

Figure 4. Perspective view of the coordination geometry of Pb^{2+} in compound **5**, which includes the "outer-sphere" ligands. Starred atoms are from neighboring molecules.

most distant equatorial ligands. The angle parameters also show the resultant distortion from a TBP geometry (in parentheses): angles $\text{S}_1\text{-Pb-O}_2$ 140.2 (180°), $\text{O}_1\text{-Pb-S}_2$ 89.8 (120°), $\text{S}_1\text{-Pb-S}_2$ 96.3 (90°), and $\text{O}_1\text{-Pb-O}_2$ 74.3 (90°); dihedral angles $(\text{S}_1, \text{S}_2, \text{O}_1)/(\text{O}_1, \text{O}_2, \text{S}_2)$ 43.1 (53.1°), $(\text{Pb}, \text{S}_1, \text{S}_2)/(\text{Pb}, \text{O}_1, \text{O}_2)$ 51.7 (60°), and $(\text{Pb}, \text{O}_1, \text{S}_2)/(\text{Pb}, \text{O}_2, \text{S}_1)$ 87.4 (90°). As in **2**, the lone pair causes the axial-axial angle to decrease nearly 40° from

linearity. The larger sulfur atoms show a resultant S-Pb-S inter-ring bond angle that is greater than the corresponding O-Pb-O angle. However, as measured by the angle between the equatorial plane ($\text{Pb}, \text{O}_1, \text{S}_2$) and the axial plane ($\text{Pb}, \text{S}_1, \text{O}_2$) of 87.4° , there is less of a twist from a C_{2v} intermediate geometry than in **2**, although the thiohydroxamate groups still span the axial and equatorial positions. There is also a difference between **5** and **2** in the outer-sphere coordination. As shown in Figure 4, there is additional weak coordination from atoms S and O_1 and O_2 of neighboring molecules.

Given their solubility, it is probable that these complexes are monomeric species in solution and may exist in both geometries described for **2** and **5** (ignoring the weak Pb-O and Pb-S bonds), which would explain the change in the UV/vis spectra of these complexes with change in polarity of the solvent. This may also explain the presence of two singlets for the NCH_3 protons in the NMR spectra of these complexes in polar solvents. If so, this represents a surprisingly slow rate of isomerization.

In conclusion, lead complexes with mono(thiohydroxamate) and bis(thiohydroxamate) ligands have been prepared and characterized. The structures of compounds **2** and **5**, determined by X-ray crystallography, will serve as models for the design of lead-chelating agents incorporating thiohydroxamate groups.

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Supplementary Material Available: Listings of general temperature factor expressions (B 's) and root-mean-square amplitudes of vibration (Tables S2, S3, S5, and S6) (4 pages); observed and calculated structure factors (Tables S1 and S4) (27 pages). Ordering information is given on any current masthead page.

Isolation and Structural Characterization of the Copper-Barium-Alkoxide Cluster $\text{Ba}_2\text{Cu}_2(\text{OR})_4(\text{acac})_4 \cdot 2\text{HOR}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{OCH}_3$) from Precursor Solutions to $\text{YBa}_2\text{Cu}_3\text{O}_7$ Thin Films

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Abstract: Attempts to identify intermediates in a solution route to thin films of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ have led to the isolation of the mixed-metal cluster $\text{Ba}_2\text{Cu}_2(\text{OR})_4(\text{acac})_4 \cdot 2\text{HOR}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{OCH}_3$) (**1**). This compound, which is the first example of a molecular barium-copper cluster, was isolated from the reaction of the copper dimer $[(\text{acac})\text{Cu}(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$ with barium 2-methoxyethoxide, the first stage in the preparation of the thin-film precursor solution. Crystallographic data for **1** are as follows: formula = $\text{Ba}_2\text{Cu}_2\text{O}_{20}\text{C}_{38}\text{H}_{72}$, $\text{FW} = 1250.5$ g/mol, $D_x = 1.57$ g/cm³, space group = $P\bar{1}$, $a = 10.797$ (3) Å, $b = 11.269$ (1) Å, $c = 12.109$ (1) Å, $\alpha = 106.18$ (1) $^\circ$, $\beta = 100.93$ (2) $^\circ$, $\gamma = 102.98$ (2) $^\circ$, $Z = 1$, $R = 0.031$ for 4059 reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 50^\circ$, $\mu = 23.5$ cm⁻¹, $\lambda(\text{Mo K}\alpha_1) = 0.70930$, $F(000) = 630$. Data were collected at 23 $^\circ\text{C}$. The metals are arranged in a rhomboid with triply bridging alkoxide oxygens above and below the two triangular planes defined by two barium atoms and one copper atom. Each metal atom is also bound to an acac ligand, and the barium is further coordinated by the methoxy oxygen of the triply bridging alkoxides and a 2-methoxyethanol. Thin films prepared from this route showed superconducting transition temperatures of 85 K, only small amounts of impurity phases by X-ray powder diffraction, and ≤ 0.1 atom % carbon as determined by nuclear reaction analysis.

Thin films of the new high-temperature superconductors, e.g., $\text{REBa}_2\text{Cu}_3\text{O}_7$, are needed for a range of technological applications. While several methods such as laser ablation, chemical vapor deposition, and electron beam evaporation are available for de-

positing these ceramic materials as thin films,¹⁻⁵ they require specialized equipment or facilities. In contrast, routes based on

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soluble precursors, which can be spun or dipped into films, appear attractive for a variety of reasons: low expense, the ability to coat large unusually shaped objects, and high homogeneity and purity.⁶ While a large number of reports on solution routes to superconducting thin films of YBa₂Cu₃O₇ have appeared in the recent literature, few describe attempts to isolate and characterize intermediates. Studies have shown that the properties of the rare earth superconductors are highly sensitive to processing conditions; metal nonstoichiometry and some grain boundary impurities are highly detrimental to the critical temperature (*T*_c) and the critical current (*J*_c) of the materials.⁷ Clearly, if solution techniques are to be of value as a source of these materials, better understanding and control of the chemistry will be necessary. To achieve this end, we have focused our research on two areas: the isolation and characterization of intermediates from proven solution routes to superconducting materials, and the design and synthesis of discrete molecular precursors for the superconductors (e.g., a YBa₂Cu₃ cluster). Ideally, these two approaches overlap, and intermediates isolated from the solution routes could be used directly or will suggest synthetic routes to more sophisticated molecular clusters that could be useful precursors to superconductors.

Chemical control of the species present in precursor solutions will enhance our ability to dictate the homogeneity, stoichiometry, and, as a result, the quality of the superconducting materials produced. At the extreme end of this control is the synthesis of a YBa₂Cu₃ cluster precursor with the metal stoichiometry and structural relationships found in the YBa₂Cu₃O₇ superconductor. The benefits of such a material could be many. For high-temperature-processing purposes, a precursor of the desired metal composition would have homogeneous metal mixing on the atomic scale, which may allow conversion to the desired product at lower temperatures. In the case of the rare earth superconductors, if the synthesis temperature is substantially lowered, the synthesis and oxygen anneal could be accomplished in a single processing step. A lower synthesis temperature could also lead to the discovery of new compounds that are thermodynamically unstable at the higher temperature (≥900 °C) of the traditional ceramic preparation using oxide starting materials. In addition, clusters that exhibit significant structural analogies with the target material could serve as a molecular models for theoretical studies.

Herein, we describe our initial attempts to map the chemistry of a solution route to thin films of YBa₂Cu₃O₇. This work was begun by examining a route reported by Fahrenholtz et al.⁸ which uses a dimeric copper acetylacetonate alkoxide with barium and yttrium alkoxides as soluble precursors. To gain a better understanding of this solution process, films of the high-*T*_c superconductor were prepared and characterized by a range of techniques. Attempts were made to isolate intermediates at key stages of the precursor solution preparation. One result of these studies was the isolation and structural characterization of the title compound, Ba₂Cu₂(acac)₄(OR)₄·2HOR (R = CH₂CH₂OCH₃) (**1**), from solutions in the first stage of the thin-film preparation. To our knowledge this cluster represents the first example of a discrete molecular barium-copper complex.

Experimental Section

General Procedures. All reactions were carried out in an inert-atmosphere (helium) drybox. Alcohols used as solvents or reactants were dried

Table I. X-ray Data

chem formula	C ₃₈ H ₇₂ O ₂₀ Cu ₂ Ba ₂
crystal system	triclinic
space group	P $\bar{1}$
<i>a</i> , Å	10.797 (3)
<i>b</i> , Å	11.269 (1)
<i>c</i> , Å	12.109 (1)
α , deg	106.18 (1)
β , deg	100.93 (2)
γ , deg	102.98 (2)
<i>V</i> , Å ³	1327.8
<i>Z</i>	1
<i>D</i> _x , g/cm ³	1.57
λ (Mo K α ₁)	0.70930
temp, °C	23
crystal color	bright blue
crystal dimens, mm	0.2 × 0.2 × 0.3
μ , cm ⁻¹	23.5
abs corr type	ϕ × sphere
sphere rad, mm	0.1
transmission	0.42, 0.32
av peak width (ω , deg)	0.8
scan range ($2\theta_{\max}$, deg)	50
scan type	θ - 2θ
scan rate	variable
target $\sigma(I)/I$	0.015
max counting time, s	90
index range	<i>h</i> , ± <i>k</i> , ± <i>l</i> , <i>h</i> = 0-12, <i>k</i> = ±13, <i>l</i> = ±14
total no. collected	5025
no. of unique reflns	4680
<i>R</i> _F equiv reflns, %	1.2
no. of <i>I</i> ≥ 2 $\sigma(I)$	4059
secondary extinction coeff (10 ⁻⁶)	5.3 (6)
no. of refined parameters	281
<i>R</i> _F obsd reflns, %	3.1
<i>R</i> _{wF} obsd reflns, %	4.8

over the sodium alkoxide and stored in an inert-atmosphere drybox. The copper dimers [(acac)Cu(OR)]₂, where R is CH₃ or CH₂CH₂OCH₃, were prepared as previously reported.^{8,9} Copper acetylacetonate and barium metal were purchased from Aldrich and used as received. Precursor solutions to superconducting thin films of YBa₂Cu₃O₇ were prepared as described by Fahrenholtz and co-workers.⁸ The resulting blue solution was spun onto single-crystal SrTiO₃(100) substrates (1500-2000 rpm) three coats at a time, with a prefire at 250 °C between each set of coats to remove residual organics. After ~10 sets of coats were applied to the substrate, the films were heated rapidly to 920 °C in argon, placed under an O₂ atmosphere, and held at 920 °C for 1 h. Films were annealed at 420 °C in oxygen for 5 h.

Preparation of Ba₂Cu₂(acac)₄(OR)₄·2HOR (R = CH₂CH₂OCH₃) (1**).**
(a) From a Solution with a 4:2 Cu:Ba Metal Ratio. The Ba₂Cu₂ cluster was isolated from the reaction of [(acac)Cu(OCH₂CH₂OCH₃)]₂ (0.150 g, 0.315 mmol) with barium 2-methoxyethoxide (0.315 mL of a 1 M solution) in 5 mL of 2-methoxyethanol as described by Fahrenholtz and co-workers for the initial step in thin-film preparation. After reaction, the precipitate of Cu(OCH₂CH₂OCH₃)₂ was filtered off, giving a dark blue solution. This solution was concentrated under flowing nitrogen to give dark blue crystals suitable for X-ray analysis.

(b) From a Solution with a 5:2 Cu:Ba Ratio. This preparation is identical with that of procedure a, with the exception that 0.187 g (0.388 mmol) of [Cu(acac)(OCH₂CH₂OCH₃)]₂ was used with the same amount of barium 2-methoxyethoxide.

Preparation of (acac)Ba(OR) (R = CH₂CH₂OCH₃) (2**).** The (acac)Ba(OR) was prepared by dissolving 0.178 g (1.30 mmol) of Ba metal in 10 mL of 2-methoxyethanol to give Ba(OCH₂CH₂OCH₃)₂. The addition of 0.130 g (0.133 mL, 1.30 mmol) of reagent grade 2,4-pentanedione gave **2** with the formation of 1 equiv of 2-methoxyethanol. This solution was stirred for 30 min prior to use.

Isolation of **1 from the Reaction of **2** with [(acac)Cu(OR)]₂.** Four milliliters of the solution of **2** (0.519 mmol) in 2-methoxyethanol was added to 0.187 g (0.388 mmol) of [Cu(acac)(OCH₂CH₂OCH₃)]₂ in 7 mL of 2-methoxyethanol. The solution was allowed to stir for 2 h. No precipitate of Cu(OCH₂CH₂OCH₃)₂ was observed during this time. The solution was slowly evaporated to dryness under a nitrogen stream, giving dark blue crystals of **1**.

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Table II. Fractional Coordinates and Thermal Parameters^a

atom	x	y	z	B_{eq} , Å ²	atom	x	y	z	B_{eq} , Å ²
Ba(1)	-0.02732 (2)	-0.13601 (3)	0.06087 (2)	3.4	O(1)	0.1716 (3)	-0.0849 (3)	0.2519 (3)	4.8
C(1)	0.2088 (5)	-0.1356 (5)	0.3270 (4)	4.5	C(2)	0.8652 (5)	0.2465 (5)	0.6596 (4)	5.3
C(3)	0.0040 (5)	-0.3206 (5)	0.2733 (4)	5.1	O(2)	-0.0609 (3)	-0.3068 (4)	0.1827 (3)	5.3
C(4)	-0.0637 (7)	-0.4313 (7)	0.3108 (6)	7.8	C(5)	0.3480 (6)	-0.0703 (7)	0.4088 (6)	6.5
Cu(1)	0.24914 (5)	0.13152 (6)	0.21439 (5)	3.4	O(3)	0.2017 (3)	0.0313 (3)	0.0469 (2)	3.7
C(6)	0.2907 (5)	-0.0226 (5)	-0.0059 (4)	4.4	C(7)	0.3056 (5)	-0.1411 (5)	0.0266 (5)	5.1
O(4)	0.1803 (4)	-0.2356 (3)	-0.0125 (3)	5.6	C(8)	0.1879 (8)	-0.3516 (6)	0.0184 (7)	9.0
O(5)	0.0665 (3)	0.1297 (3)	0.1753 (2)	3.8	C(9)	0.0097 (5)	0.1886 (5)	0.2631 (4)	4.4
C(10)	-0.0242 (5)	0.1079 (5)	0.3412 (4)	4.9	O(6)	-0.1216 (4)	-0.0116 (4)	0.2672 (3)	5.5
C(11)	-0.1706 (8)	-0.0840 (7)	0.3398 (6)	8.8	O(7)	0.2836 (3)	0.2337 (4)	0.3808 (3)	4.8
C(12)	0.3951 (5)	0.2918 (5)	0.4565 (4)	4.2	C(13)	0.5155 (5)	0.2948 (5)	0.4339 (4)	4.7
C(14)	0.5317 (5)	0.2299 (5)	0.3244 (4)	4.9	O(8)	0.4375 (3)	0.1599 (4)	0.2315 (3)	5.0
C(15)	0.6698 (6)	0.2381 (9)	0.3077 (6)	8.2	C(16)	0.6115 (7)	0.6385 (7)	0.4172 (5)	7.0
O(9)	-0.2392 (4)	-0.3695 (4)	-0.0896 (4)	5.9	C(17)	0.7785 (8)	0.5598 (6)	0.8003 (6)	7.7
C(18)	0.6253 (6)	0.6040 (6)	0.9085 (6)	6.8	C(19)	0.6176 (6)	0.6650 (7)	0.0354 (7)	8.0
O(10)	0.6658 (4)	0.6051 (4)	0.1140 (4)	6.9					

^a $B_{\text{eq}} = 100 \times (U_{11} + U_{22} + U_{33})/3$; anisotropic thermal parameters are available as supplementary material.

Table III. Selected Distances (Å) and Angles (Deg)

Distances					
Ba-Ba	3.7364 (3)	Ba-O(3')	2.749 (3)	Cu-O(1)	2.590 (3)
Ba-Cu	3.495 (1)	Ba-O(4)	2.897 (4)	Cu-O(3)	1.929 (3)
Ba-Cu'	3.737 (1)	Ba-O(5)	2.778 (3)	Cu-O(5)	1.933 (3)
Ba-O(1)	2.668 (3)	Ba-O(5')	2.833 (3)	Cu-O(7)	1.938 (3)
Ba-O(2)	2.727 (3)	Ba-O(6)	2.982 (4)	Cu-O(8)	1.948 (3)
Ba-O(3)	2.820 (3)	Ba-O(9)	2.922 (4)		
Angles					
O(1)-Cu-O(3)	87.09 (1)	O(3)-Cu-O(7)	175.67 (1)		
O(1)-Cu-O(5)	87.90 (1)	O(3)-Cu-O(8)	93.47 (1)		
O(1)-Cu-O(7)	93.14 (1)	O(5)-Cu-O(7)	93.85 (1)		
O(1)-Cu-O(8)	104.51 (1)	O(5)-Cu-O(8)	166.54 (1)		
O(3)-Cu-O(5)	81.82 (1)	O(7)-Cu-O(8)	90.69 (1)		

X-ray Diffraction Studies. Room-temperature data were collected by variable-speed θ - 2θ scans on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo K α radiation. Lattice and data collection parameters are given in Table I. The Los Alamos Crystal Structure Codes¹⁰ were used for all calculations. Data were corrected for absorption by using the relative intensity of a low-angle reflection measured as a function of Ψ (mapped to ϕ) multiplied by a spherical correction using a radius calculated from the average distance between the three most prominent directions of crystal development. The function minimized was $R_F = \sum \omega^2 [F_o - F_c]^2$, and weights were calculated as $\omega^2 = 4F^2/\sigma^2(I)$, where $\sigma(I) = \sigma_c(I) + (0.030I)^2$; $\sigma_c(I)$ is the error based on counting statistics. The structure was solved by using standard Patterson and difference Fourier methods and refined to the observed data ($I \geq 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.¹¹ A final Fourier difference map showed peaks that could be interpreted as hydrogen atoms, but they were not included in the final refinement, which was based on anisotropic thermal parameters for all atoms and a correction for secondary extinction (type II crystal assumed).¹² The resulting refined coordinates, distances, and angles are listed in Tables II and III. ORTEP projections with appropriate numbering schemes are presented in Figures 3 and 4.

Results and Discussion

Fahrenholtz and co-workers have described a solution method for the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films on platinum.⁸ According to the Fahrenholtz preparation, solutions with Y:Ba:Cu stoichiometries of 1:2:3 were obtained by reaction of the copper dimer $[\text{Cu}(\text{acac})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$ with barium 2-methoxyethoxide and yttrium isopropoxide in a ratio of 2:2:1. In the first stage of the preparation, the $[\text{Cu}(\text{acac})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$ was added to a 2-methoxyethanol solution of $\text{Ba}(\text{OR})_2$ ($\text{R} =$

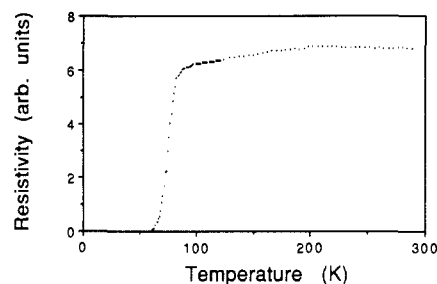
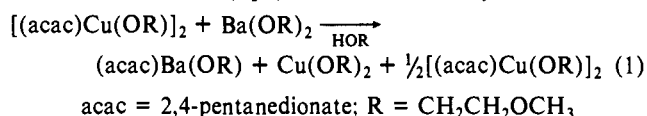


Figure 1. Resistivity (arbitrary units) vs temperature (K) plot for thin films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ on SrTiO_3 .

$\text{CH}_2\text{CH}_2\text{OCH}_3$). Insoluble copper 2-methoxyethoxide ($\text{Cu}(\text{OR})_2$) forms in this reaction (eq 1) and was removed by filtration. The



resultant solution was hydrolyzed (1–10 equiv of H_2O) and in the final step of the preparation, 1 equiv of yttrium isopropoxide ($\text{Y}(\text{O}i\text{Pr})_3$) was added. Solutions were spun onto Pt substrates, fired at 950 °C (10 min), annealed at 450 °C (10 min), and rapidly cooled to give films of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Fahrenholtz et al. report the characterization of the films by X-ray powder diffraction. Films fired in oxygen showed only small amounts of BaCO_3 and CuO impurities by X-ray diffraction and were described as generally crack-free, with some crystalline regions.

In our evaluation of solution routes to superconducting thin films, this sol-gel method met many of the criteria that we established for a solution route suitable for our investigations: readily prepared starting materials, reproducible solution chemistry and thin-film preparation, and a mostly single-phase superconducting product. We used the method reported by Fahrenholtz and co-workers to deposit films on single-crystal $\text{SrTiO}_3(100)$. Precursor solutions for these studies were prepared exactly as described by Fahrenholtz. Films were deposited by spinning multiple coats of the precursor solution onto the SrTiO_3 substrates, with pre-firing at 250 °C between successive sets of coats to remove residual organics. Superconducting films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ were obtained by heating the precursor films rapidly to 920 °C in argon or nitrogen, holding at 920 °C, and then cooling to 420 °C in flowing O_2 . This final oxygen anneal is necessary to obtain the orthorhombic superconducting phase of the material.¹³ Upon examination under a microscope, the films obtained from this procedure appeared smooth and crack-free, with no evidence of a green Y_2BaCuO_5 impurity phase. The thickness of these films was nominally 5 μm , with a surface roughness of several micrometers,

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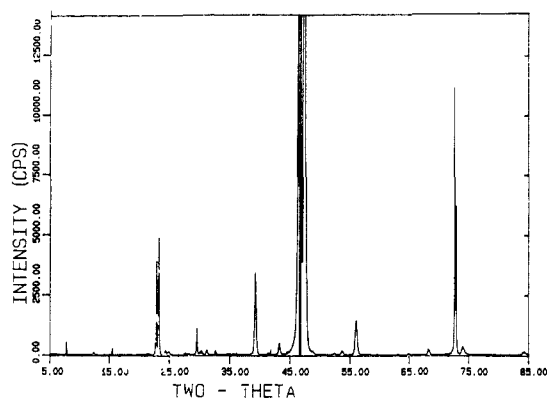


Figure 2. X-ray powder diffraction pattern of YBa₂Cu₃O₇ on SrTiO₃. The most intense peak $2\theta = 47^\circ$ is the substrate, single-crystal SrTiO₃-(100).

as determined by mechanical profilometry.

Several techniques were used to characterize the product YBa₂Cu₃O₇ films; four-point probe resistivity measurements, X-ray powder diffraction, and nuclear reaction analysis determined purity and superconducting quality. Four-point probe resistivity measurements show that the films undergo a superconducting transition at approximately 85 K and have zero resistance at 65 K. A typical plot of resistivity vs temperature for films prepared by this method is shown in Figure 1. This superconducting transition temperature is less than the optimum 93 K for bulk YBa₂Cu₃O₇ but is similar to those reported for films prepared by other solution methods.¹⁴⁻¹⁶ Both the width of the superconducting transition and the small slope of the resistance at temperatures higher than T_c suggest that the sample may be somewhat oxygen deficient. The width of the transition could also be a result of small amounts of impurities in the films. This possibility was investigated by X-ray powder diffraction.

X-ray powder diffraction shows the films to be primarily free of impurity phases, with only very small amounts of Y₂BaCuO₅ apparent in some of the films. Unlike Fahrenholtz, we did not see BaCO₃ in any of our films. Calculated lattice constants for a typical diffraction pattern from our films gave $a = 3.8205$ (5), $b = 3.8851$ (6), and $c = 11.6808$ (7) Å, within 1-2σ of those reported for bulk YBa₂Cu₃O₇.¹⁷ Alignment of the superconducting grains with the film substrate greatly enhances the current-carrying capacity of the material and as a consequence, methods that produce films with a high degree of alignment are very desirable. Diffraction studies on our films indicate at least 50% alignment of the superconducting grains. The prominent 00l reflections in the diffraction pattern (Figure 2) are manifestations of this alignment. Because this is a metal-organic route to the superconductor, we were also concerned about contamination of the films by residual carbon. The carbon content of the films, as determined by nuclear reaction analysis, ¹²C(d,p)¹³C, was <0.1 atom %.

To isolate solution intermediate(s) formed in the reaction of the copper dimer with barium alkoxide, solutions of the two were evaporated as described in the Experimental Section. Dark blue cube-shaped crystals were obtained and identified as **1** by single-crystal X-ray diffraction. This cluster is one of the few examples of a complex containing both a group II metal and copper.¹⁸⁻²⁰

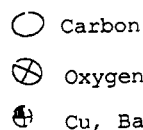
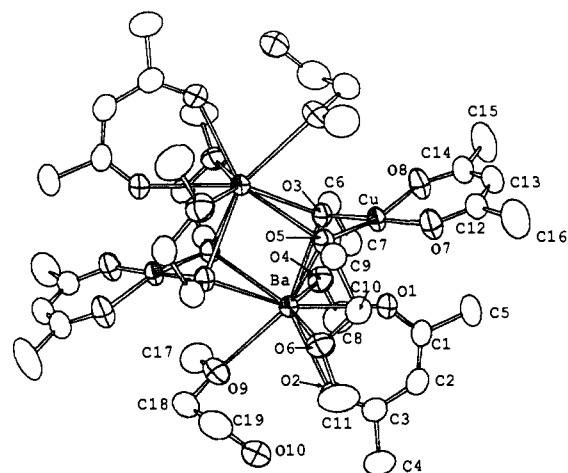


Figure 3. ORTEP representation of **1** with appropriate numbering.

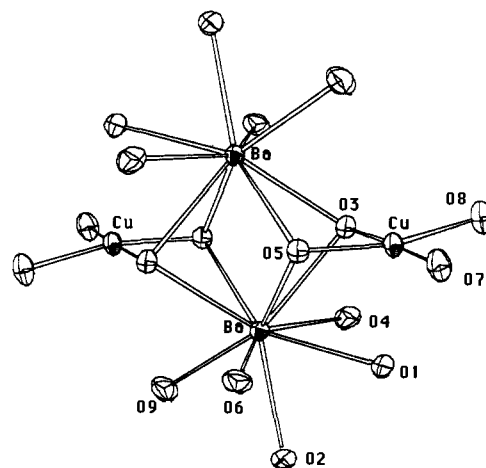


Figure 4. Metal-oxygen core of **1**.

Table IV. Comparison of Interatomic Distances (Å) for YBa₂Cu₃O₇ and Ba₂Cu₂(acac)₄(OCH₂CH₂OCH₃)₄·2HOCH₂CH₂OCH₃

YBa ₂ Cu ₃ O ₇ ¹⁷		Ba ₂ Cu ₂ cluster	
Ba-O	2.743 (2)	Ba-O(1)	2.668 (3)
Ba-O	2.897 (3)	Ba-O(2)	2.727 (3)
Ba-O	2.970 (3)	Ba-O(3)	2.820 (3)
Ba-O	2.977 (1)	Ba-O(3')	2.749 (3)
		Ba-O(4)	2.897 (4)
Cu(1)-O ^a	1.943 (3)	Ba-O(5)	2.778 (3)
Cu(1)-O ^a	1.850 (3)	Ba-O(5')	2.833 (3)
		Ba-O(6)	2.982 (4)
		Ba-O(9)	2.922 (4)
Cu(2)-O ^b	1.928 (1)	Cu-O(1)	2.590 (3)
Cu(2)-O ^b	1.962 (1)	Cu-O(3)	1.929 (3)
Cu(2)-O ^b	1.903 (3)	Cu-O(5)	1.933 (3)
		Cu-O(7)	1.938 (3)
		Cu-O(8)	1.948 (3)

^aSquare-planar copper. ^bSquare-pyramidal copper.

The structure of **1**, which lies on a crystallographic center of symmetry, is shown in Figure 3. The metals are arranged in a rhomboid with triply bridging alkoxide oxygens above and below the two triangular planes defined by the two barium atoms and

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one of the copper atoms for a total of four bridging alkoxides (see Figure 4). Each metal atom is also bound to an acac ligand. In addition, the methoxy oxygen of each of the triply bridging alkoxides is in a position to bond to barium (two to each of the barium atoms). Barium is further coordinated by the ether linkage of a neutral 2-methoxyethanol, resulting in a coordination number of 9. The resulting coordination polyhedron for barium is a distorted capped rectangular antiprism. The d^9 copper has a square-pyramidal geometry typical of Jahn–Teller distortions for Cu(II). Each copper has four shorter equatorial Cu–O distances at ~ 1.9 Å, and one long axial distance of 2.6 Å to an acac oxygen also bound to the adjacent barium.

A comparison of the bonding distances in the cluster and $\text{YBa}_2\text{Cu}_3\text{O}_7$ is given in Table IV.¹⁷ These distances demonstrate the, not unexpected, similarity in the bonding characteristics between copper and oxygen in these two materials. The square-planar CuO_4 units of **1** are also the building blocks of the Cu–O planes found in many of the high- T_c superconductors. The distorted square-pyramidal coordination geometry for copper in **1** is also found in $\text{YBa}_2\text{Cu}_3\text{O}_7$. In both compounds, the axial oxygen in the Cu coordination sphere is shared with barium. The barium coordination geometry in **1** is an irregular capped square antiprism, 9-coordinate geometry similar to that for the smaller lanthanum and strontium found in La_2CuO_4 and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. In $\text{YBa}_2\text{Cu}_3\text{O}_7$ barium is 10-coordinate in the form of a cuboctahedron which is missing two oxygen atoms trans to each other on one square capping face.

The isolation of **1** from the presumed Ba_2Cu_3 precursor solution raised the concern that the solution metal stoichiometry resulting after the precipitation of the copper 2-methoxyethoxide was not correct, that the 4:2 ratio of copper to barium did not give a final Cu:Ba stoichiometry of 3:2 in the first stage of the precursor preparation. Analysis of the metal ratios in the superconducting thin films by Rutherford backscattering spectrometry showed that the films contained roughly 25% less copper than would be required for a copper:barium ratio of 3:2. This indicates that close to 2 equiv of copper was lost as copper alkoxide in the first stage of the precursor solution preparation. Although the copper-deficient impurity phase, Y_2BaCuO_5 , was only weakly apparent in the X-ray powder patterns, the intensity of its diffraction pattern relative to the 123 material is clearly affected by the degree of orientation of the latter.

To avoid entirely the problem of copper loss via precipitation, **2** was used as the source of barium in the precursor solution preparation rather than the barium 2-methoxyethoxide. Two equivalents of **2** were reacted with 1.5 equiv of the copper dimer $[\text{Cu}(\text{acac})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$. After 2 h of stirring, a clear dark blue solution with no precipitation was obtained. The crystals isolated after evaporation of this 3:2 Cu:Ba solution were dark blue cubes, identified as **1** by comparison of cell volumes and lattice constants from single-crystal X-ray diffraction. Using the Fahrenholtz method, solutions with 3:2 Cu:Ba can be prepared if an additional equivalent of copper is added (i.e., a ratio of 5:2 rather

than 4:2 copper:barium). These solutions when concentrated under nitrogen flow also yield crystals of **1**. As suggested by Fahrenholtz et al., $(\text{acac})\text{Ba}(\text{OCH}_2\text{CH}_2\text{OCH}_3)$ appears to be an intermediate in the reaction.

Conclusions

These studies extend the solution method described by Fahrenholtz and co-workers for the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ films on Pt to SrTiO_3 substrates. We have been able to verify the production of good-quality superconducting films using this route. Rutherford backscattering measurements on the films deposited by this method indicated that more than a single equivalent of copper was lost through $\text{Cu}(\text{OR})_2$ precipitation in the initial stage of precursor solution preparation. The slightly lower superconducting transitions (85 K vs 94 K for bulk Y_{123} samples) in the films obtained from this solution method may be due to this copper deficiency. The isolation of **1** from the precursor preparation of Fahrenholtz et al. plus the observation that no precipitate of copper 2-methoxyethoxide forms in the reaction of **2** with $[\text{Cu}(\text{acac})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$ supports their proposal that **2** is an intermediate in the process.

Studies on the behavior of intermediates in this process lead us to conclude that one of the difficulties with this particular route is the inability to control metal stoichiometry in solution. Use of the identified intermediate, **2**, should allow control of the metal stoichiometry, and higher quality superconducting films could result. We plan to explore this route.

While there are structural similarities between our cluster and the solid-state target materials, which are clearly dictated by normal coordination requirements, obvious substantial differences exist. Although the syntheses of cluster complexes that are close structural analogues to the superconductors is a challenging goal, it is clear that clusters with the correct metal stoichiometry and local structural features of the oxide superconductors may well be attainable. For example, in **1** the coordination requirements for the barium atom have been completed by the ether linkage, thereby truncating the cluster. More extended clusters could possibly be prepared by using precursors with nonchelating alkoxides. We are continuing work in this area and will apply the chemical and structural information derived from these studies to the rational synthesis of precursor clusters that may model the bismuth and thallium superconductors.

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Registry No. **1**, 124153-25-9; **2**, 124153-26-0; $[(\text{acac})\text{Cu}(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$, 124153-27-1; $\text{YBa}_2\text{Cu}_3\text{O}_7$, 109064-29-1.

Supplementary Material Available: Anisotropic thermal parameters (Table Is) (1 page); structure factor amplitudes (Table IIs) (14 pages). Ordering information is given on any current masthead page.