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A Soluble Copper(II) Alkoxide for Solution-Based Syntheses of $YBa_2Cu_3O_{7-x}$

Syntheses of oxides based on hydrolysis of alkoxide precursors can have advantages over conventional methods.[1] Processing temperatures may be as much as 500 °C lower, the preparation of multinary oxides is particularly efficient, and the technique may afford gels for drawing or casting into various forms, such as fibers or films.[1] Until recently,[2] efforts to prepare cuprate–oxide superconductors from alkoxide-precursor solutions suffered from a lack of soluble copper(II) alkoxides.[3–6]

We now report the preparation of a soluble copper(II) alkoxide and its use in the hydrolytic synthesis of $YBa_2Cu_3O_{7-x}$. When our work was in progress, a similar study was published by a group from Du Pont and the University of Virginia; they prepared soluble Cu(I)–amido and Cu(II)–alkoxide precursors, and described in detail the use of a Cu(I)–amido precursor to produce submicrometer $YBa_2Cu_3O_{7-x}$ particles at very low temperatures of 650–700 °C.[2] We present results regarding the solution-phase structure of our Cu(II) precursor, homogeneous solutions obtained with it and Y(III) and Ba(II) alkoxides, the hydrated oxide obtained from hydrolysis of such solutions, and factors that influence the temperature required for converting the hydrated oxide to $YBa_2Cu_3O_{7-x}$.

The insoluble, polymeric structures of conventional copper(II) alkoxides result from extensive alkoxide bridging.[7] Decreased tendencies for bridging should improve solubility; accordingly, we sought structures containing chelating alkoxide ligands. New copper(II) alkoxides **1**–**3** were obtained as blue solids by the alcohol-exchange procedure of Mehrotra and co-workers (eq 1);[8] **3** was prepared for comparison to **1** and **2**. Complexes **1** and **3** are insoluble in a range of organic solvents.[9] In contrast, **2** is soluble in benzene, toluene, and THF, and is precipitated preparatively from benzene/hexane.[10]

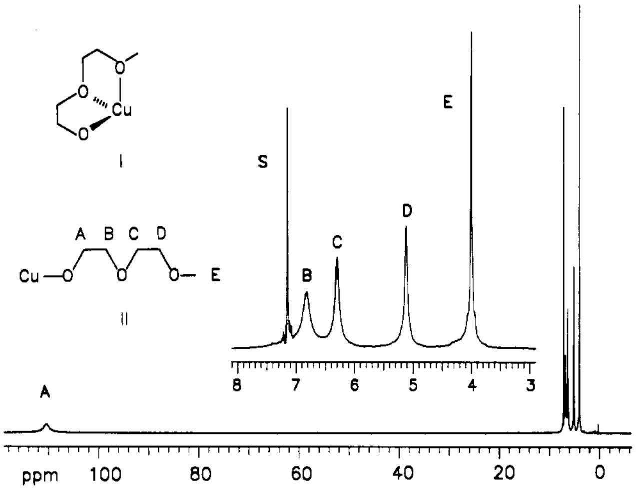

Figure 1. Room-temperature ^1H NMR spectrum of **2** in C_6D_6. An expansion of the region from δ 8.0 to δ 3.0 is inset. S marks the solvent resonance. Two limiting ligand conformations I and II are also shown; see text.

$$Cu(OMe)_2 + 2ROH \rightarrow \underset{\mathbf{1-3}}{Cu(OR)_2} + 2MeOH \qquad (1)$$

$$\begin{aligned} R = {} & CH_2CH_2OMe\ (\mathbf{1}),\ 63\% \\ & CH_2CH_2OCH_2CH_2OMe\ (\mathbf{2}),\ 93\% \\ & (CH_2)_6Me\ (\mathbf{3}),\ 68\% \end{aligned}$$

Although we have not obtained crystals of **2** suitable for X-ray crystallography, data regarding the solution-phase structure were obtained. Cryoscopic measurements in benzene indicated that **2** is oligomeric (or polymeric) conforming to $[Cu(OCH_2CH_2OCH_2CH_2OMe)_2]_n$ where $n \geq 5$. The ^1H NMR spectrum of **2**, shown in Figure 1, contains one highly shifted and broadened resonance (δ 110.4) corresponding to a single CH_2 group (A, Figure 1). The remaining resonances are only slightly shifted and broadened (B–E, Figure 1). Two limiting ligand conformations can be considered (see Figure 1); the data are most consistent with dangling conformation II for the ^1H NMR detectable ligands. For the chelating I *all* resonances should be paramagnetically shifted by Cu(II); for the dangling II the β-CH_2 group should be most strongly affected.[11] The coexistence of chelating type-I ligands (or related bridging ligands), which may

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(9) (a) Data for **1**. Anal. Calcd for $C_6H_{14}CuO_4$: C, 33.72; H, 6.60; Cu, 29.73. Found: C, 33.46; H, 6.47; Cu, 29.83. Mp: 198–200 °C dec. IR (cm^{-1}, KBr): ν_{M-O} 535 m, 480 s, 415 m. **1** is insoluble in benzene, toluene, THF, hexane, and 2-methoxyethanol. (b) Data for **3**. Anal. Calcd for $C_{14}H_{30}CuO_2$: Cu, 21.61. Found: C, 21.50. Mp: 177–179 °C dec. IR (cm^{-1}, KBr): ν_{M-O} 555 m, 495 m. **3** is insoluble in benzene, toluene, THF, and hexane.
(10) Data for **2**. Anal. Calcd for $C_{10}H_{22}CuO_6$: C, 39.80; H, 7.35; Cu, 21.05. Found: C, 39.41; H, 7.41; Cu, 20.95. Mp: 183–184 °C dec. IR (cm^{-1}, KBr): ν_{M-O} 455 s br. Magnetic moment: $\mu_{eff} = 1.18\ (7)\ \mu_B$ (in toluene, room temperature).
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have resonances broadened to invisibility, is not excluded. As in conventional copper(II) alkoxides, the oligomers of **2** are likely held together by internuclear alkoxide–oxygen bridges, but solubility is likely imparted by the presence of *some* chelating ether oxygens that reduce the extent of alkoxide bridging. The high solubility of previously reported[2] $[Cu(OCH_2CH_2OCH_2CH_2CH_2CH_3)_2]$ (one ether oxygen per ligand), and the insolubility of **3** (no ether oxygens) is consistent with this view.

Our studies of mixed-alkoxide solutions employed **2**, Ba(O-*i*-Pr)$_2$,[12] and $Y_5(O)$(O-*i*-Pr)$_{13}$.[13] Benzene or THF solutions of **2** and Ba(O-*i*-Pr)$_2$ (Ba:Cu = 2:3), or **2** and $Y_5(O)$(O-*i*-Pr)$_{13}$ (Y:Cu = 1:3) were homogeneous and blue. Addition of the third component (giving Y:Ba:Cu = 1:2:3) resulted in dark-green homogeneous solutions. NMR spectra of the mixed-alkoxide solutions (C_6D_6) were complex, and resonances for the free precursors were not present.

Hydrolysis of freshly prepared THF solutions having a total alkoxide concentration of 0.1 M (Y:Ba:Cu = 1:2:3) gave a gelatinous blue precipitate, which aged to a blue powder. Chemical analysis fit an empirical formula $YBa_2Cu_3(OH)_{13}(H_2O)_n$ (n = 0–2); carbon as residual organics was present in 1.5%.[14] The product was amorphous to X-ray powder diffraction (XRD), and crystalline grains were not detected by electron diffraction in the transmission electron microscope (TEM).[15] For comparison, the independent hydrolyses of **2**,[16] Ba(O-*i*-Pr)$_2$,[17] **2**/Ba(O-*i*-Pr)$_2$ mixtures,[18] and a **2**/$Y_5(O)$(O-*i*-Pr)$_{13}$ mixture (Y:Cu = 1:3)[19] all gave crystalline products.

Two compositionally distinct microstructures were found in TEM images: (1) lacy grains composed entirely of loosely aggregated 10–30 nm diameter particles and (2) grains similar to the first type but containing regions ca. 200 nm across with a much smoother appearance. By energy-dispersive X-ray spectroscopy (EDS),[15] the lacy grains were uniformly Cu rich (Y:Ba:Cu = 1.0:2.0:3.9), whereas the grains with smooth regions had nonuniform compositions. More of the regions analyzed in the latter were Ba rich than were Y rich; all were Cu poor. *No* regions were completely deficient in any of the three metals. Type 1 grains were more abundant than type 2 grains in the TEM specimens. Thus, the $YBa_2Cu_3(OH)_{13}(H_2O)_n$ stoichiometry above apparently represents an intimate mixture of noncrystalline phases, which does not contain expected binary or ternary hydrolysis products.

When $YBa_2Cu_3(OH)_{13}(H_2O)_n$ was fired under O_2 or air at 700–750 °C (10–15 h), XRD showed the formation of $BaCO_3$,[20] CuO,[16] $BaCuO_2$,[21] and $Y_2Cu_2O_5$[21] mixtures, which did not completely convert to $YBa_2Cu_3O_{7-x}$[22] below 900 °C. However, as in the previous study,[2] significantly lower conversion temperatures were observed by using inert atmospheres. When $YBa_2Cu_3(OH)_{13}(H_2O)_n$ was heated under a vigorous Ar or N_2 stream, some $BaCO_3$ formed below 300 °C (presumably from the residual organics) but decomposed readily at 650–700 °C with the formation of $YBa_2Cu_3O_{7-x}$. Samples heated for 10–15 h under inert atmosphere at 700 °C contained just-detectable quantities of $BaCO_3$, $BaCuO_2$, and $Y_2Cu_2O_5$, but $YBa_2Cu_3O_{7-x}$ was obtained with *no* detectable impurity phases at 750 °C (9 h). Quenching to room temperature gave tetragonal $YBa_2Cu_3O_{7-x}$, whereas samples cooled more slowly (750–400 °C in ca. 2 h) *under inert atmosphere* gave orthorhombic $YBa_2Cu_3O_{7-x}$. In cases where air was less efficiently excluded during the firing of $YBa_2Cu_3(OH)_{13}(H_2O)_n$ at 750 °C, large amounts of $BaCuO_2$ and $Y_2Cu_2O_5$ were found.

In summary, it is shown here and elsewhere[2] that syntheses based on the hydrolysis of homogeneous mixed-alkoxide solutions afford reductions of 200–250 °C in the temperature of $YBa_2Cu_3O_{7-x}$ formation. Although $BaCO_3$ decomposition may be the temperature-limiting event here, such decomposition occurs much more readily than is typical.[23] Our results suggest that O_2 may inhibit the decomposition of $BaCO_3$, and enhance the formation of $BaCuO_2$ and $Y_2Cu_2O_5$, all of which inhibit production of $YBa_2Cu_3O_{7-x}$. Work is in progress to define conditions for obtaining gels from alkoxide-precursor solutions and for subsequent conversion to fabricated superconductors.[24]

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Departments of Chemistry and Physics
Washington University
St. Louis, Missouri 63130

Subhash C. Goel[25]
Keith S. Kramer[25]
Patrick C. Gibbons[26]
William E. Buhro*,[25]

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[14] Data for $YBa_2Cu_3(OH)_{13}(H_2O)_n$. Anal. Calcd for $YBa_2Cu_3(OH)_{13}(H_2O)_1$: Ba, 34.62; Cu, 24.03; H, 1.89; C, 0.00. Found: Ba, 34.48; Cu, 24.07; H, 1.29; C, 1.49. IR (cm^{-1}, KBr): ν_{O-H} 3660–3200 s; ν_{H-O-H} 1590 m br, 1380 s br; ν_{M-O} 440 m br.

[15] JEOL 2000FX with Tracor Northern EDS instrument. Powder samples were dispersed on holey C films supported by Al grids. The EDS instrument was calibrated by measurements of single-phase orthorhombic samples with [110] twins visible in image and diffraction modes.

[16] CuO, Tenorite: JCPDS File 5-0661.

[17] γ-$Ba(OH)_2(H_2O)$: JCPDS File 24-104.

[18] 1:1 and 3:2 ratios gave products fitting empirical formulas $BaCu(OH)_4(H_2O)$ and $Ba_2Cu_3(OH)_{10}(H_2O)_2$, respectively. XRD ($d$(Å), relative intensity for the four most intense reflections). For $BaCu(OH)_4(H_2O)$: 4.38, 52%; 3.07, 95%; 3.00, 82%; 2.98, 100%. For $Ba_2Cu_3(OH)_{10}(H_2O)_2$: 5.21, 96%; 3.36, 100%; 3.28, 51%; 2.75, 36%.

[19] (a) $Ba(OH)_2(H_2O)$: JCPDS File 26-154. (b) Independent hydrolysis of $Y_5(O)$(O-*i*-Pr)$_{13}$ gave an amorphous solid.

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[24] Application of the dark green, mixed-alkoxide solution to a glass slide followed by exposure to atmospheric moisture at room temperature results in a transparent blue gel within a few minutes. The gel dries under ambient conditions to a transparent, blue, glassy film.

[25] Department of Chemistry.

[26] Department of Physics.

Observations on the Dynamics of Hydrazine Oxidation by Permanganate in Aqueous Acidic Solutions

The study of bistable and oscillatory chemical reactions, known as chemical instabilities, has been advancing rapidly in recent years.[1,2] Although early examples of such reactions were discovered accidentally, a wide variety of other chemical systems displaying nonlinear dynamic phenomena, under closed as well as open conditions, have been systematically designed within the last decade.[2,3] These recent discoveries are based on the cross-shaped phase diagram technique,[4] for which a bistable chemical system is a prerequisite. A vital but common characteristic of all known bistable and/or oscillatory systems is autocatalysis. Hence, it should be possible to design new chemical oscillators by suitable modification of a known autocatalytic reaction.[5] (It is possible that the desired modification of the chosen autocatalytic reaction may not be physically feasible). This later approach is

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