trans angle of 130.9°. This is in reasonable agreement with the result found here.

The molecular EPR $g$ values can be related to the d electron energy levels through the simple relationships[10]

$$g_z = g_0 - r_z[8\lambda/\Delta E_2] \qquad \Delta E_2 = {}^2A_2 - {}^2A_1$$
$$g_y = g_0 - r_y[2\lambda/\Delta E_3] \qquad \Delta E_3 = {}^2B_1 - {}^2A_1$$
$$g_x = g_0 - r_z[2\lambda/\Delta E_4] \qquad \Delta E_4 = {}^2B_2 - {}^2A_1$$

where $\lambda$ is the spin–orbit coupling parameter for the Cu(II) ion and the $r_i$ values are so-called reduction factors. They represent the effect of delocalization of the d electrons into the ligand orbitals. The energy level assignments were made so as to give as uniform values as possible for the reduction factors. This leads to the energy level scheme illustrated in Figure 6.

A summary of the spectral and the EPR data is presented in Table IV. The difference between $g_x$ and $g_y$ confirms the presence of a rhombic distortion as expected from the crystallographic data. This is the consequence of the substantial splitting (2360 cm$^{-1}$) between the $^2B_1$ and $^2B_2$ levels. This is not surprising in light of the nearly 0.1-Å difference between the Cu–Br(1) and Cu–Br(2) bond lengths, as well as the 17° difference in the respective *trans*-Br–Cu–Br angles. The supposition that the $^2B_1$ level (unpaired electron in a $d_{yz}$-type orbital) lies higher in energy than the $^2B_2$ level (a $d_{xz}$-type orbital) is based upon the fact that the Cu–Br(2) distance is shorter than the Cu–Br(1) distance.

The $g$ values are substantially smaller than those observed for $[CuCl_4]^{2-}$ anions with similar trans angles (cf. Gaura et al.[12]). The reduction factors are also smaller than those normally observed for copper(II) chloride complexes. These small values for the reduction factor are related to the large ligand spin–orbit coupling constants for the Br atoms and to the presence of low-lying ligand → metal charge-transfer levels. Both lead to a reduction of the deviations of $g$ values from the free electron value.[13] The lack of resolvable hyperfine structure even in the single-crystal EPR spectra of $(Ph_3AsOH)_2[CuBr_4]$ indicates the presence of the significant dipolar interaction between $[CuBr_4]^{2-}$ anions.

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**Registry No.** $(Ph_3AsOH)_2[CuBr_4]$, 139312-27-9; $[Cu(Ph_3AsO)_4][CuBr_4]$, 139312-26-8.

**Supplementary Material Available:** Tables of data collection and refinement parameters, hydrogen atom positions, and anisotropic thermal parameters and a packing diagram (4 pages); a table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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# Two New Barium–Copper–Ethylene Glycol Complexes: Synthesis and Structure of $BaCu(C_2H_6O_2)_n(C_2H_4O_2)_2$ ($n$ = 3, 6)

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Two crystalline barium–copper–ethylene glycol complexes have been isolated and structurally characterized by single-crystal X-ray diffraction. The solution-phase complex has also been investigated as a molecular precursor for use in sol–gel synthesis of high-temperature superconductors. The first crystalline form has the formula $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$ (**1**) and has been isolated directly from ethylene glycol solutions of the barium–copper salt. Crystallographic data for **1** are as follows: monoclinic space group *Cc* (No. 9), $a$ = 12.103 (6) Å, $b$ = 13.527 (3) Å, $c$ = 17.091 (8) Å, $\beta$ = 93.17 (2)°, $V$ = 2793.8 Å$^3$, $Z$ = 4, $R$ = 0.030. In this molecule, copper is coordinated to the four oxygens of two ethylene glycolate ligands in a nearly square planar geometry. Barium is coordinated by three bidentate ethylene glycol molecules and three monodentate ethylene glycol molecules; the 9-fold coordination resembles a trigonal prism with each rectangular face capped. Copper and barium moieties do not share any ethylene glycol or glycolate oxygens; they are bound by hydrogen bonding to form linear chains. The second crystal type has formula $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$ (**2**). It was prepared via crystallization of the mixed-metal alkoxide from an ethylene glycol/methyl ethyl ketone solution. Crystallographic data for **2** are as follows: monoclinic space group $P2_1/n$ (No. 14), $a$ = 12.127 (4) Å, $b$ = 11.913 (1) Å, $c$ = 12.540 (4) Å, $\beta$ = 102.47 (1)°, $V$ = 1768.9 Å$^3$, $Z$ = 4, $R$ = 0.025. As for **1**, the copper is coordinated to four oxygen atoms of two ethylene glycolate ligands in a nearly square planar arrangement. Barium is 8-coordinate in a distorted cubic geometry. It is coordinated to three bidentate ethylene glycol molecules and shares two of the oxygen atoms bound to the copper (one from each coordinated ethylene glycol) to form a discrete molecular barium–copper complex.

## Introduction

Alkoxides of yttrium, barium, and copper have recently attracted interest as molecular precursors for the sol–gel synthesis of new high-temperature superconductors, such as $YBa_2Cu_3O_{7-\delta}$.[2-8] Sol–gel synthetic routes to high-temperature superconductors offer many potential advantages over conventional solid-state reactions, including lower processing temperatures, high homogeneity and purity, and the ability to fabricate the intermediate viscous sol into a variety of forms, including thin films or fibers.

The alkoxide sol–gel synthetic route is a multistep process which begins with a solution-phase mixture of metal alkoxides in a nonaqueous solvent. The metal alkoxide solution is hydrolyzed to form a colloidal sol or an oxide gel (depending on the conditions of hydrolysis) which can subsequently be dried and fired at relatively low temperatures to form crystalline oxides. The first step

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in understanding the sol–gel process is to fully characterize the molecular alkoxide precursors—these are the building blocks which are ultimately linked together to form the gel. However, very few yttrium, barium, or copper alkoxide precursors have been structurally characterized,[9–16] and only three bimetallic alkoxide complexes involving these metals have been isolated and structurally characterized.[17–19]

In addition to limitations arising from poorly characterized alkoxides, the sol–gel synthesis of $YBa_2Cu_3O_{7-\delta}$ has been hindered by the insolubility of simple copper(II) alkoxides in common organic solvents. Many previously reported sol–gel syntheses of this compound have utilized soluble nonalkoxide sources of copper, such as copper acetylacetonate or copper carboxylates. These nonalkoxide copper complexes do not undergo hydrolysis reactions at a significant rate, and so the resulting sol or gel may be inhomogeneous with respect to mixing of copper with barium and yttrium.

We have been actively investigating diols and alkoxyalkoxides (ether alkoxides) of copper as soluble hydrolyzable copper sources for the sol–gel synthesis of $YBa_2Cu_3O_{7-\delta}$. While our work has been in progress, several groups have reported soluble alkoxyalkoxides of copper and their use in sol–gel synthesis.[2,5,20,21] In general, the alkoxyalkoxides of copper are not soluble or are only sparingly soluble in the parent alcohol, but they can be complexed by the barium salt of the same alkoxyalcohol to form complexes which are quite soluble in the parent alcohol. We have found the same holds true for diols. The copper salt of ethylene glycol is only sparingly soluble in ethylene glycol, but addition of the barium salt solubilizes the copper salts in a 1:1 molar ratio. Here we report the isolation and structural characterization of two crystalline forms of a barium–copper–ethylene glycol complex, $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$ and $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$. We also report preliminary results pertaining to the use of the soluble barium–copper–ethylene glycol complex in the sol–gel synthesis of $YBa_2Cu_3O_{7-\delta}$.

## Experimental Section

**General Procedures.** All reactions were performed under a nitrogen atmosphere, either in a drybox or on a dual manifold vacuum/nitrogen line using inert atmosphere techniques. Anhydrous methanol was purchased from Aldrich and used directly from the septum-sealed bottles. Ethylene glycol was dried over the sodium alkoxide, and methyl ethyl ketone was distilled off $CaSO_4$. $Y(NO_3)_3{\cdot}6H_2O$ and Ba granules were purchased from Aesar and used as received.

The $Cu(OMe)_2$ alkoxide used in the synthesis of the copper–ethylene glycol salt was prepared by the reaction of lithium methoxide with anhydrous copper(II) chloride (Morton Thiokol). A chloride-free source of copper(II) methoxide was found to be critical to the success of the preparation of the copper–ethylene glycol salt and the subsequent bimetallic copper–barium–ethylene glycol complex. Chloride-free copper(II) methoxide was prepared as described previously,[22] with the following exceptions. A 3-fold excess of LiOMe in methanol was added to anhydrous $CuCl_2$ and allowed to react with stirring for several hours. The insoluble $Cu(OMe)_2$ was removed by centrifugation, and reacted again with a 3-fold excess of LiOMe to ensure complete reaction. The $Cu(OMe)_2$ product was washed repeatedly with dry methanol to remove excess LiOMe and the LiCl byproduct, until no trace of chloride could be detected in the wash solution. Although three washing cycles gave a negative chloride test for $Cu(OCH_3)_2$ using a saturated $AgNO_3$ solution, a fourth wash was needed to eliminate the Cu–Cl stretches in the IR spectrum, indicating the sensitive nature of this method for detecting chloride impurities. The Cu–Cl IR stretches are visible as a single broad peak in the 700–800-$cm^{-1}$ region for chloride-contaminated $Cu(OCH_3)_2$ samples, but are resolved as two peaks at 821 and 770 $cm^{-1}$ for $Cu(OCH_3)Cl$. Finally, the chloride-free product was then vacuum dried and ground to a fine powder for use.

**Preparation of Soluble $BaCu(OR)_x$ Complexes ($R = CH_2CH_2OH$).** The copper–ethylene glycol complex was prepared by the alcoholysis reaction of 0.377 g of $Cu(OCH_3)_2$ in 50 mL of ethylene glycol. After being stirred for 15 h without heat, the reaction mixture was distilled at ~50 °C under reduced pressure to remove approximately 10 mL of ethylene glycol, along with the methanol liberated in the alcoholysis reaction. (Higher distillation temperatures resulted in formation of copper metal.) The resulting insoluble copper–ethylene glycol salt formed a turquoise suspension in ethylene glycol.

The barium–ethylene glycol salt was prepared by direct reaction of 0.4122 g of barium granules with 20 mL of ethylene glycol to yield a clear 0.15 M solution. Slow addition of all of the barium ethylene glycolate solution directly to a suspension of the copper ethylene glycolate salt as prepared above (40 mL) yielded a transparent blue 0.05 M solution of a 1:1 barium–copper complex within 10 min. Complexation and solubilization of one copper per barium appears to be the upper limit for this system.

**Isolation of $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$ (1).** Deep blue crystals of **1** were grown directly from 0.05 M solutions of the barium–copper complex in ethylene glycol. Concentrating the complex by rotary evaporation gave crystal yields up to 78%. Crystallization does not occur when the barium–copper complex concentration is less than 0.03 M, and these solutions are stable for several months under a nitrogen atmosphere. However, crystals of **1** isolated from solution decompose slowly due to loss of coordinated ethylene glycol. These crystals were found to be soluble only in ethylene glycol, precluding effective NMR analysis. The melting point of this compound was determined to be ~140 °C, above which rapid decomposition occurred. Anal. Calcd for $C_{16}H_{44}O_{16}BaCu$: C, 27.72; H, 6.39; Ba, 19.81; Cu, 9.16. Found: C, 27.88; H, 6.21; Ba, 19.90; Cu, 9.35.

**Isolation of $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$ (2).** Crystals of **2** were isolated from dilute (<0.03 M) solutions of the barium–copper complex layered with methyl ethyl ketone (MEK). These crystals, which grew near the MEK/ethylene glycol interface, were found to have the formula **2** from single-crystal X-ray crystallography. These crystals were also found to be soluble only in the parent alcohol. Because crystals of **1** also grew in the ethylene glycol-rich regions at the bottom of the layered solutions, macroscopic quantities of collected crystals from these solutions were mixtures of **1** and **2**, and it was not possible to make accurate yield calculations or to obtain quantities of pure **2** sufficient for elemental analysis.

**Preparation of $YBa_2Cu_3O_{7-\delta}$ from Ethylene Glycol Solutions.** Precursor solutions containing yttrium, barium, and copper in 1:3:3 ratios were prepared by adding the soluble nitrate salt $Y(NO_3)_3{\cdot}6H_2O$ to 0.05 M solutions of the barium–copper complex. (A 1:2:3 Y:Ba:Cu solution could not be prepared because of the fixed 1:1 Ba:Cu stoichiometry of the barium–copper complex.) The yttrium–ethylene glycol salt was not used because it is insoluble in ethylene glycol. Further hydrolysis was achieved by the addition of 5 mL of a 1:5 water–ethylene glycol solution to 40 mL of the yttrium, barium, and copper solution. The resulting sol was stirred for 72 h open to the air. During this time the sol thickened somewhat and the color changed from blue to green.

Following hydrolysis the sol was dried by rotary evaporation to produce an intimately mixed precursor powder. The powder was loaded into alumina boats and fired at 200 °C under $N_2$ for 24 h to remove organics which otherwise would react to form $BaCO_3$ above 250 °C. The resulting black powder was then fired to 950 °C (2.5 °C/min) using a 20% $O_2$, 80% $N_2$ gas mixture (oxygen was found to be necessary to prevent Cu metal formation) and annealed under oxygen at 550 °C for 5 h to produce the superconducting sample.

**Single-Crystal X-ray Diffraction Studies.** Information on the single-crystal X-ray data collection and structural refinement of $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$ (**1**) and $BaCu(C_2H_6O_2)_2(C_2H_4O_2)_2$ (**2**) is given in Table I. Twenty-five intense diffraction maxima were measured and used to obtain the cell parameters and orientation matrix. The data were treated for Lorentz and polarization effects and corrected for absorption. Data for **1** were averaged in *m* symmetry and data for **2** were averaged in 2/*m* symmetry. Structure solution was initiated using a Patterson-function

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**Table I.** Summary of X-ray Diffraction Data for $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$ and $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$

| | $BaCu(C_2H_6O_2)_6$-$(C_2H_4O_2)_2$ | $BaCu(C_2H_6O_2)_3$-$(C_2H_4O_2)_2$ |
|---|---|---|
| cryst syst | monoclinic | monoclinic |
| space group | *Cc* (No. 9) | $P2_1/n$ (No. 14) |
| *a*, Å | 12.103 (6) | 12.127 (4) |
| *b*, Å | 13.527 (3) | 11.913 (1) |
| *c*, Å | 17.091 (8) | 12.540 (4) |
| *β*, deg | 93.17 (2) | 102.47 (1) |
| temp, °C | -70 | -70 |
| *V*, $Å^3$ | 2793.8 | 1768.9 |
| *Z* | 4 | 4 |
| fw | 693.39 | 507.19 |
| $d_{calcd}$, $g/cm^3$ | 1.648 | 1.904 |
| *μ*(Mo), $cm^{-1}$ | 22.27 | 34.60 |
| radiation (graphite monochromator) | Mo K*α* | Mo K*α* |
| no. of data collcd | 8353 | 10723 |
| no. of unique data ($I > 3.0\sigma(I)$) | 3118 | 2879 |
| no. of params varied | 305 | 200 |
| $R^a$ | 0.030 (0.033)[b] | 0.025 |
| $R_w{}^a$ | 0.028 (0.032)[b] | 0.024 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, and weights used in calculating $R_w$ are proportional to $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. [b] Numbers in parentheses are for the refinement of the enantiomorph.

**Table II.** Positional and Equivalent Isotropic Thermal Parameters[a] for $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$

| atom | *x* | *y* | *z* | $B_{eq}$, $Å^2$ |
|---|---|---|---|---|
| Ba | 1.02391 (1) | 0.70067 (2) | 0.25073 (0) | 1.84 (1) |
| Cu | 0.86891 (6) | 0.68147 (4) | −0.05924 (4) | 1.85 (2) |
| O(1) | 0.8879 (3) | 0.7827 (3) | −0.1373 (2) | 2.3 (1) |
| O(2) | 0.9894 (3) | 0.7426 (3) | −0.0005 (3) | 2.4 (1) |
| O(3) | 0.7525 (4) | 0.6164 (3) | −0.1202 (3) | 2.5 (1) |
| O(4) | 0.8570 (3) | 0.5765 (3) | 0.0159 (2) | 2.5 (1) |
| O(5) | 1.2293 (3) | 0.6052 (3) | 0.3062 (3) | 2.3 (1) |
| O(6) | 1.0288 (3) | 0.5030 (3) | 0.2936 (3) | 3.1 (1) |
| O(7) | 0.8454 (4) | 0.6201 (4) | 0.1623 (3) | 3.3 (1) |
| O(8) | 0.8095 (4) | 0.7800 (4) | 0.2642 (3) | 3.6 (1) |
| O(9) | 1.0440 (5) | 0.8480 (5) | 0.3680 (4) | 4.7 (2) |
| O(10) | 0.9554 (8) | 0.6718 (4) | 0.4091 (4) | 7.4 (3) |
| O(11) | 1.0965 (4) | 0.6414 (3) | 0.1075 (3) | 2.7 (1) |
| O(12) | 1.0289 (4) | 0.4613 (4) | 0.0184 (3) | 4.3 (1) |
| O(13) | 0.9674 (4) | 0.8383 (4) | 0.1313 (3) | 2.8 (1) |
| O(14) | 0.8425 (4) | 0.9701 (4) | 0.2180 (3) | 3.9 (1) |
| O(15) | 1.2024 (3) | 0.8258 (4) | 0.2378 (3) | 2.7 (1) |
| O(16) | 1.4432 (3) | 0.8262 (3) | 0.2416 (3) | 2.7 (1) |
| C(1) | 0.9708 (5) | 0.8511 (4) | −0.1100 (4) | 2.7 (2) |
| C(2) | 1.0510 (5) | 0.7981 (5) | −0.0528 (4) | 2.6 (1) |
| C(3) | 0.7564 (5) | 0.5148 (4) | −0.0977 (4) | 2.7 (2) |
| C(4) | 0.7708 (5) | 0.5108 (5) | −0.0096 (4) | 2.9 (2) |
| C(5) | 1.1980 (5) | 0.5421 (5) | 0.3667 (4) | 3.5 (2) |
| C(6) | 1.1227 (6) | 0.4605 (5) | 0.3352 (5) | 3.6 (2) |
| C(7) | 0.7436 (7) | 0.6653 (11) | 0.1703 (8) | 9.6 (5) |
| C(8) | 0.7267 (7) | 0.7266 (8) | 0.2235 (10) | 10.0 (5) |
| C(9) | 0.9999 (9) | 0.8310 (11) | 0.4429 (7) | 9.0 (4) |
| C(10) | 0.9280 (16) | 0.7584 (9) | 0.4463 (8) | 10.7 (6) |
| C(11) | 1.1686 (6) | 0.5667 (5) | 0.0811 (4) | 3.6 (2) |
| C(12) | 1.1145 (7) | 0.4679 (5) | 0.0771 (4) | 3.9 (2) |
| C(13) | 0.9736 (6) | 0.9435 (4) | 0.1228 (4) | 3.1 (2) |
| C(14) | 0.9525 (6) | 0.9929 (5) | 0.1984 (5) | 3.5 (2) |
| C(15) | 1.2656 (6) | 0.8555 (5) | 0.1731 (4) | 3.0 (2) |
| C(16) | 1.3750 (6) | 0.8046 (5) | 0.1741 (4) | 3.4 (2) |

[a] $B_{eq} = {}^4/_3\sum_{i=1}^3\sum_{j=1}^3 (a_i \cdot a_j)\beta_{ij}$. Anisotropic thermal parameters and hydrogen atom positions are available as supplementary material.

**Table III.** Positional and Equivalent Isotropic Thermal Parameters[a] for $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$

| atom | *x* | *y* | *z* | $B_{eq}$, $Å^2$ |
|---|---|---|---|---|
| Ba | 0.27742 (2) | 0.02174 (2) | 0.00804 (2) | 1.88 (1) |
| Cu | 0.42875 (4) | 0.21785 (4) | 0.20626 (4) | 1.75 (1) |
| O(1) | 0.4276 (2) | 0.0557 (2) | 0.2040 (2) | 2.1 (1) |
| O(2) | 0.4515 (2) | 0.2123 (2) | 0.3616 (2) | 2.1 (1) |
| O(3) | 0.3895 (2) | 0.2213 (2) | 0.0494 (2) | 2.1 (1) |
| O(4) | 0.4387 (2) | 0.3786 (2) | 0.2047 (2) | 2.4 (1) |
| O(5) | 0.1097 (3) | 0.1784 (3) | −0.0026 (2) | 3.2 (1) |
| O(6) | 0.1332 (3) | 0.0187 (3) | 0.1597 (3) | 3.4 (1) |
| O(7) | 0.3794 (3) | 0.0340 (3) | −0.1715 (2) | 3.7 (1) |
| O(8) | 0.1529 (2) | 0.0699 (3) | −0.2049 (3) | 3.8 (1) |
| O(9) | 0.4174 (2) | −0.1645 (3) | 0.0032 (2) | 3.2 (1) |
| O(10) | 0.2152 (3) | −0.1926 (3) | 0.0657 (3) | 3.9 (1) |
| C(1) | 0.4103 (3) | 0.0200 (4) | 0.3072 (3) | 2.4 (1) |
| C(2) | 0.4704 (4) | 0.0999 (3) | 0.3960 (3) | 2.5 (1) |
| C(3) | 0.3510 (4) | 0.3325 (3) | 0.0197 (3) | 2.7 (1) |
| C(4) | 0.4230 (4) | 0.4156 (3) | 0.0958 (4) | 3.0 (1) |
| C(5) | 0.0763 (4) | 0.2006 (4) | 0.0971 (4) | 3.1 (1) |
| C(6) | 0.0411 (4) | 0.0951 (4) | 0.1418 (4) | 3.0 (1) |
| C(7) | 0.3216 (5) | 0.0855 (6) | −0.2689 (5) | 5.5 (2) |
| C(8) | 0.2180 (4) | 0.1381 (6) | −0.2559 (5) | 5.8 (2) |
| C(9) | 0.4097 (4) | −0.2359 (4) | 0.0919 (4) | 3.6 (1) |
| C(10) | 0.2943 (4) | −0.2822 (4) | 0.0773 (4) | 3.2 (1) |

[a] $B_{eq} = {}^4/_3\sum_{i=1}^3\sum_{j=1}^3 (a_i \cdot a_j)\beta_{ij}$. Anisotropic thermal parameters and hydrogen atom positions are available as supplementary material.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) for $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$,[a] $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$,[a] and $Ba_2Cu_2(OR)_4(acac)_4 \cdot 2HOR$ ($R = CH_2CH_2OCH_3$)[b]

| $BaCu(C_2H_6O_2)_6$-$(C_2H_4O_2)_2$ | | $BaCu(C_2H_6O_2)_3$-$(C_2H_4O_2)_2$ | | $Ba_2Cu_2(OR)_4$-$(acac)_4 \cdot 2HOR$ | |
|---|---|---|---|---|---|
| Ba–O(5) | 2.913 (4) | Ba–O(1) | 2.754 (3) | Ba–O(1) | 2.668 (3) |
| Ba–O(6) | 2.773 (4) | Ba–O(3) | 2.732 (3) | Ba–O(2) | 2.727 (3) |
| Ba–O(7) | 2.789 (5) | Ba–O(5) | 2.743 (3) | Ba–O(3) | 2.820 (3) |
| Ba–O(8) | 2.829 (5) | Ba–O(6) | 2.848 (3) | Ba–O(3′) | 2.749 (3) |
| Ba–O(9) | 2.828 (6) | Ba–O(7) | 2.797 (3) | Ba–O(4) | 2.897 (4) |
| Ba–O(10) | 2.901 (7) | Ba–O(8) | 2.829 (3) | Ba–O(5) | 2.778 (3) |
| Ba–O(11) | 2.764 (5) | Ba–O(9) | 2.802 (3) | Ba–O(5′) | 2.833 (3) |
| Ba–O(13) | 2.819 (5) | Ba–O(10) | 2.801 (3) | Ba–O(6) | 2.982 (4) |
| Ba–O(15) | 2.764 (4) | | | Ba–O(9) | 2.922 (4) |
| Cu–O(1) | 1.934 (4) | Cu–O(1) | 1.931 (3) | Cu–O(1) | 2.590 (3) |
| Cu–O(2) | 1.912 (4) | Cu–O(2) | 1.909 (3) | Cu–O(3) | 1.929 (3) |
| Cu–O(3) | 1.918 (4) | Cu–O(3) | 1.922 (3) | Cu–O(5) | 1.933 (3) |
| Cu–O(4) | 1.925 (4) | Cu–O(4) | 1.920 (3) | Cu–O(7) | 1.938 (3) |
| | | | | Cu–O(8) | 1.948 (3) |
| O(1)–Cu–O(2) | 86.5 (2) | O(1)–Cu–O(2) | 88.8 (1) | | |
| O(1)–Cu–O(3) | 93.6 (2) | O(1)–Cu–O(3) | 90.4 (1) | | |
| O(2)–Cu–O(4) | 92.9 (2) | O(2)–Cu–O(4) | 92.8 (1) | | |
| O(3)–Cu–O(4) | 86.8 (2) | O(3)–Cu–O(4) | 88.3 (1) | | |

[a] This work. [b] From ref 17.

peak-search algorithm developed by J. C. Calabrese.[23] Full-matrix least-squares refinements on all non-hydrogen positional and anisotropic thermal parameters were performed. All hydrogen atoms for **2** were located from Fourier difference maps. However, for **1** the positions of hydrogen atoms bonded to carbon were calculated for $sp^3$ carbon, and only 3 out of 12 OH hydrogen atoms were located. Hydrogen-bonding interactions for the latter compound were determined from close oxygen–oxygen contacts under 2.7 Å. Positional and equivalent isotropic thermal parameters are given in Tables II and III. Important interatomic distances and angles are given in Table IV.

## Results and Discussion

**Structural Description of $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$ (2).** This molecule may be described as composed of a $Cu(C_2H_4O_2)_2{}^{2-}$ unit connected to a $Ba(C_2H_6O_2)_3{}^{2+}$ unit by the sharing of two oxygen atoms, O(1) and O(3), as shown in Figure 1. All ethylene glycol or glycolate ligands are bidentate to copper or barium. Copper is nearly square planar in its coordination to oxygen with Cu–O bond lengths ranging from 1.91 to 1.93 Å. These distances compare quite well with the sum of ionic radii for $Cu^{2+}$ and $O^{2-}$, 1.92 Å.[24] Barium is bonded to eight oxygen atoms in a distorted cubic environment. Six of these oxygen atoms are from three

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(23) All X-ray crystallographic calculations were performed on a Digital Equipment Corp. VAX 8800 computer using a system of programs developed by J. C. Calabrese.

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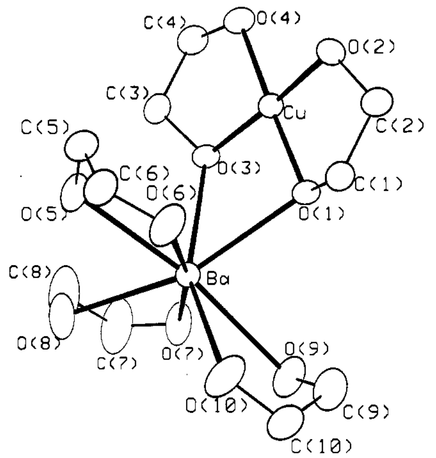

**Figure 1.** ORTEP[25] drawing of the $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$ molecule showing the oxygen-sharing $CuO_4$ and $BaO_8$ units.

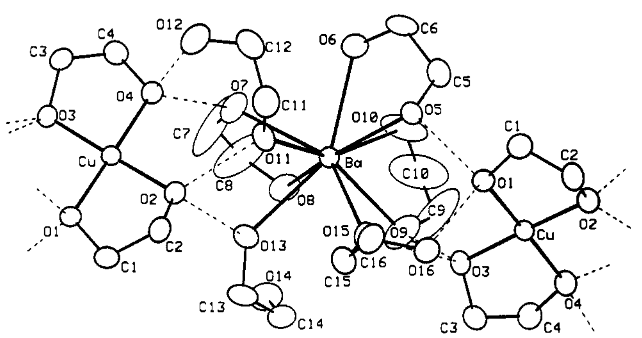

**Figure 2.** ORTEP[25] drawing showing a hydrogen-bonded chain of $Cu(C_2H_4O_2)_2^{2-}$ and $Ba(C_2H_6O_2)_6^{2+}$ units in $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$.

bidentate ethylene glycol ligands, and the remaining two are the shared oxygen atoms from a $CuO_4$ moiety. The average Ba–O distance of 2.79 Å is close in value to the sum of the ionic radii,[24] 2.77 Å.

Each $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$ molecule is hydrogen-bonded to five adjacent molecules to build the three-dimensional structure. All intermolecular hydrogen-bonding occurs between the OH atoms of Ba-bonded bidentate ethylene glycol ligands and the O atoms of Cu-bonded ethylene glycolate ligands. Hydrogen-bonding to the oxygen atoms around copper, O(1)–O(4), completes a tetrahedral coordination: O(1) and O(3) form bonds to one copper, one barium, one carbon, and one hydrogen (H bond); O(2) and O(4) bond to one copper, one carbon and two hydrogens (H bond).

**Structural Description of $BaCu(C_2H_6O_2)_6(C_2H_4O_2)_2$ (1).** In contrast to $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$, the structure of this ethylene glycol-rich compound contains discrete $Cu(C_2H_4O_2)_2^{2-}$ and $Ba(C_2H_6O_2)_6^{2+}$ units. Copper is again almost square planar in its oxygen coordination (Figure 2). Cu–O bond lengths range from 1.91 to 1.93 Å; again, these compare well with the sum of the ionic radii, 1.92 Å.[24] Barium is coordinated by nine oxygen atoms (the average Ba–O bond length is 2.82 Å): six oxygen atoms are from three bidentate ethylene glycol ligands, and the remaining three oxygen atoms come from three monodentate ethylene glycol ligands (Figure 2). The bonding environment around barium may be described as a trigonal prism of oxygen atoms with the remaining oxygen atoms capping the rectangular faces.

The Cu-containing and Ba-containing moieties are interconnected by hydrogen bonding to form chains of alternating $Cu(C_2H_4O_2)_2^{2-}$ and $Ba(C_2H_6O_2)_6^{2+}$ units. As in $BaCu(C_2H_6O_2)_3(C_2H_4O_2)_2$, these intermolecular hydrogen bonds are formed between the OH groups of the ethylene glycol ligands attached to barium and the O atoms of the ethylene glycolate ligands bonded to Cu. Hydrogen-bonding to the four oxygen atoms around copper, O(1)–O(4), creates a tetrahedral environment for each of these oxygens: each oxygen atom bonds to one copper, one carbon, and two hydrogen (H-bonded) atoms. The Cu–Ba chains are interconnected by hydrogen bonding between $Ba(C_2H_6O_2)_6^{2+}$ units.

**General Discussion.** The two crystal forms of **1** and **2** have some distinct features, such as the presence of discrete barium and copper moieties in **1** that are not present in **2**, but we have not seen evidence for two different types of solution-phase complexes. Ethylene glycol solutions of **1** and of **2** have identical EPR spectra, which are typical of $d^9$ $Cu^{2+}$ in an axial environment.

Several features of the structures of **1** and **2** are quite similar to the structure of $Ba_2Cu_2(OR)_4(acac)_4{\cdot}2HOR$ ($R = CH_2CH_2OCH_3$) recently published by Sauer et al.[17] In the dimeric barium–copper cluster structure, copper is essentially square planar, with an additional long (2.59 Å) bond to an oxygen of an acac bonded to a neighboring barium. Barium is 9-coordinate, in a distorted capped rectangular antiprism. Metal–oxygen bond distances are quite similar for all three compounds, as shown in Table IV. The similarities between the three structures may be indicative of the types of structures which are stable in solutions of soluble barium–copper–alkoxyalkoxide complexes which have so far eluded isolation and structural characterization. The prediction based on these structures would be that such complexes of alkoxyalkoxides consist of nearly square-planar copper "Lewis base" type moieties that either share bridging oxygens with or are hydrogen-bonded to solvated barium "Lewis acid" type 8- or 9-coordinate species.

Superconducting $YBa_2Cu_3O_{7-\delta}$ was prepared using solutions of the barium–copper–ethylene glycol complex as outlined above, and synthesis of the superconducting phase was confirmed by X-ray powder diffraction and magnetic susceptibility measurements. The X-ray powder diffraction pattern indicates the presence of some minor impurity phases ($Y_2BaCuO_5$ and $BaCuO_2$). Elemental analysis performed on the fired superconductor powder indicated a carbon impurity level of less than 0.06%. The onset of superconductivity was determined to be 90.8 K from dc magnetic susceptibility measurements. Although firing of thin films was not attempted with the sol, dip-processing the precursor solution on glass slides indicated good film adhesion. Further optimization of firing parameters to achieve greater purity of the superconducting phase was not pursued because the stoichiometry of the yttrium–barium–copper precursor solution (1:3:3 Y:Ba:Cu) does not match that of the desired product (i.e. 1:2:3 Y:Ba:Cu for $YBa_2Cu_3O_{7-\delta}$). Furthermore, the lack of an yttrium alkoxide source soluble in ethylene glycol necessitated the use of $Y(NO_3)_3{\cdot}6H_2O$. This salt obviously will not undergo hydrolysis and polycondensation, and so will not participate directly in the sol–gel polymerization of the barium–copper complex. Thus, hydrolysis of the yttrium–barium–copper precursor solution probably resulted in an inhomogeneous sol, making this system less than ideal for studies of the sol–gel synthesis of this material. Consequently, we have focused our attention on alkoxyalkoxide sol–gel systems which are not subject to these limitations. For example, yttrium alkoxyalkoxides are soluble in the parent alkoxy alcohols, and soluble barium copper alkoxyalkoxides with the desired 2:3 Ba:Cu stoichiometry can be prepared.[2]

## Summary and Conclusions

Two barium–copper binary alkoxides of ethylene glycol have been isolated and structurally characterized. Both are crystallized from ethylene glycol solutions of a soluble barium–copper complex, but in the case of **2**, a cosolvent (MEK) is present during crystallization. In both structures, copper is complexed by two bidentate ethylene glycolate ligands in a nearly square planar geometry. In **1**, the 9-coordinate barium complex is discrete and is bound to the copper ethylene glycolate moiety through hydrogen-bonding. In **2**, barium shares two oxygens of the copper ethylene glycolate moiety and in addition is coordinated by three bidentate ethylene glycol molecules to give an overall distorted cubic coordination.

Solution phase precursors for sol–gel synthesis of $YBa_2Cu_3O_{7-\delta}$ were produced using solutions of the barium–copper complex with a soluble nitrate salt, $Y(NO_3)_3{\cdot}6H_2O$. Hydrolysis and subsequent firing gave predominantly superconducting material, with small amounts of impurity phases. This synthetic route to superconducting $YBa_2Cu_3O_{7-\delta}$ was not pursued further because of two limitations: (1) the inability to solubilize the copper ethylene glycol salt via complexation with barium in the desired 3:2 Cu:Ba stoichiometry, and (2) the lack of a suitable yttrium alkoxide which is soluble in ethylene glycol.

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**Supplementary Material Available:** Tables giving full crystallographic information, positional parameters, anisotropic thermal parameters, hydrogen atom parameters, and interatomic distances and angles for the two compounds (15 pages); listings of observed and calculated structure factors for the two compounds (16 pages). Ordering information is given on any current masthead page.

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# Synthesis and Structure of $Ba_6Hf_5S_{16}$ and $Ba_5Hf_4S_{13}$: The $n = 5$ and 4 Members of the $A_{n+1}B_nX_{3n+1}$ Ruddlesden–Popper Phases

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Two new Ba/Hf/S phases of formula $Ba_5Hf_4S_{13}$ and $Ba_6Hf_5S_{16}$ have been prepared from BaS, Hf, and elemental sulfur at 1050 °C in $BaCl_2$ flux reactions. The compounds are the $n = 4$ and 5 members of the $Ba_{n+1}Hf_nS_{3n+1}$ series which are rare examples of Ruddlesden–Popper sulfides. The compounds contain perovskite blocks extending infinitely in *a* and *b* with double BaS layers and a 0 $^1/_2$ 0 shift every *n* layers in *c*. The Hf–S distances in both compounds average 2.48 (2) Å with regular $HfS_6$ octahedra. The 12-coordinate Ba atoms display Ba–S distances averaging 3.49 (2) Å with the Ba–S distances for the 9-coordinate Ba atoms in the double BaS layers ranging between 3.08 and 3.52 Å. Crystal data for $Ba_5Hf_4S_{13}$ (20 °C): $a = 6.977$ (1) Å, $b = 7.006$ (2) Å, and $c = 45.280$ (5) Å, $Z = 4$, $D_{calc} = 5.45$ g/cm$^3$, orthorhombic, space group *Fmmm*. Crystal data for $Ba_6Hf_5S_{16}$ (20 °C): $a = 7.002$ (1) Å, $b = 6.987$ (2) Å, and $c = 55.205$ (6) Å, $Z = 4$, $D_{calc} = 5.48$ g/cm$^3$, orthorhombic, space group *Fmmm*.

## Introduction

The oxides of general formula $A_{n+1}B_nO_{3n+1}$, first identified in the Sr/Ti/O system by Ruddlesden and Popper,[1] represent an important class of solid-state materials. The most well-known structures in the series are the $n = 1$ members, which have the $K_2NiF_4$ structure type, and the $n = \infty$ compounds, which are the $ABO_3$ perovskites.[2] Intermediate phases with $n = 2, 3$ are known for the group 4 oxides,[1,3,4] the strontium and europium vanadium oxides,[5-7] and the $La_{2-x}Sr_xCaCu_2O_6$ copper oxides[8] to name a few.[9] The copper-oxide phases are high-temperature superconductors with transition temperatures as high as 60 K.[10] In an attempt to extend the Ruddlesden–Popper phases into the metal sulfides, we[11] and others[12] have recently reported the preparation of the $Ba_2MS_4$ ($n = 1$; M = Hf and Zr) and $Ba_3Zr_2S_7$ ($n = 2$) phases. We report here the synthesis, structure, and properties of $Ba_5Hf_4S_{13}$ ($n = 4$) and $Ba_6Hf_5S_{16}$ ($n = 5$) that, together with $BaHfS_3$ ($n = \infty$),[13] are the third and fourth Ba–Hf–S phases characterized to date. To our knowledge, these compounds are the first $A_{n+1}B_nX_{3n+1}$ phase with $n > 3$ to be structurally characterized (excluding $n = \infty$).

## Experimental Section

**General Procedures.** All sample manipulations were conducted in a Vacuum Atmospheres Co. drybox system. All reagents were purchased from Cerac Inorganics and used as received. Powder X-ray data were collected on a modified Phillips XRG 2000 diffractometer interfaced with a Radix databox and MDI software system.

**Synthesis of $Ba_5Hf_4S_{13}$ and $Ba_6Hf_5S_{16}$.** BaS, Hf powder, and elemental sulfur in a 3:2:4 ratio, respectively, were ground and loaded into a silica ampule along with 25% $BaCl_2$ by weight. The tube was sealed under vacuum and placed inside a larger silica tube which was also sealed under vacuum. The material was heated to 1050 °C at 0.3 °C/min and fired at 1050 °C for an additional 20 h. The sample was then quickly cooled to room temperature ($^1/_2$ h.). The resulting material was washed with water to dissolve the $BaCl_2$ flux, leaving two types of well-formed crystals: orange-brown plates and darker brown parallelepipeds. A lighter orange-brown powder primarily composed of elemental sulfur and some BaS was also present. The single crystals accounted for ca. 70% of the reaction mixture. The synthesis is reproducible.

**Table I.** Summary of Crystallographic Data for $Ba_5Hf_4S_{13}$ and $Ba_6Hf_5S_{16}$

| | $Ba_5Hf_4S_{13}$ | $Ba_6Hf_5S_{16}$ |
|---|---|---|
| fw | 1817.49 | 2229.51 |
| space group | *Fmmm* | *Fmmm* |
| cell dimens at 20 °C | | |
| *a*, Å | 6.977 (1) | 7.002 (1) |
| *b*, Å | 7.006 (2) | 6.987 (2) |
| *c*, Å | 42.280 (5) | 55.205 (6) |
| *V*, Å$^3$ | 2213 (1) | 2700 (1) |
| *Z* | 4 | 4 |
| linear abs coeff, cm$^{-1}$ | 284.35 | 287.53 |
| rel. transm factors: max; min | 1.0; 0.59 | 1.0; 0.09 |
| no. of unique data | 757 | 541 |
| data with $I > 3.0\sigma(I)$ | 686 | 469 |
| no. of variables | 42 | 49 |
| shift/esd final cycle | 0.01 | 0.27 |
| $R(F_o)^a$ | 0.054 | 0.079 |
| $R_w(F_o)^a$ | 0.085 | 0.130 |
| density, g/cm$^3$ | 5.45 | 5.48 |

[a] $R(F_o) = \sum|F_o - F_c|/\sum F_o$; $R_w(F_o) = (\sum w|F_o - F_c|^2/\sum wF_o^2)^{1/2}$.

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