ba1–O4	2.74(3)	Cu4–N11	2.17(3)	O9–C49	1.07(7)	N10–C41	1.45(6)
Ba1–O5	2.88(2)	Cu4–N2	1.87(3)	O10–C49	1.24(6)	N11–C42	1.45(7)
Ba1–O6	2.97(3)	F7–C52	1.31(4)	O11–C51	1.16(6)	N11–C43	1.24(5)
Ba1–O7	2.86(2)	F8–C52	1.31(5)	O12–C51	1.27(5)	N11–C44	1.53(5)
Ba1–O8	2.88(2)	F9–C52	1.31(5)	N5–C21	1.36(7)	N12–C46	1.51(5)
Cu1–O5	2.02(3)	F1–C50	1.51(8)	N5–C22	1.59(6)	N12–C47	1.57(8)
Cu1–O8	2.00(2)	F2–C50	1.2(1)	N5–C23	1.45(7)	N12–C48	1.53(6)
Cu1–N5	2.04(4)	F3–C50	1.0(1)	N6–C25	1.54(5)	C23–C24	1.56(7)
Cu1–N4	1.97(2)	F4–C50	1.27(8)	N6–C26	1.30(5)	C24–C25	1.40(7)
Cu2–O6	1.80(2)	F5–C50	1.2(1)	N6–C27	1.42(7)	C30–C31	1.51(6)
Cu2–O7	2.07(3)	F6–C50	1.70(9)	N7–C28	1.61(5)	C31–C32	1.55(6)
Cu2–O12	2.23(3)	Cu1–O10	2.33(2)	N7–C29	1.40(6)	C37–C38	1.41(6)
Cu2–N7	2.04(3)	Cu3–O11	2.33(2)	N7–C30	1.54(5)	C38–C39	1.48(5)
Cu2–N3	1.98(2)	O1–C1	1.24(3)	N8–C32	1.42(7)	C44–C45	1.56(6)
Cu3–O6	2.10(3)	O2–C6	1.21(3)	N8–C33	1.35(6)	C45–C46	1.54(5)
Cu3–O7	2.10(2)	O3–C11	1.31(3)	N8–C34	1.44(6)	C49–C50	1.61(7)
Cu3–N9	2.16(3)	O4–C16	1.23(4)	N9–C35	1.50(5)	C51–C52	1.59(4)
Cu3–N1	1.92(2)	O5–C24	1.45(5)	N9–C36	1.39(6)		
			Angles				
O3–Ba1–O5	121.2(6)	N8–C32–C31	117(5)	O11–C51–O12	135(4)	C25–N6–C26	108(3)
O3–Ba1–O6	80.8(7)	N9–C37–C38	121(4)	O11–C51–C52	111(3)	C25–N6–C27	113(4)
O3–Ba1–O7	66.9(6)	O7–C38–C37	101(3)	O12–C51–C52	114(4)	C26–N6–C27	112(4)
O3–Ba1–O8	80.5(6)	O7–C38–C39	102(2)	Ba1–O6–C31	128(2)	Cu2–N7–C28	114(3)
O4–Ba1–O5	84.3(7)	C37–C38–C39	116(4)	Cu2–O6–Cu3	97(1)	Cu2–N7–C29	118(2)
O4–Ba1–O6	130.2(7)	N10–C39–C38	108(3)	Cu2–O6–C31	119(3)	Cu2–N7–C30	108(2)
O4–Ba1–O7	83.6(8)	N11–C44–C45	110(3)	Cu3–O6–C31	129(2)	C28–N7–C29	103(3)
O4–Ba1–O8	64.9(6)	O8–C45–C44	109(3)	Ba1–O7–Cu2	86.9(8)	C28–N7–C30	105(2)
O5–Ba1–O6	135.3(7)	O8–C45–C46	106(3)	Ba1–O7–Cu3	87.0(7)	C29–N7–C30	108(3)
O5–Ba1–O7	167.0(9)	C44–C45–C46	105(3)	Ba1–O7–C38	141(2)	C32–N8–C33	114(4)
O5–Ba1–O8	50.9(6)	N12–C46–C45	116(3)	Cu2–O7–Cu3	89(1)	C32–N8–C34	109(4)
O6–Ba1–O7	52.7(8)	O9–C49–O10	122(4)	Cu2–O7–C38	128(2)	C33–N8–C34	115(4)
O6–Ba1–O8	158.9(7)	O9–C49–C50	129(5)	Cu3–O7–C38	108(2)	Cu3–N9–C35	115(3)
O7–Ba1–O8	126.7(6)	O10–C49–C50	106(5)	Ba1–O8–Cu1	87.9(6)	Cu3–N9–C36	110(2)
O1–Ba1–O2	108.0(7)	Cu1–N4–C16	110(2)	Ba1–O8–Cu4	86.1(7)	Cu3–N9–C37	97(2)
O1–Ba1–O3	147.3(7)	Cu1–N4–C20	130(1)	Ba1–O8–C45	138(2)	C35–N9–C36	106(3)
O1–Ba1–O4	84.0(8)	Cu2–N3–C11	111(1)	Cu1–O8–Cu4	91.1(8)	C35–N9–C37	118(3)
O1–Ba1–O5	90.6(7)	Cu2–N3–C15	129(2)	Cu1–O8–C45	131(2)	C36–N9–C37	111(4)
O1–Ba1–O6	70.0(8)	Cu3–N1–C1	111(2)	Cu4–O8–C45	106(2)	C39–N10–C40	110(5)
O1–Ba1–O7	83.4(7)	Cu3–N1–C5	128(2)	Cu4–O9–C49	134(3)	C39–N10–C41	113(3)
C47–N12–C48	116(4)	Cu4–N2–C6	111(2)	Cu2–O12–C51	119(3)	C40–N10–C41	98(4)
N5–C23–C24	116(3)	Cu4–N2–C10	129(2)	O13–O13–C54	71(8)	Cu4–N11–C42	111(3)
O5–C24–C23	107(3)	O1–C1–C2	127(2)	O13–O13–C54	73(8)	Cu4–N11–C43	113(3)
O5–C24–C25	111(4)	O1–C1–N1	113(2)	C54–O13–C54	87(6)	Cu4–N11–C44	103(2)
C23–C24–C25	116(3)	O2–C6–C7	123(2)	Cu1–N5–C21	113(3)	C42–N11–C43	111(4)
N6–C25–C24	115(4)	O2–C6–N2	117(3)	Cu1–N5–C22	111(3)	C42–N11–C44	110(3)
N7–C30–C31	105(3)	O3–C11–C12	124(2)	Cu1–N5–C23	100(3)	C43–N11–C44	109(4)
O6–C31–C30	110(3)	O3–C11–N3	116(2)	C21–N5–C22	106(4)	C46–N12–C47	109(4)
O6–C31–C32	116(4)	O4–C16–C17	125(2)	C21–N5–C23	118(4)	C46–N12–C48	109(3)
C30–C31–C32	110(3)	O4–C16–N4	114(2)	C22–N5–C23	109(3)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

the bdmap$^-$ ligand. This could be attributed to the contribution of the ketone resonance form (b) of the PyO$^-$ which enhances the



a



b

electron density on the nitrogen atom of the PyO$^-$ ligand. Such a resonance form is not available for the bdmap ligand. It is of interest to notice that only one of the amino groups from each bdmap ligand is coordinated, while the other amino group is away from the copper centers. A similar bonding mode of bdmap ligand has been observed previously in the $Cu_3(bdmap)_4Cl_2$ compound.[7] It can be shown by simple molecular modeling that it is the ring strain that prevents all the amino groups of the bdmap ligand from coordinating to the copper centers in the dinuclear unit. The dicopper unit is capped by a trifluoroacetate ligand through the formation of one long and one normal Cu–O bond: Cu1–O10 = 2.33(2) Å, Cu4–O9 = 2.15(3) Å; Cu2–O12 = 2.23(3) Å, Cu3–O11 = 2.33(2) Å. It has not been understood by us why the trifluoroacetate ligand is asymmetrically coordinated to the two copper centers since the coordination environment around each copper atom is nearly identical. Nevertheless, each copper center has an approximately square-pyramidal geometry. Similar square-pyramidal geometry has been observed in the Y_2Cu_8 and Ln_2Cu_8 complexes.[4,8]

The most important feature of this structure is that a barium ion is sandwiched between the two anionic dicopper units. All oxygen atoms from the PyO$^-$ ligands are coordinated exclusively to the barium center in a nonplanar fashion. The dihedral angle between the planes of Ba1–O2–O3 and Ba1–O1–O4 is 50.7°, and the averaged bond distance of these four Ba–O bonds is 2.71 Å. The barium ion is also coordinated by the additional four oxygen atoms from the bdmap ligands in a nonplanar fashion,

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with a dihedral angle of 38.0° between the planes of Ba1–O5–O8 and Ba1–O6–O7. The averaged bond distances of these four Ba–O bonds is 2.90 Å, which is much longer than the Ba–O bonds formed by the barium atom and oxygen atoms from the PyO ligands. The coordination geometry of the barium ion can be described as a distorted square antiprism. The bridging of three metal centers by the oxygen atom of the bdmap ligand has been observed previously.[5] Barium–oxygen bond distances reported in known compounds span a considerable range,[2f,3,9] 2.60–3.00 Å. In the unit cell of $YBa_2Cu_3O_{7-x}$, a BaO_4 layer is sandwiched by a Cu_4O_2 layer and a Cu_4O_4 layer.[10] The Ba–O distance in the BaO_4 layer is 2.750(3) Å, while the Ba–O distances between the Ba atom and the oxygen atoms in the Cu_4O_4 and Cu_4O_2 layers are much longer, 2.915 Å being the average.[10b] The features displayed by the molecule of **1**, such as sharing of the oxygen atom from the bdmap ligand between two copper and one barium centers, the two distinct sets of Ba–O bonds, and the sandwich structure resemble those found in the $YBa_2Cu_3O_{7-x}$ structure. The geometry of the $BaCu_4$ unit can be best described as two triangles sharing a corner and twisted by 38.3°. The Cu–Ba distances in **1** do not vary significantly: Ba1–Cu1 = 3.449(6), Ba1–Cu2 = 3.438(6), Ba1–Cu3 = 3.460(6), Ba1–Cu4 = 3.440(6) Å. These distances are close to the sum of metallic radii[11] of copper and barium, 3.451 Å. Similar Cu–Ba distances have also been found in $YBa_2Cu_3O_{7-x}$ and the Ba_2Cu_2 complex reported by Ryan and co-workers.[3a,10] A similar sandwich structure involving barium ion has also been observed in the complex $BaZr_4(O^iPr)_{18}$ reported recently by Caulton and co-workers.[12]

Since only one amino group of the bdmap ligand is coordinated to the copper center in **1**, it is conceivable that the bdmap ligand could be replaced by a 2-(dialkylamino)ethanol ligand and the analogous compound of **1** could be obtained. Indeed, a new Ba–Cu complex with the formula of $BaCu_4(deae)_4(PyO)_4(O_2CCF_3)_2$ (**2**) was obtained when the bdmap ligand was replaced by the 2-(diethylamino)ethanol ligand.

Synthesis and Characterization of $BaCu_4(deae)_4(PyO)_4(O_2CCF_3)_2$ (2). Compound **2** was obtained from the reaction of $Cu(OCH_3)_2$, $Ba(O_2CCF_3)_2$ and PyOH with deaeH ligand in the ratio of 4:1:4:4 in about 50% yield (eq 4). Compound **2** was

$$Ba(O_2CCF_3)_2 + 4Cu(OCH_3)_2 + 4PyOH + 4deaeH \rightarrow \underset{\mathbf{2}}{BaCu_4(deae)_4(PyO)_4(O_2CCF_3)_2} \quad (4)$$

characterized by elemental analysis and single-crystal X-ray diffraction analysis. The crystals of **2** decomposed rapidly upon isolation from the solution due to the loss of the THF solvent molecules. As a result of considerable intensity loss and disorder of atoms in the crystal lattice, the structure was only partially resolved. Nevertheless, from the incomplete structural data, it was unambiguously established that the structure of **2** is very similar to that of **1** as shown in Figure 2. Positional and thermal parameters are given in Table IV. Selected bond lengths and angles are given in Table V.

In the two anionic dicopper units, two copper atoms are bridged by the two oxygen atoms of the deae ligands in a similar fashion as found in **1**. Each copper atom is coordinated by two nitrogen atoms, one from the deae ligand and the other one from the PyO^- ligand. Dinuclear copper(II) complexes of the general formula $Cu_2(L)_2X_2$ (L = 2-(dialkylamino)ethanolato, X = halogen or NCO) with (dialkylamino)ethanolato ligands as the bridging ligand have been well characterized previously.[13] These complexes typically dimerize to form tetramers with tetrahedral geometry in the solid through the formation of intermolecular Cu–O bonds at the fifth coordination site of the copper atom. In contrast, in complex **2**, the fifth position of the copper atom is occupied by the oxygen atom of the trifluoroacetate ligand. The two oxygen atoms of the trifluoroacetate ligand are bonded to two copper atoms in a similar fashion as found in **1** with one short Cu–O bond (Cu1–O1 = 2.24(4), Cu2–O3 = 2.22(5) Å) and one long Cu–O bond (Cu3–O6 = 2.28(4), Cu4–O5 = 2.35(4) Å). The Cu1–Cu3 and Cu2–Cu4 separations are 2.954(9) and 2.950(9) Å, respectively. The Ba–Cu distances are comparable to those in **1**: Ba–Cu1 = 3.450(7), Ba–Cu2 = 3.440(7), Ba–Cu3 = 3.427(8), Ba–Cu4 = 3.460(7) Å. The averaged bond distance between the barium and the four oxygen atoms of the PyO^- ligands is 2.65 Å, much shorter than the averaged Ba–O distance between the barium ion and the oxygen atom of the deae ligand, 2.84 Å in average. As observed in **1**, the averaged Cu–N (PyO^-) bond length, 1.93 Å, is shorter than that of Cu–N (deae), 2.09 Å. The averaged bond length of Cu–O (deae) bonds is 1.97 Å, similar to those found in the known (dialkylamino)ethanolato copper(II) dimers.[13] The dihedral angle between the Cu1–Cu3–Ba plane and the Cu2–Cu4–Ba plane, 45°, is much larger than that of **1**.

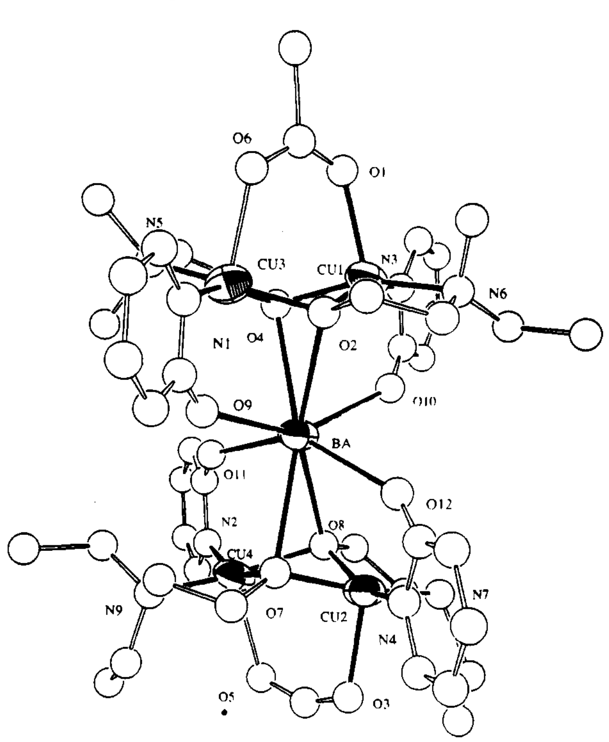

Figure 2. ORTEP diagram showing the partially resolved structure of **2** with labeling scheme. The disordered CF_3 groups are not shown.

The successful syntheses of **1** and **2** demonstrated that bifunctional ligands with both neutral and negatively charged coordination sites such as 2-hydroxypyridine, 1,3-bis(dimethylamino)-2-propanol and 2-(dialkylamino)ethanol are able to bind to the copper and the barium ions selectively. Although no bimetallic Ba–Cu complexes have been isolated directly from our precursor solutions of the $YBa_2Cu_3O_{7-x}$ superconductor, Ba–Cu complexes involving both acetate ligand and the bdmap ligand could exist in the precursor solution since the bdmap ligand is capable of binding the copper(II) ion and the barium(II) ion together through the oxygen atom as indicated in the structure of **1**. It was also demonstrated here that anionic polynuclear

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Table IV. Positional and Thermal Parameters for **2**

atom	x	y	z	B_{eq},[a] Å^2
Ba	0.7508(2)	0.0724(2)	0.7337(1)	4.7(2)
Cu1	0.6613(4)	0.0457(4)	0.6267(2)	5.3(4)
Cu2	0.7184(4)	−0.0232(4)	0.8325(2)	5.4(4)
Cu3	0.8338(4)	0.1159(4)	0.6357(2)	5.7(4)
Cu4	0.7906(4)	0.1475(4)	0.8407(2)	5.3(4)
O1	0.680(2)	0.077(2)	0.556(1)	8(1)
O2	0.775(2)	0.009(2)	0.647(1)	6.3(9)
O3	0.747(3)	−0.027(3)	0.905(2)	12(2)
O4	0.723(2)	0.149(2)	0.650(1)	4.3(7)
O5	0.767(2)	0.117(3)	0.914(1)	10(1)
O6	0.819(2)	0.093(2)	0.561(1)	9(1)
O7	0.822(2)	0.034(2)	0.820(1)	4.9(8)
O8	0.683(2)	0.087(2)	0.8171(9)	4.3(7)
O9	0.910(2)	0.073(2)	0.714(1)	6.6(8)
O10	0.592(2)	0.060(2)	0.703(1)	8(1)
O11	0.766(2)	0.226(2)	0.763(1)	6.4(9)
O12	0.743(2)	−0.093(2)	0.756(1)	4.8(7)
N5	0.851(3)	0.250(3)	0.628(2)	8(1)
N6	0.639(4)	−0.086(4)	0.627(2)	12(2)
N7	0.594(2)	−0.045(3)	0.841(1)	8(1)
N9	0.917(2)	0.167(3)	0.847(2)	7(1)
C21	0.713(4)	−0.125(4)	0.642(2)	8(2)
C22	0.600(3)	0.108(3)	0.828(2)	7(2)
C23	0.564(4)	0.044(5)	0.855(3)	14(2)
C24	0.957(3)	0.096(4)	0.824(2)	7(2)
C25	0.543(3)	−0.209(3)	0.647(2)	8(2)
C26	0.65(1)	−0.13(1)	0.914(6)	17(6)
C27	0.952(4)	0.171(5)	0.894(3)	13(2)
C28	0.756(4)	0.089(4)	0.485(2)	9(2)
C29	0.706(3)	0.241(4)	0.638(2)	8(2)
C30	0.641(4)	−0.102(4)	0.581(2)	11(2)
C31	0.792(3)	−0.077(3)	0.632(1)	5(1)
C32	0.768(6)	0.296(5)	0.623(3)	16(3)
C33	0.941(5)	0.370(6)	0.590(3)	20(3)
C35	0.921(4)	0.252(5)	0.926(3)	15(3)
C36	0.751(4)	0.083(4)	0.541(2)	9(2)
C37	0.934(3)	0.245(3)	0.823(2)	7(1)
C38	0.590(6)	−0.100(6)	0.893(3)	17(3)
C39	0.908(3)	0.018(3)	0.834(2)	7(1)
C40	0.560(3)	−0.106(4)	0.648(2)	8(2)
C41	0.891(6)	0.295(6)	0.674(4)	22(4)
C42	0.763(6)	0.035(7)	0.919(3)	16(3)
C43	1.040(3)	0.264(3)	0.821(2)	8(2)
C44	0.472(8)	−0.122(8)	0.881(4)	11(4)
C45	0.546(5)	−0.077(5)	0.540(3)	16(3)
C47	0.82(2)	0.06(2)	1.06(1)	
C48	0.928(4)	0.255(5)	0.590(2)	13(2)
C1	0.962(2)	0.051(2)	0.689(1)	4(1)
C2	1.035(2)	0.009(2)	0.704(1)	10(2)
C3	1.091(2)	−0.018(2)	0.673(2)	12(2)
C4	1.072(2)	−0.002(2)	0.628(1)	9(2)
C5	0.998(2)	0.040(2)	0.6134(8)	4(1)
N1	0.943(1)	0.067(2)	0.644(1)	7(1)
C6	0.733(2)	0.280(2)	0.790(1)	4(1)
C7	0.696(2)	0.355(2)	0.7756(9)	6(1)
C8	0.668(2)	0.411(2)	0.807(1)	8(2)
C9	0.678(2)	0.391(2)	0.852(1)	8(2)
C10	0.716(2)	0.316(2)	0.8657(8)	6(1)
N2	0.744(2)	0.260(2)	0.835(1)	7(1)
C11	0.532(2)	0.095(2)	0.677(1)	6(1)
N3	0.548(1)	0.089(2)	0.633(1)	5(1)
C15	0.487(2)	0.113(2)	0.5993(8)	8(1)
C14	0.409(2)	0.143(2)	0.610(1)	9(2)
C13	0.393(2)	0.150(2)	0.654(1)	6(1)
C12	0.454(2)	0.126(2)	0.688(1)	8(2)
C16	0.773(2)	−0.157(2)	0.777(1)	7(1)
C17	0.810(2)	−0.235(2)	0.769(1)	8(2)
C18	0.838(2)	−0.286(2)	0.805(1)	5(1)
C19	0.830(2)	−0.259(2)	0.848(1)	9(2)
C20	0.793(2)	−0.182(2)	0.8558(9)	7(1)
N4	0.764(2)	−0.131(1)	0.820(1)	6(1)
F1	0.816(4)	0.050(5)	0.479(3)	16(4)
F3	0.681(4)	0.060(5)	0.469(2)	10(2)
F5	0.756(5)	0.170(3)	0.482(2)	10(2)
F7	0.691(4)	0.133(5)	0.480(3)	11(2)
F8	0.821(3)	0.104(5)	0.476(2)	8(2)
F9	0.730(5)	0.004(3)	0.478(3)	14(3)
C47	0.792(3)	0.043(3)	0.982(1)	24(1)
F4	0.733(3)	−0.004(3)	0.996(2)	24(1)
F10	0.866(3)	0.006(3)	0.990(2)	24(1)
F2	0.793(3)	0.116(2)	1.002(2)	24(1)

[a] $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j$.

copper complexes could be used as ligands to bind highly electropositive metal ions such barium and yttrium. The rational design of such anionic polynuclear copper complexes and the use of bifunctional ligands could lead to the successful syntheses of Cu_4BaCu_4, Cu_4YCu_4 or $BaCu_4YCu_4$ species with sandwich structures. Such research efforts are being conducted in our laboratory.

Magnetic Properties of Compounds 1 and 2. In both compounds **1** and **2** all copper atoms have a formal oxidation state +2 and electronic configuration $3d^9$. However, both compounds do not have any detectable ESR signals in the solid at 23 °C, an indication of the presence of magnetic exchange. In order to understand the magnetic properties of these compounds, magnetic susceptibility measurements over the temperature range 4–300 K at the field strength of 0.5 kG were performed. The data of molar susceptibility and the reciprocal of molar susceptibility for **1** and **2** are given in Figures 3 and 4, respectively. These data were corrected for diamagnetism. The plots of molar susceptibility for both compounds are quite similar. No maximum was observed for both compounds in the experimental temperature range. The plots of the reciprocal of molar susceptibility, χ^{-1}, for both compounds are not linear over the entire temperature range. The χ^{-1} data of **1** are linear at 4–120 K and obey the Curie law with a nearly zero intercept at the temperature axis. A curvature appears at about 125 K. The χ^{-1} data at 125–300 K are essentially linear and obey the Curie–Weiss law with a negative intercept at the temperature axis, an indication of antiferromagnetism.[14] **1** has a magnetic moment of 4.61 μ_B at 295 K and 3.61 μ_B at 4.66 K. The plot of magnetic moment μ vs T (Figure 5) shows that magnetic moment of **1** slowly decreases with the decrease of temperature, another indication of the presence of weak antiferromagnetic coupling. Similar behavior was also observed for compound **2**. The χ^{-1} data of **2** are nearly linear at above 100 K with a negative intercept at the temperature axis. Significant curvature appears below 100 K. The low-temperature data are also nearly linear with a negative intercept at the temperature axis. The plot of magnetic moments μ vs T of **2** (Figure 6) shows that the magnetic moment of **2** is temperature-dependent. It decreases gradually with the decrease of temperature. A sharp decrease appears below about 60 K. **2** has a magnetic moment of 4.45 μ_B at 297 K and a magnetic moment of 1.79 μ_B at 5 K. From the data, it is apparent that the magnetic moment of **2** decreases much faster with the decrease of temperature than that of **1**. This implies that the antiferromagnetic coupling in **2** is probably stronger than that in **1**. The magnetic susceptibility data shown here were reproducible for samples from different batches of syntheses. These samples were analytically pure as indicated by the elemental analysis results. Although a small percentage of paramagnetic impurity may be present in the sample, we believe that their contributions to the total susceptibility is not significant. The susceptibility data of both compounds suggest that these compounds have a singlet ground state and the gap between the singlet and triplet state is small.

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[14] Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1977.

Table V. Selected Bond Distances (Å) and Angles (deg) for Compound **2**[a]

	Distances		
Ba–O2	2.87(3)	Ba–O4	2.81(3)
Ba–O7	2.83(3)	Ba–O8	2.84(3)
Ba–O9	2.65(3)	Ba–O10	2.62(3)
Ba–O11	2.61(3)	Ba–O12	2.72(3)
Cu1–O1	2.24(4)	Cu1–O2	1.94(3)
Cu1–O4	2.01(3)	Cu1–N6	2.12(6)
Cu1–N3	1.95(3)	Cu2–O3	2.22(5)
Cu2–O7	1.95(3)	Cu2–O8	1.88(3)
Cu2–N7	2.06(4)	Cu2–N4	1.91(3)
Cu3–O2	2.00(3)	Cu3–O4	1.92(3)
Cu3–N5	2.16(5)	Cu3–N1	1.90(2)
Cu4–O7	1.99(3)	Cu4–O8	2.03(3)
Cu4–N9	2.03(4)	Cu4–N2	1.94(3)
Cu3–O6	2.28(4)	Cu4–O5	2.35(4)
O1–C36	1.26(8)	O6–C36	1.21(7)
O3–C42	1.1(1)	O5–C42	1.3(1)
	Angles		
O2–Ba–O4	49.4(9)	O2–Ba–O7	134.1(8)
O2–Ba–O8	158.8(8)	O2–Ba–O9	65.7(9)
O2–Ba–O10	81.6(9)	O2–Ba–O11	129(1)
O2–Ba–O12	83.9(9)	O4–Ba–O7	161.3(8)
O4–Ba–O8	136.7(8)	O4–Ba–O9	82.6(9)
O4–Ba–O10	69.2(9)	O4–Ba–O11	84.5(9)
O4–Ba–O12	129.1(8)	O7–Ba–O8	49.1(8)
O7–Ba–O9	84.1(9)	O7–Ba–O10	127.3(9)
O7–Ba–O11	82.6(9)	O7–Ba–O12	65.6(8)
O8–Ba–O9	130.1(8)	O8–Ba–O10	83.7(9)
O8–Ba–O11	69.6(9)	O8–Ba–O12	80.3(8)
O9–Ba–O10	146(1)	O9–Ba–O11	91(1)
O9–Ba–O12	96.8(9)	O10–Ba–O11	104(1)
O10–Ba–O12	87.4(9)	O11–Ba–O12	146.1(9)
O1–Cu1–O2	100(1)	O1–Cu1–O4	93(1)
O1–Cu1–N6	105(2)	O1–Cu1–N3	103(1)
O2–Cu1–O4	74(1)	O2–Cu1–N6	81(2)
O2–Cu1–N3	156(1)	O4–Cu1–N6	152(2)
O4–Cu1–N3	96(1)	N6–Cu1–N3	101(2)
O3–Cu2–O7	96(1)	O3–Cu2–O8	108(2)
O3–Cu2–N7	89(2)	O3–Cu2–N4	97(2)
O7–Cu2–O8	76(1)	O7–Cu2–N7	161(2)
O7–Cu2–N4	92(1)	O8–Cu2–N7	85(1)
O8–Cu2–N4	153(2)	N7–Cu2–N4	106(1)
O2–Cu3–O4	75(1)	O2–Cu3–N5	158(2)
O2–Cu3–N1	94(1)	O4–Cu3–N5	83(2)
O4–Cu3–N1	158(1)	N5–Cu3–N1	107(1)
O7–Cu4–O8	72(1)	O7–Cu4–N9	84(1)
O7–Cu4–N2	156(1)	O8–Cu4–N9	154(2)
O8–Cu4–N2	96(1)	N9–Cu4–N2	104(1)
Ba–O2–Cu1	89(1)	Ba–O2–Cu3	88(1)
Ba–O4–Cu1	90(1)	Ba–O4–Cu3	91(1)
Ba–O7–Cu2	90(1)	Ba–O7–Cu4	90(1)
Ba–O8–Cu2	91(1)	Ba–O8–Cu4	89(1)
Cu1–O2–Cu3	97(1)	Cu1–O4–Cu3	98(1)
Cu2–O7–Cu4	97(1)	Cu2–O8–Cu4	98(1)
O1–C36–O6	128(6)	O3–C42–O5	151(10)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

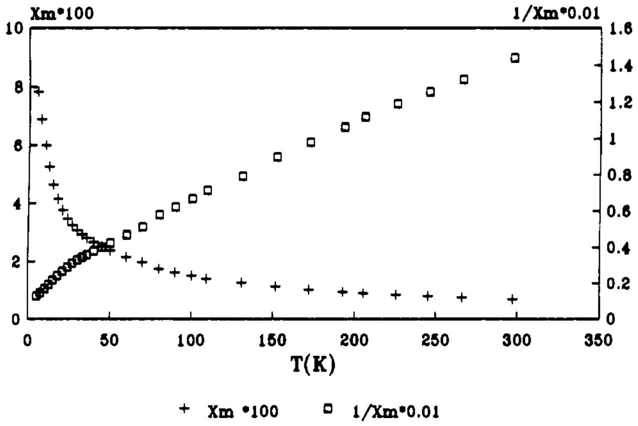

Figure 3. Data of molar susceptibility and the reciprocal of molar susceptibility of **1**.

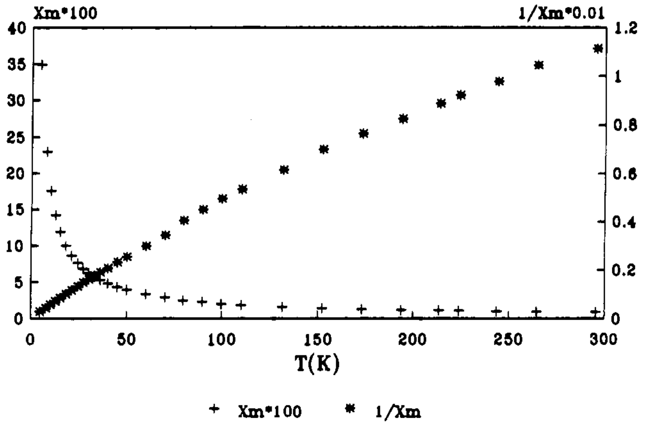

Figure 4. Data of molar susceptibility and the reciprocal of molar susceptibility of **2**.

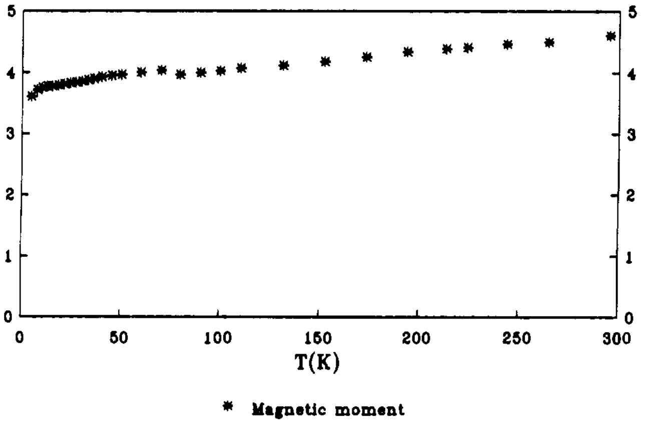

Figure 5. Plot of magnetic moment vs temperature for **1**.

Magnetic behavior of dimeric copper(II) complexes have been studied extensively previously.[6,13c] Dimeric copper(II) complexes with two oxygen bridges such dialkoxo and dihydroxo complexes typically have a singlet ground state. The electron spin exchange is usually dominated by antiferromagnetism. However, it has been demonstrated previously that the energy gap between the singlet and triplet state is very sensitive to the Cu–O–Cu angle and the Cu–Cu distance in the alkoxo and hydroxo copper(II) dimers.[6b] In the case of dihydroxo compounds a linear relationship between the Cu–O–Cu angle, the Cu–Cu distance and the $-2j$ value has been observed. The $-2j$ value in dihydroxo copper(II) complexes increases with the increase of the Cu–O–Cu angle and the Cu–Cu distances. For example, in the compound[13c] $[Cu(bipy)OH]_2(NO_3)_2$ the Cu–O–Cu angle and Cu–Cu distance are 95.6(1)° and 2.847 Å, respectively. The $-2j$ value for this compound is -172 cm^{-1}. In the compound[13c] $[Cu(tmeen)OH)]_2$ (tmeen = *N,N,N′,N′*-tetramethylethylenediamine) the Cu–O–Cu angle and Cu–Cu distance are 104.1(2)° and 3.000(4) Å, respectively. The observed $-2j$ value of this compound is 509 cm^{-1}. Although such a linear relationship is not obvious for alkoxo copper(II) dimers due to the complication of the R group bonded to the oxygen atom, a linear relationship between the Cu–O–Cu angle and the $-2j$ value has been observed for the Cu_2(dialkylamino)ethanolato)$_2X_2$ complexes (X = halogen or NCO), where the $-2j$ value increases with the increase of the Cu–O–Cu angle.[13c] The averaged Cu–O–Cu angles in **1** and **2** are 94.0 and 97.5°, respectively. The averaged Cu–Cu distances in **1** and **2** are 2.92 and 2.95 Å, respectively. They are between the extreme cases observed for the (dialkylamino)ethanolato complexes. The fact that the antiferromagnetic coupling in **2** appears stronger than that in **1** could be related to the relatively larger Cu–O–Cu angle and Cu–Cu distance of **2**, since it is in agreement with the

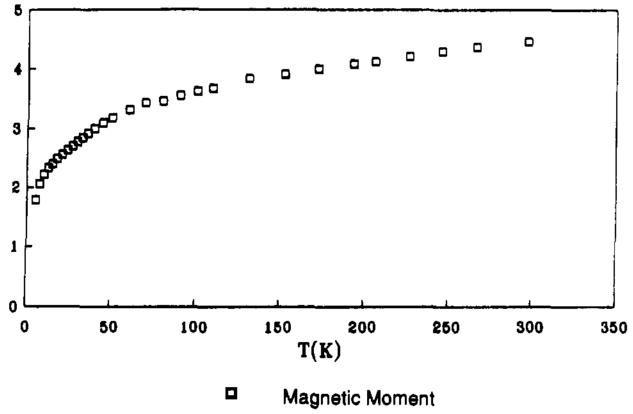

Figure 6. Plot of magnetic moment vs temperature for **2**.

observed trend in the (dialkylamino)ethanolato and dihydroxo copper(II) dimer complexes. Preliminary fitting on the data using a simple dimer model indicated that the $-2j$ values of both compounds are on the order of 10 cm^{-1}. The g value obtained from the fitting is about 3.0. The unrealistic large g value implies that a better theoretical model which includes the interaction between the two copper dimers is needed, even though the Cu–Cu separation between dimers is more than 6 Å. Such effort will be undertaken by our group.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, hydrogen parameters, anisotropic thermal parameters, bond lengths, and bond angles, in addition to an ORTEP diagram for the entire molecule of **1** and an ORTEP diagram for the disordered THF solvent molecule in **1** (28 pages). Ordering information is given on any current masthead page.