A New Chemical Precursor System to the $YBa_2Cu_3O_{7-x}$ Superconductor using Acetic Acid and 1,3-Bis(dimethylamino)propan-2-ol (bdmapH), Isolation and Characterization of a Polynuclear Copper(II) Complex $[Cu_4(OAc)_6(bdmap)_2(H_2O)_6]_n$ with a Two-dimensional Hydrogen-bonded Network

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A new chemical precursor system to the $YBa_2Cu_3O_{7-x}$ (1-2-3) superconductor using acetic acid and 1,3-bis(dimethylamino)propan-2-ol (bdmapH) has been developed, a polynuclear complex $[Cu_4(OAc)_6(bdmap)_2(H_2O)_6]_n$ with a two-dimensional network linked by hydrogen bonds has been isolated and characterized from this system.

Chemical processing of high-temperature superconductors has attracted the attention of chemists and material scientists because it provides a way to overcome some of the inherent weaknesses of ceramic superconductors and conventional processing methods such as difficulty of fabrication, poor homogeneity and low critical current.[1,2] We have been interested in using multicomponent molecular compounds as precursors because multicomponent molecular compounds with appropriate compositions and structures can not only reduce the number of variables in the synthesis and the

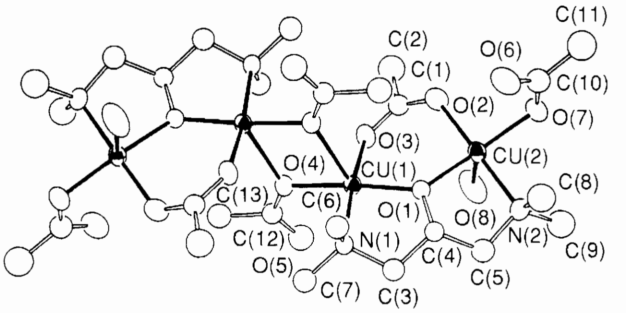

Fig. 1 The molecular structure of **1**. Selected bond distances and angles: Cu(1)–O(1) 1.912(4), Cu(1)–O(3) 1.964(4), Cu(1)–N(1) 2.064(5), Cu(1)–O(4) 1.950(4), Cu(1)–O(4′) 2.460(5), Cu(2)–O(1) 1.930(4), Cu(2)–O(2) 1.973(5), Cu(2)–N(2) 2.065(6), Cu(2)–O(7) 1.959(4), Cu(2)–O(8) 2.336(5) Å; O(1)–Cu(1)–O(4) 175.4(2), N(1)–Cu(1)–O(3) 171.1(2), O(1)–Cu(2)–O(7) 164.5(2), O(2)–Cu(2)–N(2) 179.0(2)°.

inhomogeneity of the product, but also provide the possible preferential alignment of microstructures of the material and hence increase the critical current. Precursor systems using multicomponent molecular compounds are scarce. In 1989 Rupich and coworkers reported a polynuclear complex with the composition of $Cu_3O_3Ba_2Y(OCH_2CH_2OMe)_7$, which was used directly as a precursor for the $YBa_2Cu_3O_{7-x}$ superconductor.[3] The existence of a two-dimensional network of CuO_2 in this material was proposed. In our recent effort to synthesize multicomponent molecular compounds related to the 1-2-3 superconductor by using bifunctional ligands, we have found that 1,3-bis(dimethylamino)propan-2-ol (bdmapH) is an excellent ligand for binding to multiple metal centres.[4] This prompted us to examine the possibility of developing a new precursor system for the 1-2-3 superconductor using the bdmapH and acetate ligands. Indeed, an excellent precursor system was obtained. The results are reported here.

$Y(OAc)_3$, $Ba(OAc)_2$ and $Cu(OAc)_2(H_2O)$ were mixed in a 1 : 2 : 3 ratio in acetic acid. This mixture was heated to boiling temperature. In the absence of the bdmapH ligand a blue-green solution was obtained. Upon concentration and cooling to ambient temperature, coprecipitation occurred and a mixed microcrystalline material was obtained. In contrast, upon addition of the bdmapH ligand (1 : 2 ratio of Cu/bdmapH), the solution changed colour rapidly to dark-blue. After being concentrated and cooled to ambient temperature a viscous blue gel was obtained. Fibres can be drawn readily from this gel. The gel formed films readily on the surface of ordinary laboratory glassware. Upon further concentration a dark-blue glass material was obtained. This material can be readily converted into the $YBa_2Cu_3O_{7-x}$ superconductor after calcination and sintering at 875 °C under an oxygen atmosphere. The compressed pellet made from this material displayed the Meissner effect in liquid nitrogen. Magnetic susceptibility measurements for the powder sample at 19 G in the temperature range of 40–120 K revealed that the sample has an onset superconducting temperature of 92 K. The X-ray powder diffraction pattern of this sample is consistent with that of the $YBa_2Cu_3O_{7-x}$ superconductor.[1b]

In order to understand the role of the bdmap ligand played in this system, the reaction of $Cu(OAc)_2(H_2O)$, $Ba(OAc)_2$ and $Y(OAc)_3$ with the bdmapH ligand was investigated. A polynuclear copper(II) species with the formula of $[Cu_4(OAc)_6(bdmap)_2(H_2O)_6]_n$ **1** has been isolated. This compound can also be synthesized by the reaction of $Cu_2(OAc)_4(H_2O)_2$ with bdmapH in 1 : 1 ratio in nearly quantitative yield. **1** is an air-stable, dark-blue crystalline material and was fully characterized by IR, elemental analysis, and single-crystal X-ray diffraction.† The molecular structure of **1** is given in Fig. 1. **1** consists of four Cu^{II} ions in a zig-zag chain arrangement. The molecule has an inversion centre. Cu(1) and Cu(2) are bridged by an acetate ligand and an oxygen atom of the bdmap ligand. The Cu(1)–Cu(2) separation is 3.496(2) Å. The coordination geometry of Cu(1) can be described as a square-pyramid with the O(4′) atom of an acetate ligand occupying the fifth position, Cu(1)–O(4′) = 2.460(5) Å. Similarly the geometry of Cu(2) can also be described as a square-pyramid with the H_2O ligand occupying the fifth position, Cu(2)–O(8) = 2.336(5) Å. This dimer is linked to the other dimer through the O(4) atom of the acetate ligand to form a zig-zag chain with the Cu(1)–Cu(1′) separation of 3.537(3) Å. Tetranuclear copper(II) complexes with zig-zag chain structures have been reported previously.[5] It is well known that the acetate ligand typically bridges two metal centres through both oxygen atoms. The single oxygen atom bridging mode of the acetate ligand observed in this compound is uncommon, but has been observed previously in a few dinuclear copper(II) complexes such as the $[Cu_2(1\text{-methylimidazole})_4(O_2CCH_3)_4]\cdot(H_2O)_6$ complex.[6]

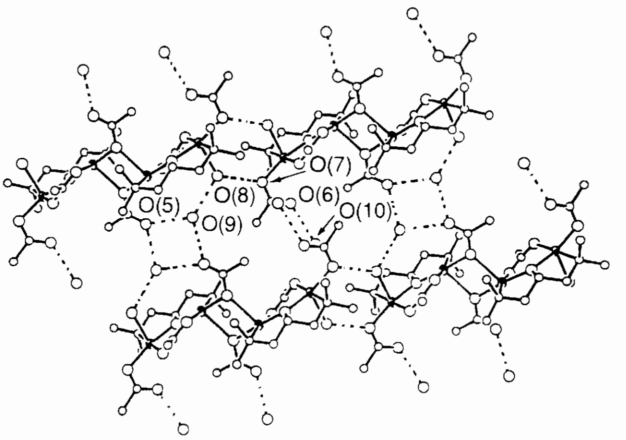

Fig. 2 A diagram showing the two-dimensional hydrogen-bonded network of **1**.

There are extensive hydrogen bonds[7] in **1** as shown in Fig. 2. The zig-zag Cu_4 chains are linked together to form a one-dimensional chain through intermolecular hydrogen bonds between the O(7) atom of the acetate ligand bonded to the Cu(2) atom and the O(8″) atom of the water ligand bonded to Cu(2″), O(7)–O(8″) = 2.764(7) Å. The Cu(2)–Cu(2″) separation is 5.435(3) Å. The coordination-free oxygen atom O(6) of the acetate forms a hydrogen bond with the water molecule O(10), O(6)–O(10) = 2.806(8) Å. A similar situation has been observed in the compound[4b] $[Cu_4(bdmap)_2(OH)_2(H_2O)(OAc)_3][PF_6]$. The one-dimensional chain is further linked together through hydrogen bonds between the chains. The O(8) atom forms an additional hydrogen bond with another water molecule O(9), O(8)–O(9) = 2.787(8) Å. The O(9) atom is further linked to the O(5) and O(5″) atoms of acetate ligands through the formation of two

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† IR for **1** (KBr): ν/cm^{-1} 3200–3600 (s, br), OH.

Crystal data for **1**: triclinic, $P\bar{1}$, $Z = 1$, $M = 1006.9$, $a = 10.554(5)$, $b = 11.611(3)$, $c = 9.406(3)$ Å, $\alpha = 102.87(2)$, $\beta = 99.87(3)$, $\gamma = 101.88(3)$°, $V = 1070.7(7)$ Å^3. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo-Kα radiation. The structure solution and refinements were carried out by using the TEXSAN software program package on a VAX workstation 3520. The structure was solved by heavy-atom methods. Atoms heavier than the carbon atom were refined anisotropically. Convergence to final R values of $R = 0.045$ and $R_w = 0.052$ was achieved by using 2087 reflections $[F^2 \geqslant 3\sigma(F^2)]$ and 179 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

hydrogen bonds, O(9)–O(5) = 2.796(8), O(9)–O(5″) = 2.854(9) Å. As a consequence, this compound has a two-dimensional extended structure in the solid. The formation of two hydrogen bonds of the O(5) atom with two water molecules may be the cause of the single oxygen bridge mode of the acetate ligand. Hydrogen bonds have been known to play an important role in the hydrolysis and condensation process of sol–gel.[2b] However, structure data are scarce. The structure of **1** provides evidence that hydrogen bonds may have played a critical role in the solution process of the precursor system. The gel formation in our precursor system could be the direct result of the two-dimensional hydrogen-bonded copper network observed in **1**.

Magnetic susceptibility of **1** was measured in the temperature range 4–297 K on a SQUID device. The data were fitted by using a tetramer chain model[8] involving two exchange constants, $J_{21} = J_{1'2'} = J_1$, $J_{11'} = J_2$. The best fit yielded $J_1 = -85.6\ \mathrm{cm}^{-1}$, $J_2 = 13.1\ \mathrm{cm}^{-1}$ and $g = 2.23$. These results suggest that the electron spin exchange in **1** is dominated by antiferromagnetism.

Although we have not been able to isolate any heterometallic species from this system, some clues regarding the possible bimetallic Y–Cu species in this system may be obtained from a new compound $LaCu_2(O_2CCF_3)_4(bdmap)_3$, **2** synthesized recently by our group.[9] In the $LaCu_2(O_2CCF_3)_4(bdmap)_3$ compound, the $La(O_2CCF_3)_3$ unit is linked to a dimeric $[Cu_2(O_2CCF_3)(bdmap)_3]$ unit through the oxygen atoms of the three bdmap ligands. We believe that the acetate analogue of **2** involving yttrium may be present in the precursor solution. Further study of this system is in progress.

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References

1 (*a*) D. Segal, *Chemical Synthesis of Advanced Ceramic Materials*, CUP, Cambridge, 1989; (*b*) C. P. Pool, Jr., T. Datta and H. A. Farach, *Copper Oxide Superconductors*, Wiley, New York, 1988.

2 (*a*) *Better Ceramics through Chemistry, Mater. Res. Soc. Symp. Proc.*, ed. C. J. Brinker, D. E. Clark, D. R. Ulrich, Pittsburg, PA, Vol. 121; 1988, B. J. J. Zelinski, C. J. Brinker, D. E. Clark and D. R. Ulrich vol. 180, 1990; (*b*) C. J. Brinker, *Sol–Gel Science*, Academic Press, Inc., Boston, 1990; (*c*) D. R. Ulrich, *Chem. Eng. News*, January 1, 1990, 28.

3 M. W. Rupich, B. Lagos and J. P. Hachey, *Appl. Phys. Lett.*, 1989, 1989, **55**, 2449.

4 (*a*) J. C. Zheng, R. J. Rousseau and S. Wang, *Inorg. Chem.*, 1992, **31**, 106; (*b*) S. Wang, S. J. Trepanier, J. C. Zheng, Z. Pang and M. J. Wagner, *Inorg. Chem.*, 1992, **31**, 2118.

5 C. A. Bear, J. M. Waters and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1974, 1059; R. R. Gagne, R. S. Gall, G. C. Lisensky, R. E. Marsh and L. M. Speltz, *Inorg. Chem.*, 1979, **18**, 771.

6 P. Y. Boukari, A. Busnot, F. Busnot, A. Leclaire and M. A. Bernard, *Acta Crystallogr., Sect. B.* 1982, **38**, 2458.

7 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, W. A. Benjamin, Inc., New York, 1968; A. Novak, *Struct. Bonding* (*Berlin*), 1974, **18**, 177.

8 K. E. Halvorson, T. Grigereit and R. D. Willett, *Inorg. Chem.*, 1987, **26**, 1716.

9 S. Wang, Z. Pang, Y. S. Hua and M. J. Wagner, *Inorg. Chem.*, 1992, submitted for publication.