Syntheses and Characterization of Polynuclear Metal Complexes related to a Chemical Precursor System for the $YBa_2Cu_3O_{7-x}$ Superconductor†

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A chemical precursor system for the $YBa_2Cu_3O_{7-x}$ superconductor has been investigated. From $[Cu_2(O_2CCH_3)_4(H_2O)_2]$, $Ba(O_2CCH_3)_2$, and $[Y(O_2CCH_3)_3(H_2O)_4]$ as starting materials and acetic acid and 1,3-bis(dimethylamino)propan-2-ol (Hbdmap) as the cross-linking agents, the $YBa_2Cu_3O_{7-x}$ powder sample obtained had an onset superconducting temperature of 92 K. Polynuclear metal complexes related to this system have been characterized. Thus $[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$, $[LaCu_2(bdmap)_3(O_2CCF_3)_4]$ and $[Cu_3(bdmap)_3(O_2CCF_3)_2]_2[Y_2(bdmap)_2(O_2CCF_3)_6]$ have been characterized structurally and their thermal and magnetic properties have been studied. The compounds decompose to the corresponding oxides when heated under an oxygen atmosphere.

Chemical processing of ceramic materials has attracted much recent attention because it provides an alternative to overcome the weakness associated with traditional processing methods such as poor homogeneity and difficulty of fabrication.[1] The most commonly used chemical processing methods are chemical vapour deposition and polymer pyrolysis. The former requires volatile molecular precursor compounds while the latter requires cross-linking reagents to bring different metal components together. Although several precursor systems employing soluble molecular complexes and cross-linking agents have been developed for the production of high-temperature superconductors by polymer pyrolysis, the chemistry involved in the process has not been well studied.[2] We have been interested in polynuclear compounds involving yttrium, lanthanides, copper and barium because these not only could be useful in chemical processing of ceramic superconductors but also could provide valuable information on the intermediate species involved in the chemical process and give clues for the design of suitable precursor systems. Recently, in a preliminary communication,[3] we reported a chemical precursor system for the $YBa_2Cu_3O_{7-x}$ superconductor where 1,3-bis(dimethylamino)propan-2-ol (Hbdmap) and acetic or trifluoroacetic acid were used as the complexing agents. The structure of a copper(II) complex isolated from this system, having a two-dimensional network linked by hydrogen bonds, was described. Although we have not been able to isolate any crystalline heterometallic species directly from this precursor system owing to the oily nature of these solutions, it was believed that heteropolynuclear species may be present in the precursor solution because we demonstrated earlier that the bdmap ligand is capable of bringing several metal ions together.[4] In an effort further to understand the roles of the bdmap and carboxylate ligands in this system and their interactions with the metal ions involved, we have carried out the synthesis of heterometallic complexes involving copper, yttrium (lanthanides), and barium with bdmap and trifluoroacetate as ligands. Several heteronuclear complexes have been characterized and the details are reported here.

Experimental

All reactions were carried out under a nitrogen atmosphere. Solvents were freshly distilled prior to use. The compounds $LnCl_3$ and $Ag(O_2CCF_3)$ were obtained from Strem Chemicals, 1,3-bis(dimethylamino)propan-2-ol from Spectrum Chemical and $Cu(OCH_3)_2$ from Aldrich. Thermogravimetric analyses were performed on a Perkin Elmer TGA-7 analyser. X-Ray powder diffraction experiments were performed on a Rigaku diffractometer. Elemental analyses were performed at Guelph Chemical Laboratories, Guelph, Ontario and Desert Analytics, Tucson, AZ.

Syntheses.—The $YBa_2Cu_3O_{7-x}$ *superconductor.* The compounds $[Y(O_2CCH_3)_3(H_2O)_4]$, $Ba(O_2CCH_3)_2$, $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ and Hbdmap were mixed in a 1:2:3:1.5 molar ratio in a beaker containing acetic acid–tetrahydrofuran (thf) (1:2, 30 cm^3). This mixture was heated to boiling and a homogeneous blue solution was obtained. The solution was concentrated by boiling off the solvents on a hot-plate until a viscous dark blue gel was obtained. This was transferred to a crucible and fired at 850 °C for 2 h under an oxygen atmosphere. The resulting powder was pressed into a pellet and reheated to 875 °C under oxygen for 5 h. X-Ray powder diffraction and magnetic susceptibility measurements confirmed that the product is the $YBa_2Cu_3O_{7-x}$ superconductor.[1b] The replacement of acetate by trifluoro-acetate resulted in a similar blue gel. However, owing to the toxicity of fluorinated hydrocarbons, the conversion into the superconductor was not performed.

$[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$ **1**. 1,3-Bis(dimethylamino)propan-2-ol (200 mg, 1.37 mmol) was mixed with $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ (547 mg, 1.37 mmol) in thf (5 cm^3) at 23 °C. A deep sapphire-blue solution was obtained. It was stirred for 1 h and filtered. The addition of diethyl ether to the filtrate resulted in the formation of dark blue crystals of compound **1** in > 70% yield. The compound changes gradually from blue to green at temperatures above 95 °C and melts at 200 °C (Found: C, 31.90; H, 6.40; N, 5.65. Calc. for $C_{26}H_{64}Cu_4N_4O_{20}$: C, 31.00; H, 6.35; N, 5.55%).

$[LaCu_2(bdmap)_3(O_2CCF_3)_4]$ **2a**. A sample of $LaCl_3$ (97 mg, 0.40 mmol) was placed in thf (150 cm^3) and $CuCl_2$ (27 mg, 0.20 mmol) and $Ag(O_2CCF_3)$ (351 mg, 1.60 mmol) were added. After being stirred for 24 h at 23 °C, a blue solution with purple

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

precipitation was obtained. The compounds $Cu(OCH_3)_2$ (75 mg, 0.60 mmol) and Hbdmap (174 mg, 1.20 mmol) were then added. After being stirred for 48 h, the solution was filtered. The blue filtrate was concentrated in vacuum to about 10 cm^3. After a few days blue crystals of compound **2a** were obtained (210 mg, 0.18 mmol, yield 46%) (Found: C, 30.15; H, 4.15; N, 6.95. Calc. for $C_{29}H_{51}Cu_2F_{12}LaN_6O_{11}$: C, 30.15; H, 4.40; N, 7.30%).

Compound **2b**, $[NdCu_2(bdmap)_3(O_2CCF_3)_4]$, was synthesised by the same method in 22% yield (Found: C, 30.10; H, 4.35; N, 7.10. Calc. for $C_{29}H_{51}Cu_2F_{12}NdN_6O_{11}$: C, 30.05; H, 4.40; N, 7.25%).

$[Cu_3(bdmap)_3(O_2CCF_3)_2]_2[Y_2(bdmap)_2(O_2CCF_3)_6]$ **3**. Copper(II) chloride (27 mg, 0.20 mmol) and YCl_3 (39 mg, 0.20 mmol) were dissolved in thf (20 cm^3), then $Ag(O_2CCF_3)$ (220 mg, 1.00 mmol) was added. After this mixture was stirred for 24 h at 23 °C, a blue solution with AgCl precipitation was obtained. The compounds $Cu(OCH_3)_2$ (50 mg, 0.40 mmol) and 1,3-bis(dimethylamino)propan-2-ol (116 mg, 80 mmol) were added. After being stirred for 48 h, the solution was filtered and concentrated to about 10 cm^3 *in vacuo*. After a few days standing at 23 °C, green-blue crystals of compound **3** were obtained (180 mg, 0.06 mmol, yield 62%), m.p. 205 °C (Found: C, 32.55; H, 5.05; N, 7.60. Calc. for $C_{76}H_{136}Cu_6F_{30}N_{16}O_{28}Y_2 \cdot C_4H_8O$: C, 32.85; H, 4.95; N, 7.65%).

Magnetic Susceptibility Measurements.—The magnetic susceptibilities for compounds **1**, **2a** and **3** were measured on a SQUID device (S.H.E. variable-temperature susceptometer) at Michigan State University. The sample was quenched to 4 K at zero applied field. The field was cycled to minimize the residual field. The samples were located in a nitrogen-filled glove-bag and measured in an Al–Si alloy bucket.

X-Ray Diffraction Analysis.—Blue single crystals of compounds **1**–**3** were obtained from thf–diethyl ether solution by slow diffusion of solvents at 23 °C. The crystals were mounted on glass fibres and sealed with epoxy glue. Data were collected at 22 °C over the range $3 < 2\theta < 45°$ for **1**, $2 < 2\theta < 47°$ for **2a** and **3** on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å), operated at 50 kV and 35 mA. The initial orientation matrix for **1** was obtained from 20 reflections ($8 < 2\theta < 14°$). High-angle cell refinements were not performed for this compound. The initial orientation matrix for **2a** was obtained from 20 reflections ($11 < 2\theta < 13°$) located by the SEARCH[5] routine. This matrix was refined successfully with 20 high-angle reflections ($15 < 2\theta < 32°$). The initial orientation matrix for **3** was obtained from 20 reflections ($10 < 2\theta < 14°$). No further refinement for this matrix was performed. Three standard reflections were measured every 147. No significant decay was observed for all crystals. Data were processed on a VAX workstation 3520 using the TEXSAN crystallographic package (version 5.0).[5] Data were corrected for Lorentz-polarization effects. Empirical absorption corrections were applied for all crystals.

Crystals of compounds **1** and **3** belong to the triclinic crystal system, space group $P\bar{1}$. Those of **2a** crystallized in the orthorhombic crystal system. The systematic absences agreed with two possible space groups, *Pnma* and $Pna2_1$. The centric space group *Pnma* was chosen. The correctness of this choice was confirmed by the successful solution and refinement of the structure. The crystals of **2b** are isomorphous with those of **2a** as indicated by the unit-cell parameters, a = 24.836(9), b = 14.747(9), c = 13.675(8) Å, U = 5009(5) Å^3, although the dimensions are slightly smaller than those of **2a**. The positions of the metal atoms in **1** and **3** were determined by heavy-metal methods (Patterson map), while those in **2a** were located by the direct method (MITHRIL).[6] Other non-hydrogen atoms were located by subsequent Fourier difference syntheses. The molecules of **1** and **3** have an inversion centre, while **2** possesses a reflection mirror plane.

Full-matrix least-squares refinements were applied to all structures. Neutral atom scattering factors were taken from Cromer and Waber.[7] Atoms heavier than carbon in compound **1** were refined anisotropically. Only metal atoms and the non-disordered fluorine atoms were refined anisotropically in **2a**. The CF_3 group bonded to the C(14)O(4)(5) acetate ligand in **2a** displayed a C_2 rotation disorder with respect to the C(14)–C(15) bond. Two sets of fluorine atoms were located and refined successfully. Each set has about 50% occupancy. A small degree of disorder was also observed for other CF_3 groups as indicated by the relatively large thermal parameters of the fluorine atoms. Owing to the limited data these disorders were ignored. The crystal of **3** had twinning problems. All fluorine atoms displayed varied degrees of disorder. Owing to limited data, only two of the CF_3 groups were treated as disordered with two sets of fluorine atoms of 50% occupancy being located and refined successfully. All CF_3 groups were refined as rigid groups. Only the metal atoms were refined anisotropically. A thf solvent molecule was located in the lattice and was only partially resolved due to the quality of the data. The positions of the hydrogen atoms except those bonded to the disordered thf molecule were calculated. Their thermal parameters were tied to those of the carbon atoms to which they are bonded (multiplied by 1.10) and their contribution in structural-factor calculations was included. The high R factor for **3** was attributed to the disorder of the molecule and the quality of the data. The data for the X-ray diffraction analyses of **1**–**3** are summarized in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—Carboxylates have frequently been employed in precursor solutions for producing the $YBa_2Cu_3O_{7-x}$ superconductor.[2] However, in the absence of additional cross-linking reagents, precipitations often occur in these systems. Precipitation not only can change the stoichiometry of the solution, but also destroy the homogeneity of the precursor system. In order to make high-quality superconducting films, it is essential to have a homogeneous precursor solution with a desired viscosity so that spinning- or dip-coating techniques can be applied prior to pyrolysis. When $[Y(O_2CCH_3)_3(H_2O)_4]$, $Ba(O_2CCH_3)_2$ and $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ were mixed in boiling thf and acetic acid without the Hbdmap ligand a blue-green solution was initially obtained. Upon concentration and cooling to ambient temperature, coprecipitation occurred and a mixed microcrystalline material was obtained. In contrast, after the addition of Hbdmap (1:2 ratio of Cu:Hbdmap) the solution changed colour rapidly to dark blue. After being concentrated and cooled to ambient temperature a homogeneous viscous blue gel was obtained. The viscosity can be adjusted by regulating the amount of solvents. Fibres can be drawn readily from this gel and it formed films readily on the surface of ordinary laboratory glassware. Upon further concentration a dark blue glass material was obtained. Owing to the lack of adequate equipment, no attempt was made to produce a superconducting film. Superconducting powder, however, was obtained readily by calcination and sintering of the glass material at 875 °C under an oxygen atmosphere. The compressed pellet made of this material displayed the Meissner effect in liquid nitrogen. Magnetic susceptibility measurements for the powder sample at 19 G (1.9×10^{-3} T) in the temperature range 40–120 K revealed that the sample has an onset superconducting temperature of 92 K as shown in Fig. 1(*a*). X-Ray powder diffraction analysis revealed that this sample consists of essentially the pure $YBa_2Cu_3O_7$ superconducting phase[1b] as shown in Fig. 1(*b*). A similar precursor system was also obtained by replacing acetate with trifluoroacetate.

The Hbdmap ligand apparently has played an important role in promoting the solubility and homogeneity of the precursor

Table 1 Crystallographic data

	1	**2a**	**3**
Formula	$C_{26}H_{64}Cu_4N_4O_{20}$	$C_{29}H_{51}Cu_2F_{12}LaN_6O_{11}$	$C_{80}H_{144}Cu_6F_{30}N_{16}O_{29}Y_2$
Formula weight	1006.90	1153.8	2923.07
Crystal symmetry	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	*Pnma* (no. 62)	$P\bar{1}$
a/Å	10.554(5)	24.95(1)	16.60(1)
b/Å	11.611(3)	14.806(4)	16.923(8)
c/Å	9.406(3)	13.724(4)	13.494(9)
α/°	102.87(2)	90	96.72(5)
β/°	99.87(3)	90	112.90(5)
γ/°	101.88(3)	90	83.10(5)
U/Å^3	1070.7(7)	5069(3)	3457(4)
Z	1	4	1
D_c/g cm^{-3}	1.54	1.51	1.47
Crystal size/mm	0.20 × 0.20 × 0.10	0.10 × 0.20 × 0.20	0.10 × 0.20 × 0.15
μ(Mo-Kα)/cm^{-1}	20.4	17.56	18.42
2θ Range/°	3–45	3–47	3–45
Reflections			
measured	$+h, \pm k, \pm l$, 3136	$+h, +k, +l$, 4197	$+h, \pm k, \pm l$, 8444
observed $[F_o^2 \geqslant 3\sigma(F_o^2)]$	2087	1537	2548
No. of parameters, N_p refined	179	180	347
R^a	0.045	0.080	0.115
R'^b	0.052	0.087	0.086
Largest shift/e.s.d. in final cycle	0.001	0.11	0.25
Largest electron-density peak/e Å^{-3}	0.680	1.057	1.32
Goodness-of-fit,^{c} S	2.029	2.00	3.36

^{a} $R = \sum_{i=1}^{n}(|F_o|_i - |F_c|_i) / \sum_{i=1}^{n}|F_o|_i$. ^{b} $R' = [\sum_{i=1}^{n} w_i(|F_o|_i - |F_c|_i)^2 / \sum_{i=1}^{n} w_i|F_o|_i^2]^{\frac{1}{2}}$, where $w = 1/\sigma^2(F_o)$. ^{c} $S = \sum_{i=1}^{n}(|F_o|_i - |F_c|_i)/\sigma(N_o - N_p)$.

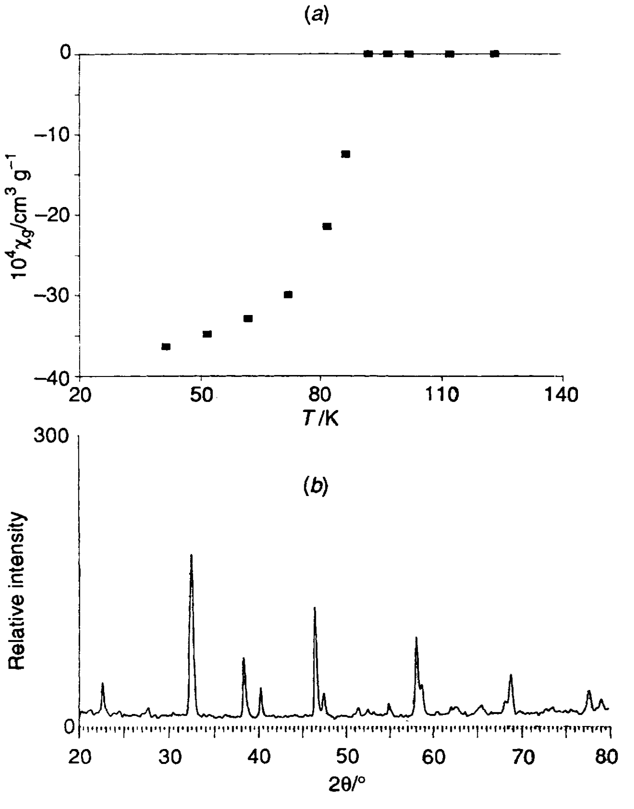


Fig. 1 Magnetic susceptibility data (χ_g) (*a*) and X-ray powder diffraction diagram (*b*) for the $YBa_2Cu_3O_{7-x}$ superconductor

compounds. Our previous studies demonstrated that it is capable of linking several metal ions through both amino groups and the alkoxy group.[4] Therefore, we believed that polynuclear species may exist in the precursor solution. Attempts to isolate these species directly from the precursor system were unsuccessful due to the high viscosity of the solution. However, in the absence of an excess of acetic acid, a crystalline polynuclear copper(II) complex, $[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$ **1**, was isolated from the mixture of $[Y(O_2CCH_3)_3(H_2O)_4]$, $Ba(O_2CCH_3)_2$, $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ and Hbdmap in thf. Compound **1** can also be obtained readily from the reaction of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ and Hbdmap in a 2:1 ratio. Heteronuclear complexes were not identified structurally from the acetate and bdmap mixture due to the difficulty of crystallization. In an effort to obtain crystalline materials, we replaced the acetate by trifluoroacetate and yttrium with lanthanides. Two heteronuclear complexes with the formula $[LnCu_2(bdmap)_3(O_2CCF_3)_4]$ (Ln = La **2a**, or Nd **2b**) and $[Y_2Cu_6(bdmap)_8(O_2CCF_3)_{10}]$ **3** were obtained. Both compounds can be prepared by independent syntheses according to equations (1) and (2).

$$\left.\begin{array}{l} LnCl_3 + 0.5CuCl_2 + 4Ag(O_2CCF_3) \\ \quad 1.5Cu(OCH_3)_2 + 3Hbdmap \end{array}\right\} \xrightarrow{thf} [LnCu_2(bdmap)_3(O_2CCF_3)_4] \quad (1)$$

$$\left.\begin{array}{l} YCl_3 + CuCl_2 + 5Ag(O_2CCF_3) \\ \quad 2Cu(OCH_3)_2 + 4Hbdmap \end{array}\right\} \xrightarrow{thf} [Y_2Cu_6(bdmap)_8(O_2CCF_3)_{10}] \quad (2)$$

The compound $Cu(OCH_3)_2$ has frequently been used by our group as a starting material. It has been demonstrated previously that it reacts readily with aminoalcohol ligands to form soluble monomeric $Cu(OR)_2$ species where OR is the deprotonated aminoalcohol ligand.[8] We have found that $[Cu(bdmap)_2]$ can serve as a good precursor for the formation of polymetallic complexes in the presence of other bridging ligands. It was believed that the reaction of $CuCl_2$ and $LnCl_3$ or YCl_3 with $Ag(O_2CCF_3)$ yielded $Cu_2(O_2CCF_3)_4$ and $Ln(O_2CCF_3)_3$ or $Y(O_2CCF_3)_3$ *in situ*, which subsequently reacted with $[Cu(bdmap)_2]$ to form the bimetallic compounds **2** and **3**.

Heteronuclear complexes of barium and copper with bdmap, acetate or trifluoroacetate are oily materials and have not been characterized structurally, although a $BaCu_4$ compound[4c] with mixed ligands and the formula $[BaCu_4(bdmap)_4(O_2CCF_3)_2(pyo)_4]$ **4** has been obtained and reported recently by our group (pyo = deprotonated 2-hydroxypyridine).

Compounds **1**–**3** are blue crystalline materials and were fully characterized by single-crystal X-ray diffraction and elemental analyses.

Crystal Structure of $[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$ **1**.—The molecular structure of compound **1** is shown in Fig. 2. Positional parameters are given in Table 2, selected bond lengths and angles in Table 3. Compound **1** consists of four copper(II) ions in a zigzag chain arrangement. The molecule has an inversion centre. Atoms 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 co-ordination 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. 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 zigzag chain with Cu(1) ··· Cu(1′) 3.537(3) Å. Tetranuclear copper(II) complexes with zigzag chain structures have been reported previously.[9] 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 $[Cu_2(mim)_4(O_2CCH_3)_4]\cdot 6H_2O$ (mim = *N*-methylimidazole).[10] The zigzag Cu_4 chains are linked together to form a one-dimensional chain through intermolecular hydrogen bonds[11] between the O(7) atom of the acetate ligand bonded to Cu(2) and O(8″) 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 unco-ordinated 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] $[Cu_4(bdmap)_2(OH)_2(O_2CCH_3)_3(H_2O)][PF_6]$. The one-dimensional chain is further linked together through hydrogen bonds between the chains. The atom O(8) forms an additional hydrogen bond with another water molecule O(9), O(8) ··· O(9) 2.787(8) Å. Atom O(9) is further linked to O(5) and O(5″) of acetate ligands through two hydrogen bonds, O(9) ··· O(5) 2.796(8) and O(9) ··· O(5″) 2.854(9) Å. As a consequence, this compound has a two-dimensional extended structure in the solid (Fig. 3). Hydrogen bonds are known to play an important role in the hydrolysis and sol–gel condensation process.[2b] However, structural 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. Gel formation in our precursor system could be the direct result of the two-dimensional hydrogen-bonded copper network observed in **1**.

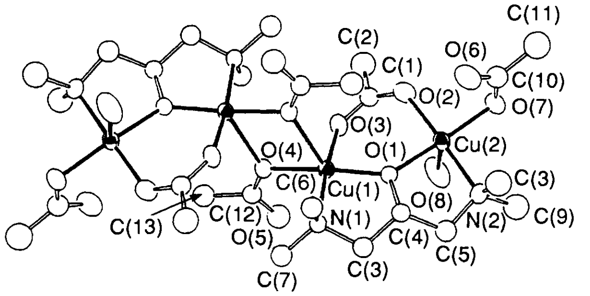


Fig. 2 The molecular structure of compound **1** with labelling scheme and 50% thermal ellipsoids

Table 2 Positional parameters for compound **1**

Atom	*x*	*y*	*z*
Cu(1)	0.154 21(8)	0.057 17(7)	−0.367 96(9)
Cu(2)	0.287 12(8)	0.306 63(7)	−0.052 8(1)
O(1)	0.230 2(4)	0.135 9(4)	−0.160 4(5)
O(2)	0.189 9(5)	0.358 6(4)	−0.215 8(5)
O(3)	0.180 5(5)	0.212 6(4)	−0.422 7(5)
O(4)	0.088 3(4)	−0.029 6(4)	−0.579 6(5)
O(5)	0.294 5(5)	−0.019 0(5)	−0.603 9(6)
O(6)	0.102 7(5)	0.379 3(5)	0.090 9(6)
O(7)	0.307 8(5)	0.466 6(4)	0.085 0(5)
O(8)	0.469 6(5)	0.339 3(5)	−0.161 9(6)
O(9)	0.502 5(7)	−0.127 7(7)	−0.650(1)
O(10)	−0.155 0(6)	0.381 3(5)	0.129 0(7)
N(1)	0.158 4(5)	−0.100 5(5)	−0.302 5(6)
N(2)	0.388 8(5)	0.249 6(5)	0.115 2(6)
C(1)	0.186 8(7)	0.320 1(6)	−0.352 9(8)
C(2)	0.187 1(8)	0.414 2(8)	−0.443(1)
C(3)	0.275 3(7)	−0.057 6(6)	−0.172 8(8)
C(4)	0.266 9(7)	0.059 4(6)	−0.071 7(7)
C(5)	0.397 5(7)	0.126 4(7)	0.036 9(8)
C(6)	0.035 4(7)	−0.142 2(6)	−0.250 8(8)
C(7)	0.176 5(7)	−0.205 2(7)	−0.412 0(8)
C(8)	0.315 5(9)	0.241 7(8)	0.233(1)
C(9)	0.523 6(9)	0.328 2(8)	0.185(1)
C(10)	0.201 4(8)	0.469 1(7)	0.130 0(8)
C(11)	0.198(1)	0.583 6(8)	0.240(1)
C(12)	0.174 4(7)	−0.053 4(6)	−0.655 1(8)
C(13)	0.119 5(8)	−0.129 7(7)	−0.815 1(9)

Crystal Structure of $[LaCu_2(bdmap)_3(O_2CCF_3)_4]$ **2a**.—Positional parameters of compound **2a** are given in Table 4, selected bond distances and angles in Table 5. The compound consists of two copper atoms and one lanthanum atom arranged in a triangular geometry with a Cu ··· Cu separation of 3.265(6) Å and La ··· Cu separation of 3.632(4) Å, as shown in Fig. 4. Half of the molecule is related to the other half by reflection in a mirror plane. The two copper atoms are bridged by one trifluoroacetate ligand and one bdmap ligand. Each is co-ordinated by one additional bdmap ligand through one nitrogen and one oxygen atom. The co-ordination geometry of the copper centre is square pyramidal with atom N(3) occupying the axial position as indicated by the O(1)–Cu–O(3) angle, 170.4(6)°, O(2)–Cu–N(2) angle, 170.2(8)°, and the

Table 3 Selected bond distances (Å) and angles (°) for compound **1**

Cu(1)–O(1)	1.912(4)	O(6)–C(10)	1.248(9)
Cu(1)–O(3)	1.964(4)	O(7)–C(10)	1.270(8)
Cu(1)–O(4)	1.950(4)	N(1)–C(3)	1.490(9)
Cu(1)–N(1)	2.064(5)	N(1)–C(6)	1.489(9)
Cu(2)–O(1)	1.930(4)	N(1)–C(7)	1.475(8)
Cu(2)–O(2)	1.973(5)	N(2)–C(5)	1.483(8)
Cu(2)–O(7)	1.959(4)	N(2)–C(8)	1.46(1)
Cu(2)–N(2)	2.065(6)	N(2)–C(9)	1.47(1)
O(1)–C(4)	1.412(7)	C(1)–C(2)	1.52(1)
O(2)–C(1)	1.260(8)	C(3)–C(4)	1.503(9)
O(3)–C(1)	1.256(8)	C(4)–C(5)	1.51(1)
O(4)–C(12)	1.282(8)	C(10)–C(11)	1.50(1)
O(5)–C(12)	1.223(8)	C(12)–C(13)	1.51(1)
O(1)–Cu(1)–O(4)	175.4(2)	Cu(1)–O(1)–Cu(2)	131.0(2)
O(1)–Cu(1)–O(3)	92.8(2)	Cu(1)–O(1)–C(5)	139.6(3)
O(1)–Cu(1)–N(1)	83.7(2)	O(1)–Cu(1)–O(4′)	110.1(2)
O(4)–Cu(1)–O(3)	89.3(2)	O(4)–Cu(1)–O(4′)	73.9(2)
O(4)–Cu(1)–N(1)	93.6(2)	O(2)–Cu(2)–O(8)	86.8(2)
O(3)–Cu(1)–N(1)	171.1(2)	O(1)–Cu(2)–O(8)	92.3(2)
O(3)–Cu(1)–O(4′)	91.3(2)	O(7)–Cu(2)–O(8)	103.0(2)
N(1)–Cu(1)–O(4′)	97.6(2)	N(2)–Cu(2)–O(8)	92.9(2)
O(1)–Cu(2)–O(7)	164.5(2)	O(7)–Cu(2)–N(2)	91.2(2)
O(1)–Cu(2)–O(2)	93.7(2)	O(2)–Cu(2)–N(2)	179.0(2)
O(1)–Cu(2)–N(2)	85.4(2)	Cu(1)–O(4)–Cu(1′)	106.1(2)
O(7)–Cu(2)–O(2)	89.7(2)		

Cu–N(3) distance, 2.48(2) Å. Atom O(4) of another trifluoroacetate ligand is 2.94(2) Å from the copper atom, and may be considered as the sixth ligand with very weak interactions. The structure of the copper dimer portion of this molecule is very similar to those found in $[LnCu_2(bdmap)_3(O_2CCF_3)(O_2CCH_3)(hfacac)_2]$ **5** (Hhfacac = hexafluoroacetylacetone),[12] and tetrameric $[Cu^{II}_4(bdmap)_3(OH)(O_2CCH_3)_2(HO_2CCH_3)(H_2O)][PF_6]_2$.[6] In the Cu_4 complex the dimer unit is linked to another dicopper unit through two of the bdmap ligands, while in compounds **2a** and **5** this dimer is linked to a $Ln(O_2CCF_3)_3$ unit and a $Ln(O_2CCF_3)(hfacac)_2$, respectively, through the oxygen atoms of all three bdmap ligands as illustrated. The Cu • • • Cu distance [3.265(6) Å] in **2a** is comparable with those in the Cu_4 compound [3.307(3) Å] and in **5** [3.165(5) Å]. With respect to the $LaCu_2$ plane, two of the bdmap ligands with the oxygen atom bridging one copper atom and the lanthanum ion are *cis* to each other and *trans* to the third bdmap ligand which has a μ_3-oxygen atom bridging the two copper atoms and the lanthanum ion. Two of the trifluoroacetate ligands are bonded to the lanthanum ion through only one oxygen atom, La–O(5) 2.52(2) and La–O(7) 2.49(2) Å. The third trifluoroacetate ligand is bonded to the La atom through both oxygen atoms, La–O(6) 2.67(1) Å. The bond distances between the three oxygen atoms from the three bdmap ligands and the La atom vary considerably, La–O(1) 2.42(1) Å and La–O(2) 2.84(2) Å. This difference could be attributed to the fact that O(2) is bonded to two copper centres while O(1) is bonded only to one. The negative charge on O(2) is therefore significantly reduced, in comparison with

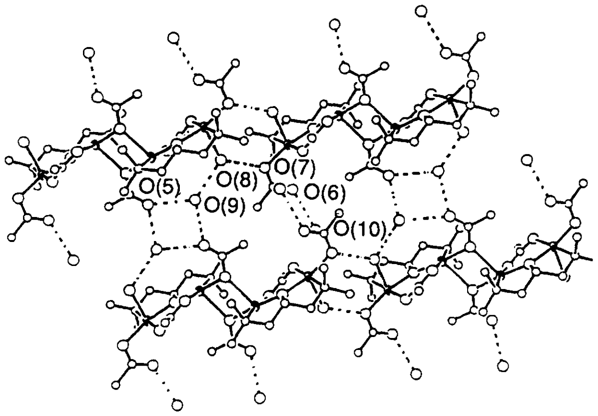


Fig. 3 The extended hydrogen-bonding network of compound **1**

Table 4 Positional parameters for compound **2a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
La	0.755 24(9)	1/4	0.941 5(1)	N(2)	0.630 1(9)	0.032(1)	1.101(1)
Cu	0.630 3(1)	0.139 7(2)	1.006 8(2)	N(3)	0.601 1(8)	0.082(1)	0.846(1)
F(1)	0.444(1)	1/4	1.009(2)	C(1)	0.781(1)	0.046(2)	1.068(2)
F(2)	0.463 5(9)	0.320(1)	1.134(2)	C(2)	0.723 6(8)	0.038(2)	1.040(1)
F(3)	0.787(3)	1/4	1.309(5)	C(3)	0.690(1)	0.022(2)	1.129(1)
F(4)	0.722(2)	0.319(3)	1.339(3)	C(4)	0.865(1)	0.109(2)	1.039(2)
F(5)	0.768(1)	0.324(2)	1.315(2)	C(5)	0.820(1)	0.036(2)	0.909(2)
F(6)	0.699(3)	1/4	1.350(5)	C(6)	0.599(1)	0.055(2)	1.193(2)
F(7)	0.695(1)	1/4	0.586(2)	C(7)	0.604(1)	−0.050(2)	1.054(2)
F(8)	0.765(1)	0.319(1)	0.573(1)	C(8)	0.601(1)	1/4	0.850(2)
F(9)	0.957(1)	1/4	0.712(2)	C(9)	0.612(1)	0.164(2)	0.791(2)
F(10)	0.951(1)	0.317(2)	0.851(2)	C(10)	0.630(1)	0.009(2)	0.805(2)
O(1)	0.705 0(5)	0.117(1)	0.989(1)	C(11)	0.543(1)	0.060(2)	0.843(2)
O(2)	0.641 5(8)	1/4	0.928(1)	C(12)	0.536(1)	1/4	1.061(2)
O(3)	0.555 2(6)	0.174(1)	1.046(1)	C(13)	0.477(2)	1/4	1.088(3)
O(4)	0.675(1)	1/4	1.165(2)	C(14)	0.723(2)	1/4	1.183(2)
O(5)	0.763(1)	1/4	1.125(2)	C(15)	0.741(3)	1/4	1.293(4)
O(6)	0.744 3(7)	0.175(1)	0.766(1)	C(16)	0.748(2)	1/4	0.727(2)
O(7)	0.847(1)	1/4	0.868(2)	C(17)	0.743(2)	1/4	0.612(3)
O(8)	0.859(2)	1/4	0.713(3)	C(18)	0.874 9(2)	1/4	0.796(3)
N(1)	0.812 3(7)	0.091(1)	0.995(1)	C(19)	0.934(2)	1/4	0.805(4)

Table 5 Selected bond lengths (Å) and angles (°) for compound **2a**

La–O(1)	2.42(1)	O(1)–C(2)	1.43(2)	F(2)–C(13)	1.26(2)	N(2)–C(3)	1.55(3)
La–O(2)	2.84(2)	O(2)–C(8)	1.47(3)	F(3)–C(15)	1.16(9)	N(2)–C(6)	1.52(3)
La–O(5)	2.52(2)	O(3)–C(12)	1.24(2)	F(4)–C(15)	1.29(5)	N(2)–C(7)	1.52(3)
La–O(6)	2.67(1)	O(4)–C(14)	1.20(4)	F(5)–C(15)	1.32(4)	N(3)–C(9)	1.47(3)
La–O(7)	2.49(2)	O(5)–C(14)	1.29(4)	F(6)–C(15)	1.31(8)	N(3)–C(10)	1.42(3)
La–N(1)	2.85(2)	O(6)–C(16)	1.24(2)	F(7)–C(17)	1.25(6)	N(3)–C(11)	1.49(3)
Cu–O(1)	1.91(1)	O(7)–C(18)	1.21(3)	F(8)–C(17)	1.28(3)	C(1)–C(2)	1.49(3)
Cu–O(2)	1.98(1)	O(8)–C(18)	1.20(4)	F(9)–C(19)	1.40(5)	C(2)–C(3)	1.50(3)
Cu–O(3)	2.01(1)	N(1)–C(1)	1.43(3)	F(10)–C(19)	1.25(3)	C(8)–C(9)	1.53(3)
Cu–N(2)	2.06(2)	N(1)–C(4)	1.47(3)	C(12)–C(13)	1.52(5)	C(14)–C(15)	1.57(6)
F(1)–C(13)	1.35(4)	N(1)–C(5)	1.44(3)	C(16)–C(17)	1.59(5)	C(18)–C(19)	1.47(5)
O(1)–La–O(1′)	108.5(7)	O(5)–La–N(1)	72.9(5)	O(2)–La–O(5)	98.1(7)	O(1)–Cu–O(3)	170.4(6)
O(1)–La–O(2)	60.1(4)	O(6)–La–O(6′)	49.5(6)	O(2)–La–O(6)	80.8(5)	O(1)–Cu–N(2)	86.9(8)
O(1)–La–O(5)	76.6(5)	O(6)–La–O(7)	74.2(6)	O(2)–La–O(7)	152.4(7)	O(2)–Cu–O(3)	94.0(7)
O(1)–La–O(6)	81.5(5)	O(6)–La–N(1)	86.4(5)	O(2)–La–N(1)	121.0(4)	O(2)–Cu–N(2)	170.2(8)
O(1)–La–O(6′)	122.1(5)	O(6)–La–N(1′)	129.0(5)	O(2)–La–C(16)	82.6(9)	O(3)–Cu–N(2)	91.4(7)
O(1)–La–O(7)	125.7(3)	O(7)–La–N(1)	69.3(4)	O(5)–La–O(6)	155.2(3)	La–O(2)–Cu	96.1(6)
O(1)–La–N(1)	61.1(5)	N(1)–La–N(1′)	111.7(8)	O(5)–La–O(7)	109.5(7)	Cu–O(2)–Cu′	111.3(9)
O(1)–La–N(1′)	149.3(5)	O(1)–Cu–O(2)	86.4(7)	La–O(1)–Cu	113.4(7)		

that of O(1), which leads to a weaker La–O interaction and a longer separation, since the lanthanide–ligand interaction is dominated by the electrostatic force.[13] Steric factors may also be responsible for these observed variations in bond lengths. Two amino groups of the bdmap ligands are also bonded to the La atom with a very long bond length, La–N(1) 2.85(2) Å, which is apparently caused by the poor affinity of the neutral amino group for the lanthanum ion, in comparison to the negatively charged oxygen centres. As a result, the lanthanum ion has a co-ordination number of nine and an irregular polyhedral geometry, as has frequently been observed in lanthanide(III) compounds.[13]

Several $LnCu_2$ compounds have been reported previously, where the three metal atoms have a bent-chain arrangement without any bridging ligands between the copper atoms.[14] A triangular structure similar to that of **2a** has been observed in the compound[15] $[YCu_2(OCH_2CH_2OCH_3)_3(hfacac)_2(tmhd)_2]$ where tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate.

Compound **2b** is isostructural with **2a** as confirmed by the crystal unit-cell parameters.

Crystal Structure of $[Y_2Cu_6(bdmap)_8(O_2CCF_3)_{10}]$ **3**.—The positional parameters for compound **3** are listed in Table 6, selected bond lengths and angles in Table 7. Compound **3** consists of one anionic yttrium dimer, $[Y_2(bdmap)_2(O_2CCF_3)_6]^{2-}$, and two cationic copper trimers, $[Cu_3(bdmap)_3(O_2CCF_3)_2]^+$. The yttrium dianion is situated in between the two Cu_3 cations as shown in Fig. 5. In the Y_2 anion the two yttrium ions are bridged by the oxygen atom of the bdmap ligand (Fig. 6). A neutral dimer compound[12] $[Ln_2(bdmap)_2(hfacac)_4(H_2O)_2]$ with the similar bdmap bridges has been synthesised recently by our group. The Y ··· Y separation 3.748(5) Å in this dimer is similar to those of previously reported polynuclear yttrium complexes.[16] Each yttrium centre is co-ordinated by three trifluoroacetate ligands through one oxygen atom with Y–O distances ranging from 2.19(3) to 2.28(3) Å, and also by two amino groups of the bdmap ligand with very long Y–N separations, Y(1)–N(7) 2.72(5) and Y(1)–N(8) 2.64(4) Å, similar to those observed in compound **2a**. Its geometry can best be described as a distorted pentagonal bipyramid. It appears that the stability of this Y_2 anion is dependent on the Cu_3 cation because independent syntheses in the absence of the copper(II) complex were unsuccessful.

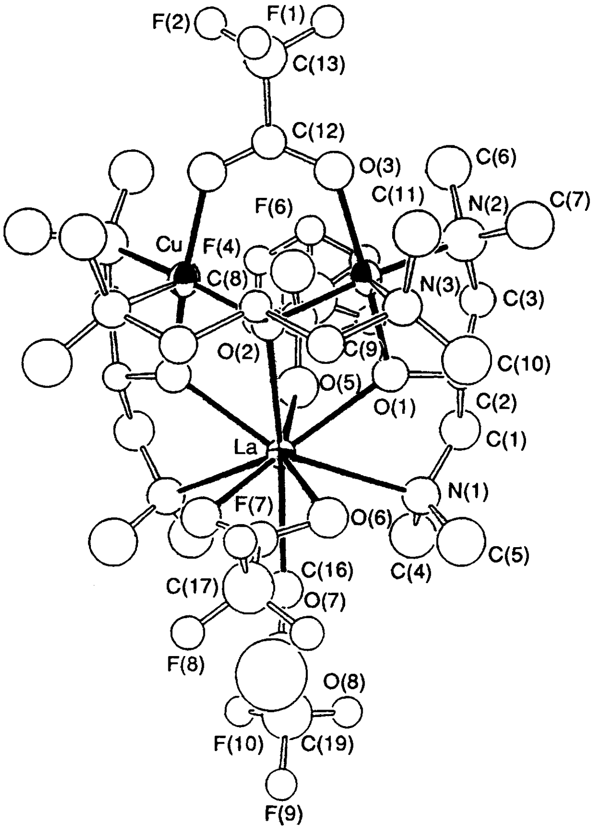
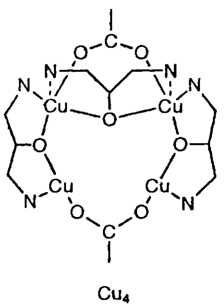
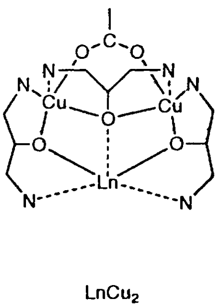


Fig. 4 The molecular structure of compound **2a** with labelling scheme and 50% thermal ellipsoids



Cu_4



$LnCu_2$

The $[Cu_3(bdmap)_3(O_2CCF_3)_2]^+$ cation has an unusual cyclic structure (Fig. 7). The three copper(II) ions are bridged by three oxygen atoms of the bdmap ligands to form a six-membered ring with nearly identical Cu ··· Cu distances, Cu(1) ··· Cu(2) 3.454(9), Cu(1) ··· Cu(3) 3.411(7) and Cu(2) ··· Cu(3) 3.436(7) Å. Although a cyclic structure has been observed previously in some Cu_3 complexes, very often a μ_3-bridging ligand such as OH^- and O^{2-} is present.[17] The cyclic structure observed in **3** without any triply bridging ligands is rare for copper(II) complexes. The $[Cu_3(bdmap)_3(O_2CCF_3)_2]^+$ cation has an approximate C_2 symmetry. Atoms Cu(1) and

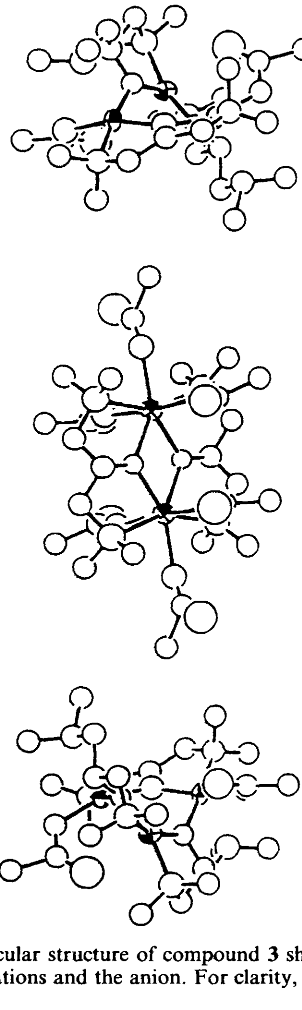


Fig. 5 The molecular structure of compound **3** showing the relative positions of the cations and the anion. For clarity, fluorine atoms are omitted

Table 6 Positional parameters for compound **3**

Atom	x	y	z
Y(1)	0.1042(3)	0.4346(2)	0.0238(3)
Cu(1)	0.7141(3)	0.1273(3)	0.5016(4)
Cu(2)	0.7653(3)	0.2038(3)	0.3090(4)
Cu(3)	0.7218(3)	0.0074(3)	0.2833(4)
F(1)	0.849(2)	−0.103(3)	0.708(4)
F(2)	0.833(3)	−0.155(4)	0.646(5)
F(3)	0.770(4)	−0.173(3)	0.570(4)
F(4)	0.694(3)	−0.129(3)	0.575(4)
F(5)	0.710(3)	−0.094(3)	0.663(5)
F(6)	0.768(4)	−0.074(3)	0.729(3)
F(7)	0.701(3)	0.064(1)	−0.079(4)
F(8)	0.748(2)	0.181(2)	−0.039(3)
F(9)	0.610(2)	0.167(2)	−0.097(3)
F(10)	0.099(1)	0.382(2)	0.347(2)
F(11)	0.187(2)	0.460(2)	0.466(2)
F(12)	0.237(2)	0.358(2)	0.390(2)
F(13)	0.346(6)	0.211(4)	0.138(8)
F(14)	0.357(4)	0.275(5)	0.201(5)
F(15)	0.388(5)	0.329(4)	0.197(5)
F(16)	0.417(4)	0.349(3)	0.135(6)
F(17)	0.427(8)	0.222(3)	0.102(9)
F(18)	0.435(8)	0.259(6)	0.084(9)
F(19)	0.088(2)	0.491(2)	−0.288(3)
F(20)	0.121(2)	0.371(2)	−0.341(3)
F(21)	−0.007(2)	0.428(2)	−0.421(2)
O(1)	0.744(2)	0.203(2)	0.434(2)
O(2)	0.798(2)	0.091(1)	0.309(2)
O(3)	0.663(2)	0.071(1)	0.364(2)
O(4)	0.729(2)	0.034(2)	0.583(2)
O(5)	0.804(2)	−0.042(2)	0.497(3)
O(6)	0.745(2)	0.208(1)	0.165(2)
O(7)	0.645(2)	0.107(2)	0.095(2)
O(8)	−0.036(2)	0.441(1)	−0.002(2)
O(9)	0.142(2)	0.446(1)	0.199(2)
O(10)	0.196(2)	0.541(2)	0.330(3)
O(11)	0.231(2)	0.356(2)	0.048(2)
O(12)	0.271(2)	0.262(2)	−0.056(3)
O(13)	0.077(2)	0.414(1)	−0.154(2)
O(14)	−0.007(2)	0.328(2)	−0.293(3)
N(1)	0.765(2)	0.195(2)	0.639(3)
N(2)	0.724(2)	0.316(2)	0.313(3)
N(3)	0.813(2)	−0.062(2)	0.253(3)
N(4)	0.931(2)	0.198(2)	0.360(2)
N(5)	0.558(2)	0.158(2)	0.472(3)
N(6)	0.609(2)	−0.052(2)	0.210(3)
N(7)	0.217(3)	0.542(2)	0.031(3)
N(8)	0.056(2)	0.292(2)	0.026(3)
C(1)	0.759(4)	0.275(3)	0.602(5)
C(2)	0.733(4)	0.285(4)	0.489(6)
C(3)	0.726(4)	0.336(3)	0.414(5)
C(4)	0.733(3)	0.202(3)	0.713(4)
C(5)	0.864(3)	0.157(3)	0.687(4)
C(6)	0.634(3)	0.339(2)	0.251(3)
C(7)	0.778(3)	0.373(3)	0.293(3)
C(8)	0.890(3)	−0.027(3)	0.317(3)
C(9)	0.878(3)	0.072(2)	0.305(3)
C(10)	0.950(3)	0.114(2)	0.380(3)
C(11)	0.832(3)	−0.147(3)	0.289(4)
C(12)	0.800(3)	−0.062(2)	0.138(4)
C(13)	0.988(3)	0.247(2)	0.454(3)
C(14)	0.952(2)	0.219(2)	0.271(3)
C(15)	0.549(3)	0.009(3)	0.229(3)
C(16)	0.584(3)	0.052(2)	0.342(3)
C(17)	0.522(3)	0.125(2)	0.358(3)
C(18)	0.577(3)	−0.074(3)	0.095(4)
C(19)	0.608(3)	−0.116(3)	0.265(4)
C(20)	0.535(3)	0.108(2)	0.541(3)
C(21)	0.517(3)	0.237(3)	0.479(3)
C(22)	0.775(4)	−0.022(3)	0.567(4)
C(23)	0.777(4)	−0.102(3)	0.634(4)
C(24)	0.695(3)	0.163(3)	0.101(4)
C(25)	0.688(2)	0.137(2)	−0.038(2)
C(26)	0.167(5)	0.608(5)	−0.029(6)
C(27)	−0.081(3)	0.369(3)	−0.006(4)
C(28)	−0.015(5)	0.311(4)	0.052(5)
C(29)	0.257(3)	0.519(3)	−0.049(3)
C(30)	0.274(3)	0.546(3)	0.131(4)
C(31)	0.116(4)	0.257(3)	0.121(5)
C(32)	0.050(3)	0.239(3)	−0.063(4)
C(33)	0.167(4)	0.479(3)	0.287(5)
C(34)	0.173(2)	0.415(1)	0.376(2)
C(35)	0.283(4)	0.292(3)	0.027(5)
C(36)	0.385(5)	0.269(4)	0.113(6)
C(37)	0.031(4)	0.371(3)	−0.252(4)
C(38)	0.058(2)	0.421(1)	−0.328(2)
C(39)	0.492(5)	0.327(5)	0.747(7)
C(40)	0.405(6)	0.341(5)	0.702(7)
C(41)	0.454(7)	0.385(6)	0.869(8)
C(42)	0.430(9)	0.421(8)	0.81(1)

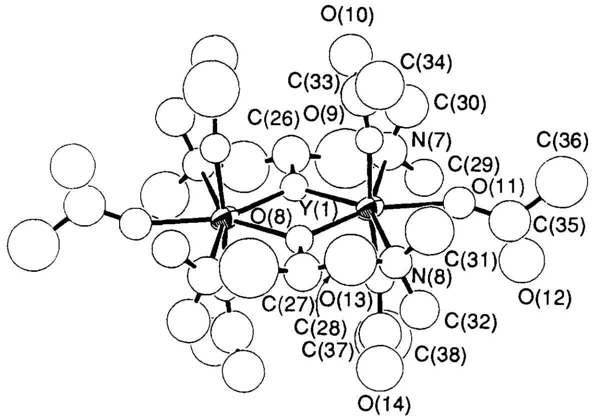


Fig. 6 The structure of the Y_2^{2-} anion in compound **3** with labelling scheme and 50% thermal ellipsoids. Fluorine atoms are omitted

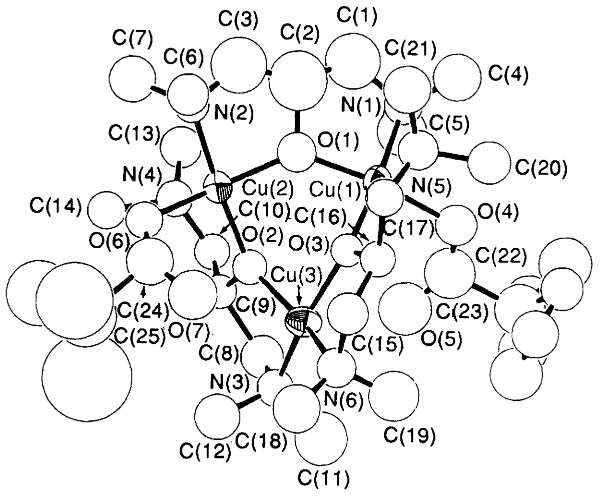


Fig. 7 The structure of the Cu_3^+ cation in compound **3** with labelling scheme and 50% thermal ellipsoids

Cu(2) have a square-pyramidal geometry with N(4) and N(5) being the fifth ligand, respectively, Cu(1)–N(5) 2.46(3) and Cu(2)–N(4) 2.55(3) Å, while Cu(3) has an elongated octahedral geometry with O(5) and O(7) occupying the fifth and sixth positions, Cu(3)–O(5) 2.84(3) and Cu(3)–O(7) 2.97(3) Å. The co-ordination geometries of Cu^{II} observed in this cation have frequently been observed previously.[17] Copper(II) ions in the

Table 7 Selected bond distances (Å) and angles (°) for compound **3**

Y(1)···Y(1′)	3.748(5)	Y(1)–O(8′)	2.21(3)	N(1)–C(5)	1.60(6)	N(2)–C(3)	1.35(8)
Y(1)–O(8)	2.26(2)	Y(1)–O(9)	2.19(3)	N(2)–C(6)	1.43(5)	N(2)–C(7)	1.50(7)
Y(1)–O(11)	2.28(3)	Y(1)–O(13)	2.25(3)	N(3)–C(8)	1.39(5)	N(3)–C(11)	1.53(6)
Y(1)–N(7)	2.72(5)	Y(1)–N(8)	2.64(4)	N(3)–C(12)	1.48(6)	N(4)–C(10)	1.45(5)
Cu(1)–O(1)	1.86(3)	Cu(1)–O(3)	1.91(2)	N(4)–C(13)	1.49(5)	N(4)–C(14)	1.46(6)
Cu(1)–O(4)	1.97(3)	Cu(1)–N(1)	2.00(3)	N(5)–C(17)	1.48(5)	N(5)–C(20)	1.51(7)
Cu(2)–O(1)	1.86(3)	Cu(2)–O(2)	1.92(2)	N(5)–C(21)	1.44(6)	N(6)–C(15)	1.42(6)
Cu(2)–O(6)	1.85(3)	Cu(2)–N(2)	1.95(3)	N(6)–C(18)	1.45(6)	N(6)–C(19)	1.39(7)
Cu(3)–O(2)	1.92(3)	Cu(3)–O(3)	1.89(3)	N(7)–C(26)	1.43(8)	N(7)–C(29)	1.48(7)
Cu(3)–N(3)	1.94(4)	Cu(3)–N(6)	2.06(3)	N(7)–C(30)	1.31(6)	N(8)–C(28)	1.35(10)
O(1)–C(2)	1.52(7)	O(2)–C(9)	1.35(5)	N(8)–C(31)	1.42(6)	N(8)–C(32)	1.38(6)
O(3)–C(16)	1.31(5)	O(4)–C(22)	1.20(6)	C(1)–C(2)	1.4(1)	C(2)–C(3)	1.4(1)
O(5)–C(22)	1.22(8)	O(6)–C(24)	1.20(5)	C(8)–C(9)	1.68(6)	C(9)–C(10)	1.44(5)
O(7)–C(24)	1.32(7)	O(8)–C(27)	1.48(6)	C(15)–C(16)	1.53(5)	C(16)–C(17)	1.56(5)
O(9)–C(33)	1.20(6)	O(10)–C(33)	1.20(6)	C(22)–C(23)	1.70(9)	C(26)–C(27)	1.7(1)
O(11)–C(35)	1.38(6)	O(12)–C(35)	1.13(7)	C(24)–C(25)	1.85(6)	C(33)–C(34)	1.68(7)
O(13)–C(37)	1.42(6)	O(14)–C(37)	0.99(7)	C(27)–C(28)	1.43(8)	C(37)–C(38)	1.62(8)
N(1)–C(1)	1.46(7)	N(1)–C(4)	1.29(7)	C(35)–C(36)	1.67(9)		
Y(1)–O(8)–Y(1′)	113(1)	O(8)–Y(1)–O(8′)	66(1)	Cu(1)–O(3)–Cu(3)	127(1)	Cu(2)–O(2)–Cu(3)	126(1)
O(8)–Y(1)–O(9)	91.2(9)	O(8)–Y(1)–O(11′)	147.1(10)	O(1)–Cu(1)–O(3)	88(1)	O(1)–Cu(1)–O(4)	158(1)
O(8)–Y(1)–O(13)	93.4(9)	O(8)–Y(1)–N(7′)	135(1)	O(1)–Cu(1)–N(1)	87(1)	O(3)–Cu(1)–O(4)	94(1)
O(8)–Y(1)–N(8)	68(1)	O(8)–Y(1)–O(9′)	94.1(8)	O(3)–Cu(1)–N(1)	174(1)	O(4)–Cu(1)–N(1)	90(1)
O(8)–Y(1)–O(11)	146(1)	O(8)–Y(1)–O(13′)	91.1(8)	O(1)–Cu(2)–O(2)	91(1)	O(1)–Cu(2)–O(6)	160(1)
O(8)–Y(1)–N(7)	68(1)	O(8)–Y(1)–N(8′)	135(1)	O(1)–Cu(2)–N(2)	85(1)	O(2)–Cu(2)–O(6)	94(1)
O(9)–Y(1)–O(11)	88.4(9)	O(9)–Y(1)–O(13)	174.1(9)	O(2)–Cu(2)–N(2)	174(1)	O(6)–Cu(2)–N(2)	88(1)
O(9)–Y(1)–N(7)	93(1)	O(9)–Y(1)–N(8)	86(1)	O(2)–Cu(3)–O(3)	89(1)	O(2)–Cu(3)–N(3)	85(1)
O(11)–Y(1)–O(13)	85.7(9)	O(11)–Y(1)–N(7)	77(1)	O(2)–Cu(3)–N(6)	156(1)	O(3)–Cu(3)–N(3)	159(1)
O(11)–Y(1)–N(8)	78(1)	O(13)–Y(1)–N(7)	86(1)	O(3)–Cu(3)–N(6)	87(1)	N(3)–Cu(3)–N(6)	105(1)
O(13)–Y(1)–N(8)	91(1)	N(7)–Y(1)–N(8)	155(1)	Cu(1)–O(1)–Cu(2)	136(1)	Cu(1)–O(1)–C(2)	108(3)

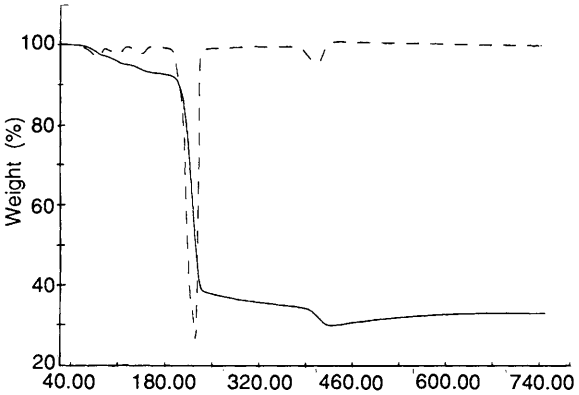


Fig. 8 The TGA diagram for compound **1**. Sample weight: 17.153 mg. Scanning rate 10 °C min^{-1}

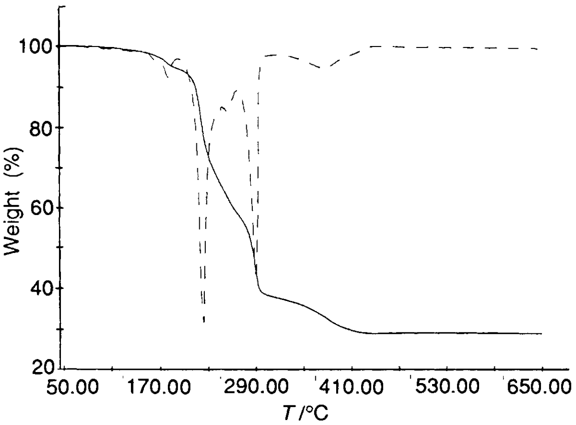


Fig. 9 The TGA diagram for compound **2a**. Sample weight: 7.946 mg. Scanning rate 20 °C min^{-1}

presence of bdmap and carboxylate ligands tend to form cyclic Cu_4 compounds.[4b] The unusual cyclic Cu_3 cation could not be obtained by alternative synthesis where no yttrium anion was involved. The mutual dependence of the cation and anion complexes in **3** is a fascinating phenomenon which is not understood.

Thermal Properties.—The thermal properties of compounds **1**–**3** were investigated by thermal gravimetric analysis (TGA) experiments carried out under an oxygen atmosphere. The TGA diagrams for compounds **1**, **2a** and **3** are given in Figs. 8–10, respectively. The dashed lines shown are the first derivatives of the weight-loss curves. Compound **1** underwent initial weight loss in the temperature range 130–160 °C which can be attributed to the partial loss of the water molecules in the lattice. A rapid weight loss occurred at 190–230 °C. The residual mass at 236 °C (about 40%) corresponds to the formula $Cu_4O_2(CO_3)_2$ (41%). A third major weight loss occurred at 400–425 °C, the residual mass at 425 °C being consistent with the formula Cu_4O_4 (31%). Interestingly, a steady weight increase occurred after this temperature. A steady residual mass (33%) was obtained after about 700 °C. The origin of this weight increase is not understood. In order to confirm it, we examined the residue by X-ray powder diffraction analysis, which revealed an essentially pure CuO phase. Compound **2a** underwent several stages of weight loss in the temperature range 150–430 °C. A major weight loss occurred at 190–310 °C, the residual mass at 310 °C being consistent with the formula $LaCu_2(O_3C)_3O_{0.5}$. After 430 °C no further weight loss occurred. The mass of the final pyrolysis product corresponds to 28% of compound **2a**, in agreement with the empirical formula $LaCu_2O_{3.5}$. Compound **2b** decomposes similarly to yield the residue $NdCu_2O_{3.5}$. Compound **3** lost about 1.8% weight in the temperature range 101–126 °C which corresponds to the loss of a thf molecule. The weight of the sample became constant after 530 °C. The residual mass is 25% of that of compound **3**, in agreement with the empirical formula $Y_2Cu_6O_9$. The $BaCu_4$ compound mentioned earlier also decomposed to the corresponding oxide $BaCu_4O_{10}$ at about 400 °C.[12] For all the bimetallic compounds no formation of copper(III) oxides was observed. Although the details of the pyrolysis process are not understood and the phases of these oxide products not identified, the TGA results clearly indicated that mixed-metal complexes with bdmap and carboxylate do decompose to the corresponding oxides at moderate temperatures and carbonate intermediates may be involved.

Magnetic Properties.—The magnetic susceptibilities of compounds **1**, **2a** and **3** were measured in the temperature range 4–300 K. All data were corrected for diamagnetism. The contributions from temperature-independent paramagnetism and monomeric impurities were taken into consideration in the fitting of the data according to equation (3), where ρ is

$$\chi_{obs} = (1 - \rho)\chi_{calc} + \chi_{tip} + \rho\chi_{mono} + \chi_{diam} \qquad (3)$$

the percentage of monomer impurity. The function $\Sigma(\chi_{obs} - \chi_{calc})^2T^2$ was minimized. The R factor is defined as $[\Sigma(\chi_{obs} - \chi_{calc})^2T^2/\Sigma(\chi_{obs}T)^2]^{\frac{1}{2}}$. The data for compound **1** were fitted by using a tetramer chain model[18] involving two exchange constants, $J_{21} = J_{1'2'} = J_1$ and $J_{11'} = J_2$. The data for **2a** were fitted by using the standard dimer model[19] with one exchange contant J. A substantial monomer contribution (11%) was necessary. The best fit was obtained by fixing the g value at 2.0. The origin of the monomer contribution is not clear since repeated measurements using analytically pure samples produced the same results. Compound **3** was treated as two independent trimers and the data were fitted by using a trimer model involving two independent exchange contants, $J_{13} = J_{23} = J_1$ and $J_{12} = J_2$, derived by Kambe's method.[20] A contribution from intertrimer interaction was considered by including a Weiss contant θ. Several comparable best-fit solutions were obtained for this compound and all of them produced a low g value. One solution, which we consider more plausible, yielded $J_1 = -66(1)$ cm^{-1} and $J_2 = 276.5(3)$ cm^{-1} with g being fixed at 1.92. The J_1 value is much less definitive than J_2. Compound **3** is a complicated magnetic system. Similar problems have also been encountered in trinuclear copper(II) compounds reported previously.[21] A better theoretical approach than Kambe's model may be needed to obtain a greater understanding and interpretation of the magnetic behaviour of the tricopper system. The experimental data, magnetic moments, and the theoretical fitting (the solid line) for these three compounds are shown in Figs. 11–13. The parameters are summarized in Table 8. Although the nature of the magnetic exchange in **3** remains inconclusive, the data show clearly that the magnetic exchanges in compounds **1** and **2a** are dominated by antiferromagnetism.

Table 8 Parameters from the susceptibility fitting

Compound	J/cm^{-1}	ρ (%)	g	$10^3\chi_{tip}$	θ
1	$J_1 = -84.7(1)$ $J_2 = 10.0(1)$	0.23	2.24(1)	2.115	
2a	$J = -6.0(1)$	11	2.0	1.997	
3	$J_1 = -66(1)$ $J_2 = 276.5(3)$	0.23	1.92	7.117	−0.61

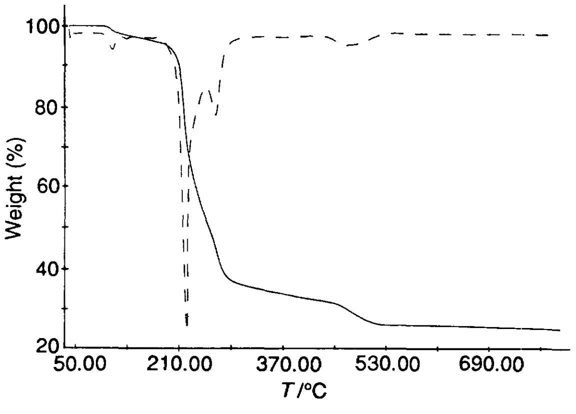


Fig. 10 The TGA diagram for compound **3**. Sample weight: 7.885 mg. Scanning rate: 20 °C min^{-1}

Conclusion

The precursor system with Hbdmap and carboxylic acid as the cross-linking reagents could be useful for the formation of the $YBa_2Cu_3O_{7-x}$ superconducting film. Homo- and hetero-nuclear species linked by bdmap and carboxylate ligands with versatile structures related to this precursor system have been characterized. These polynuclear complexes with bdmap and trifluoroacetate ligands readily decompose to the corresponding oxides when heated under an oxygen atmosphere, which may account for the ready formation of the superconductor in this system. The magnetic exchange is dominated by antiferromagnetism in compounds with even numbers of copper(II) ions. Further theoretical study is needed unambiguously to establish the nature of the magnetism in the Y_2Cu_6 compound.

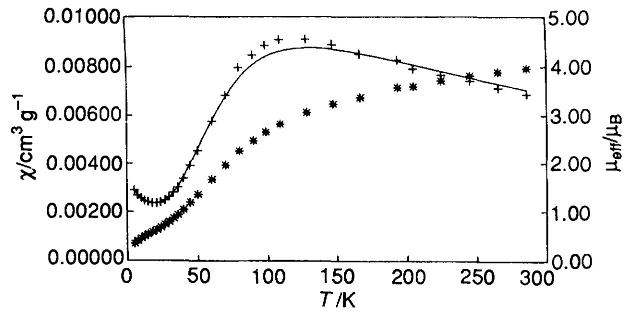


Fig. 11 Plots of molar susceptibility (+) and magnetic moment (*) *versus* temperature for compound **1**

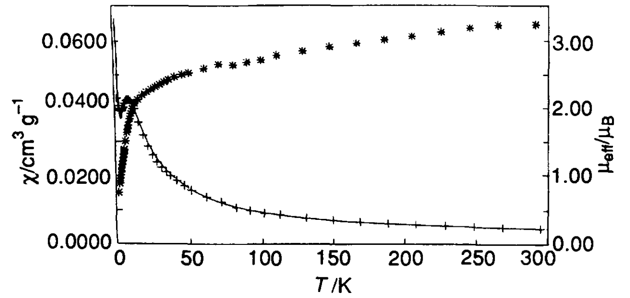


Fig. 12 Plots of molar susceptibility (+) and magnetic moment (*) *versus* temperature for compound **2a**

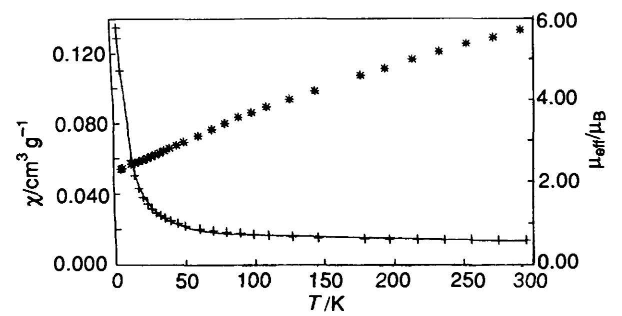


Fig. 13 Plots of molar susceptibility (+) and magnetic moment (*) *versus* temperature for compound **3**

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