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STRUCTURE AND PROPERTIES OF HETEROMETALLIC ALKOXIDES CONTAINING COPPER(I)

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Abstract—The heterometallic Cu^I alkoxides $Li_4Cu_4(OCMe_3)_8$ (**1**) and $Ba_2Cu_4(OCEt_3)_8$ (**3**) were synthesized from the component single metal alkoxides in anhydrous THF solution. Only **1** sublimes without decomposition under vacuum (150°C); **3** is non-volatile. Crystal structures were determined for **1**, **3** and the previously reported $Na_4Cu_4(OCEt_3)_8$ (**2**). Compounds **1** and **2** have nearly identical $M_4Cu_4O_8$ cores consisting of two puckered M_2O_2 rings related by a centre of symmetry and joined at the oxygens by two bridging copper atoms, and at the M edges by two nearly linear O—Cu—O units. Compound **3** has a $Ba_2(OR)_2$ ring containing the centre of symmetry and is bridged by two $Cu_2(OR)_3$ units that are nearly perpendicular to the Ba_2O_2 ring. The two $BaCu_2O_3$ planes in **3** are parallel, but separated by 0.48 Å. Hydrolysis of compounds **1**–**3** in THF afforded an orange or orange–brown solid that was converted to the mixed metal oxide by thermolysis, but copper and Cu_2O were also produced from the $Li_4Cu_4(OCMe_3)_8$ hydrolysis product.

The discovery of cuprate superconductors has prompted numerous researchers to synthesize alkoxide and acetylacetonate precursors for copper oxides.[1] While a fair number of mixed metal alkoxides containing Cu^{II} have been isolated and characterized, few heterometallic Cu^I alkoxides are known. Those reported to date include two zirconium–copper(I) alkoxides, $Cu_2Zr_2(OCHMe_2)_{10}$ and $Cu_4Zr_4(OCHMe_2)_{18}$,[2] the sparingly soluble solids $(NaCu(OCMe_3)_2)_n$ and $(BaCu_2(OCMe_3)_4)_n$, and the tetramer $(NaCu(OCEt_3)_2)_4$.[3] Of the latter, only the zironium complexes have been structurally characterized. Here we report the synthesis and structure of two more Cu^I mixed metal alkoxides, $Li_4Cu_4(OCMe_3)_8$ and $Ba_2Cu_4(OCEt_3)_8$, the crystal structure of $Na_4Cu_4(OCEt_3)_8$ and the hydrolysis reactions of all three compounds.

EXPERIMENTAL

General comments

All manipulations were performed under helium in a Vacuum-Atmospheres Dri-Lab, in a Pyrex bulb equipped with a stirbar and a Kontes valve, or on the vacuum line. All non-deuterated solvents were dried by distillation from sodium benzophenone ketyl before use, deuterated solvents were distilled from sodium/potassium. The alkoxides $LiOCMe_3$, $Ba(OCEt_3)_2$, $(CuOCMe_3)_4$, $(CuOCEt_3)_4$ and $Na_4Cu_4(OCEt_3)_8$ were prepared as described previously.[3,4] NMR spectra were recorded on a Bruker MSL-300 or a Bruker AC-300 instrument. The 2-D COLOC spectra for **2** and **3** were obtained with a standard COLOC sequence[5] using 0.03 s and 0.015 s as the polarization and refocussing delays, respectively. Elemental analyses were performed by E+R Microanalytical Laboratories Inc., Corona, NY.

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Synthesis of $Li_4Cu_4(OCMe_3)_8$ (**1**)

A THF solution of $LiOCMe_3$ (60 mg, 0.75 mmol) was added to a hot THF solution of $(CuOCMe_3)_4$ (101 mg, 0.185 mmol) in a round-bottomed flask and allowed to stand for 16 h (total volume ≈ 50 cm^3). The liquid was decanted and the colourless crystals were washed with THF and dried *in vacuo*; 121 mg (75%) were isolated. Compound **1** was also made in low yield from a reaction between $Cu(N(CN)_2)_2$[6] (0.203 g, 1.04 mmol) and $LiOCMe_3$ (0.333 g, 4.16 mmol) in boiling THF (25 cm^3). Yellowish crystals of **1** (95 mg) precipitated from the brown solution over several weeks. Found (Calc.) for $Li_4Cu_4O_8C_{32}H_{72}$: C, 44.5 (44.3); H, 8.2 (8.4); Li, 2.9 (3.2); Cu, 29.3 (29.3).

Synthesis of $Ba_2Cu_4(OCEt_3)_8$ (**3**)

A THF solution of $CuOCEt_3$ (0.2575 g, 1.44 mmol, 10 cm^3) was added to $Ba(OCEt_3)_2$ (0.2496 g, 0.679 mmol) and boiled for 30 min in a round-bottomed flask. Some of the $Ba(OCEt_3)_2$ did not dissolve. After standing stoppered for 4 days, the mixture was filtered through a fine frit and the solvent removed *in vacuo*. The resulting solid was redissolved in hot hexane containing a few drops of THF, and after cooling to room temperature, the solution was transferred to a stoppered vial and allowed to evaporate slowly to dryness (over several months) in the Dri-Lab. A large colourless crystal of $Ba_2Cu_4(OCEt_3)_8$ was mechanically separated with a scalpel from impurities, isolated yield 126 mg (25%). Found (Calc.) for $Ba_2Cu_4C_{56}H_{120}O_8$: C, 46.3 (46.4); H, 8.1 (8.3); Ba, 18.8 (18.9); Cu, 17.3 (17.5).

A repeat reaction involving $CuOCEt_3$ (0.508 g, 2.84 mmol), a slight excess of $Ba(OCEt_3)_2$ (0.530 g, 1.44 mmol) and THF (15 cm^3) was stirred in a bulb at room temperature for 12 h and 70°C for 6 h, and filtered. After solvent removal, the filtrate was redissolved in benzene and filtered through dry talc. Solvent removal *in vacuo* afforded a slightly yellowed solid, 0.668 g (64%). The NMR spectrum indicates a slight amount of impurities; the latter material was used for two-dimensional NMR experiments.

Hydrolysis experiments

The alkoxides (40–200 mg) were dissolved in 5–10 cm^3 dry THF [$Li_4Cu_4(OCMe_3)_8$ had to be heated to dissolve] and frozen at -196°C. An excess of H_2O (at least two-fold) was condensed onto the THF solution. The mixture was slowly warmed to ambient temperature, stirred for several hours and filtered to isolate the orange (Ba) or orange–brown (Li, Na) solid. The solids were heated under dynamic vacuum to 475°C for conversion to LiCuO or NaCuO, and 800°C for $BaCu_2O_2$.

Crystal structure determinations

Suitable crystals of **1, 2** and **3** were mounted in thin-walled glass capillaries under inert gas atmosphere. Data were collected in the θ–2θ mode on an automated Siemens R3m/V diffractometer equipped with an incident beam graphite monochromator (Mo-K_α, $\lambda = 0.71073$ Å) at 233 K. Data were corrected for Lorentz and polarization effects and semi-empirical absorption corrections were applied. Maximum and minimum transmissions were 0.88 and 0.60, 0.46 and 0.14, and 0.53 and 0.46, respectively for **1, 2** and **3**. In each case the structures were determined by direct methods and refined using full matrix least-squares methods as implemented by the program SHELXTL.[7] In all the structures the parameters refined included the coordinates and anisotropic thermal parameters for all but the hydrogen atoms. Hydrogen atoms were placed in idealized positions (C—H = 0.96 Å) and the coordinate shifts for carbon were applied to the bonded hydrogens. The isotropic thermal parameters for the hydrogens were fixed. In each of the complexes one or more of the alkoxide groups showed some evidence of disorder; however, it was not possible to discretely model the disorder. Additional data collection and refinement parameters are given in Table 1, and selected distances and angles in Table 2. Atom coordinates and complete listings of bond angles and distances have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Synthesis and properties

The mixed Cu^I alkoxides were all synthesized from the direct reaction of the component alkoxides in dry THF under an inert atmosphere:

$$M(OR)_x + xCu(OR) \rightarrow 1/n(MCu_x(OR)_{2x})_n \qquad (1)$$

$Li_4Cu_4(OCMe_3)_8$ (**1**)

$Na_4Cu_4(OCEt_3)_8$ (**2**)

$Ba_2Cu_4(OCEt_3)_8$ (**3**)

X-ray crystallography reveals both **1** and **2** to have identical atomic arrangements of their centrosymmetric $M_4Cu_4O_8$ cores (Figs 1 and 2), while **3** has the unique structural arrangement of a

Table 1. Crystal and refinement data

	1	**2**	**3**
Formula	$[LiCu(OC(CH_3)_3)_2]_4$	$[NaCu(OC(CH_2CH_3)_3)_2]_4$	$[BaCu_2(OC(CH_2CH_3)_3)_4]_2$
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.822(5)	11.926(3)	13.396(6)
b (Å)	11.273(5)	12.771(2)	13.040(5)
c (Å)	11.655(4)	12.860(3)	20.401(8)
α (°)	68.62(3)	64.11(2)	90.00
β (°)	72.97(3)	74.68(2)	97.93(3)
γ (°)	88.21(4)	78.75(2)	90.00
V (Å^3)	1144.8(9)	1692.3(7)	3530(2)
Z	1	1	2
Formula weight	866.8	1267.6	1450.4
F(000)	456	680	1496
ρ(*calc*) (*g cm*$^{-3}$)	1.257	1.310	1.365
Crystal dim. (mm)	0.18 × 0.42 × 0.42	0.18 × 0.34 × 0.58	0.30 × 0.32 × 0.45
μ, absorption coeff. (mm^{-1})	1.87	1.31	2.32
2θ max. (°)	50	45	45
2θ scan speed (° min^{-1})	variable 10–30	variable 10–30	variable 7.5–30
2θ scan range (°)	$2.0+\Delta_{\alpha1\alpha2}$	$2.4+\Delta_{\alpha1\alpha2}$	$2.0+\Delta_{\alpha1\alpha2}$
Data collected, h,k,l	−8 to 11, −13 to 13, −13 to 13	−12 to 0, −13 to 13, −13 to 13	−14 to 14, 0 to 14, −22 to 0
Unique data	4067	4432	4604
R_{int}	0.021	0.010	0.010
Unique data, $F_0 > 4\sigma(F_0)$	3016	3423	3273
Parameters refined	229	326	319
Weighting function, g[a]	0.00023	0.00023	0.00023
R[b], R_w[c], S[d]	0.060, 0.073, 2.57	0.056, 0.063, 2.27	0.091, 0.078, 1.96
Fourier excursions (e Å^{-3})	1.60, −0.81	0.88, −0.58	1.84, −1.74

[a] $w^{-1} = \sigma^2(F_0)+gF_0^2$.
[b] $\Sigma|\Delta|/\Sigma|F_0|$.
[c] $[\Sigma(w\Delta^2)/\Sigma(wF_0^2)]^{1/2}$.
[d] $[\Sigma w(\Delta^2)/(N_0-N_p)]^{1/2}$.

$Ba_2(OR_2)$ ring bridged by two $Cu_2(OR)_3$ units (Fig. 3). The solution NMR spectra (Table 3) are consistent with the crystal structures; the spectra for compounds **1** and **2** show two magnetically inequivalent OR groups in a 1 : 1 ratio, while **3** has three different $OCEt_3$ groups in a 1 : 2 : 1 ratio. Sharp resonance lines were observed in all cases. Examination of the ^1H NMR data in Table 3 shows that the chemical shift of sodium and lithium alkoxides are generally upfield from the copper(I) alkoxides, as one would expect based on electronegativity considerations. It is difficult to extend this to compounds **1** and **2** because the peaks are too close together to definitively distinguish between the alkoxy groups bridging Cu(1) or Cu(1A) to two alkali metal atoms, and the bridging alkoxides between Cu(2) and a single alkali metal atom. The peaks in **3** are, however, more easily assigned. Based on their integrals, the ^1H peaks at δ 0.99 and 1.34 in **3** must belong to the four $OCEt_3$ groups bridging between barium and copper. The resonances at δ 1.07 and 1.67 are probably from the two $OCEt_3$ groups bridging Ba(1) to Ba(1A), and the CH_3 and CH_2 peaks at 1.34 and 1.81 respectively should be from the bridges between two copper atoms. The correspondence between the CH_3 and CH_2 peaks on any given ethyl group was verified with a standard two-dimensional COSY spectrum.

The trend in the ^{13}C spectra is similar for the α-carbons (to the oxygen), and opposite for the γ-carbons (alkali metals cause a downfield shift for the latter). No clear trend is evident for the β-carbons. Standard HETCOR and COLOC[5] two-dimensional spectra were used to unambiguously associate the carbon and proton spectra of the $OCEt_3$ complexes **2** and **3**. Clearly, the trend noted

Table 2. Selected bond lengths (Å) and angles (°)

1		**2**		**3**	
Cu(1)—Cu(1A)	2.920(2)	Cu(1)—Cu(1A)	3.374(2)	Ba(1)—Ba(1A)	3.963(3)
Cu(1)—Cu(2)	3.507(2)	Cu(1)—Cu(2)	4.373(2)	Cu(1)—Cu(2)	3.008(3)
Li(1)—Cu(1)	2.89(1)	Na(1)—Cu(1)	3.180(4)	Cu(1)—Ba(1A)	3.539(3)
Li(1)—Cu(2)	2.81(1)	Na(1)—Cu(2)	3.137(2)	Ba(1)—Cu(2)	3.571(3)
Li(1)—Cu(1A)	2.88(1)	Na(1)—Cu(1A)	3.256(4)	Cu(1)—O(1)	1.82(1)
Li(1)—Li(2A)	2.65(1)	Na(1)—Na(2A)	3.286(3)	Cu(1)—O(2)	1.83(1)
Li(2)—Cu(1)	2.89(1)	Na(2)—Cu(1)	3.170(2)	Cu(2)—O(3)	1.83(1)
Li(2)—Cu(1A)	2.90(1)	Na(2)—Cu(1A)	3.111(3)	Cu(2)—O(1)	1.84(1)
Li(2)—Cu(2)	2.79(1)	Na(2)—Cu(2)	3.142(3)	Ba(1)—O(2A)	2.58(1)
Cu(1)—O(1)	1.850(5)	Cu(1)—O(1)	1.843(4)	Ba(1)—O(3)	2.59(1)
Cu(1)—O(2)	1.855(5)	Cu(1)—O(2)	1.834(4)	Ba(1)—O(4)	2.51(1)
Cu(2)—O(3)	1.823(5)	Cu(2)—O(3)	1.822(5)	Ba(1)—O(4A)	2.54(1)
Cu(2)—O(4)	1.831(5)	Cu(2)—O(4)	1.825(5)	C—O(Avg)	1.42(2)
Li(1)—O(1)	1.94(1)	Na(1)—O(1)	2.292(6)	C—C(Avg)	1.50(4)
Li(1)—O(2A)	1.94(1)	Na(1)—O(2A)	2.314(5)		
Li(1)—O(3)	1.80(1)	Na(1)—O(3)	2.179(5)		
Li(2)—O(1A)	1.93(1)	Na(2)—O(1A)	2.333(5)		
Li(2)—O(2)	1.93(1)	Na(2)—O(2)	2.318(5)		
Li(2)—O(4)	1.79(1)	Na(2)—O(4)	2.192(5)		
C—O (Avg)	1.43(1)	C—O (Avg)	1.44(1)		
C—C (Avg)	1.51(1)	C—C (Avg)	1.53(2)		
O(1)—Cu(1)—O(2)	175.6(2)	O(1)—Cu(1)—O(2)	174.7(2)	O(1)—Cu(1)—O(2)	174.9(5)
O(3)—Cu(2)—O(4)	175.5(2)	O(3)—Cu(2)—O(4)	171.2(2)	O(3)—Cu(2)—O(1)	177.4(5)
Cu(1)—O(1)—Li(1)	99.3(4)	Cu(1)—O(1)—Na(1)	100.0(2)	O(3)—Ba(1)—O(2A)	134.5(3)
Cu(1)—O(1)—Li(2A)	99.8(4)	Cu(1)—O(1)—Na(2A)	95.6(2)	O(2)—Ba(1A)—O(4)	104.3(3)
Cu(1)—O(2)—Li(2)	99.5(4)	Cu(1)—O(2)—Na(2)	98.9(2)	O(4)—Ba(1)—O(2A)	111.1(3)
Cu(2)—O(3)—Li(1)	102.0(4)	Cu(2)—O(3)—Na(1)	102.9(2)	O(3)—Ba(1)—O(4A)	99.3(3)
Cu(2)—O(4)—Li(2)	100.8(5)	Cu(2)—O(4)—Na(2)	102.5(2)	O(3)—Ba(1)—O(4)	111.9(3)
O(1)—Li(1)—O(3)	131.8(7)	O(1)—Na(1)—O(3)	138.5(2)	O(4)—Ba(1)—O(4A)	76.5(3)
O(1)—Li(1)—O(2A)	91.4(5)	O(1)—Na(1)—O(2A)	88.1(2)	Cu(1)—O(1)—Cu(2)	110.4(3)
O(3)—Li(1)—O(2A)	129.9(5)	O(3)—Na(1)—O(2A)	125.9(2)	Cu(1)—O(2)—Ba(1A)	105.4(4)
O(2)—Li(2)—O(4)	131.9(5)	O(2)—Na(2)—O(4)	137.7(2)	Cu(2)—O(3)—Ba(1)	106.4(5)
O(2)—Li(2)—O(1A)	92.0(5)	O(2)—Na(2)—O(1A)	87.1(2)	Ba(1)—O(4)—Ba(1A)	103.5(3)
O(4)—Li(2)—O(1A)	129.6(7)	O(4)—Na(2)—O(1A)	130.1(2)		
Li(1)—O(1)—Li(2A)	86.3(5)	Na(1)—O(1)—Na(2A)	90.6(2)		
Li(2)—O(2)—Li(1A)	86.3(5)	Na(2)—O(2)—Na(1A)	90.4(2)		
Symmetry operation denoted by suffix A					
$(-x, 1.0-y, 1.0-z)$		$(-x, 1.0-y, 2.0-z)$		$(1.0-x, -y, -z)$	

above for the α-carbons does not hold for **3**. The two-dimensional heteronuclear spectra for **3** are reproduced in Fig. 4.

Only **1** sublimes completely under vacuum, while **2** sublimes with decomposition and **3** decomposes when heated under vacuum. There is a marked difference in solubility between the t-butoxides and t-heptoxides; **1** is only a little more soluble than the previously reported sodium and barium copper(I)-t-butoxides,[3] while the t-heptoxides are very soluble in organic solvents. This suggests the use of the t-heptoxides as sol–gel precursors for copper oxides. To test this hypothesis, we hydrolysed **1–3** in THF solution:

$$\mathrm{MCu}_x(\mathrm{OR})_{2x} + \text{excess}\ \mathrm{H_2O} \xrightarrow{\mathrm{THF}} \xrightarrow{475\text{–}800^\circ\mathrm{C,\ vac}} \mathrm{MCu}_x\mathrm{O}_x. \tag{2}$$

The ternary $\mathrm{Cu^I}$ oxides NaCuO and $\mathrm{BaCu_2O_2}$ were obtained from **2** and **3** respectively, while the LiCuO from **1** contained copper and $\mathrm{Cu_2O}$ impurities. These aforementioned oxides were identified by comparison of their X-ray powder patterns with

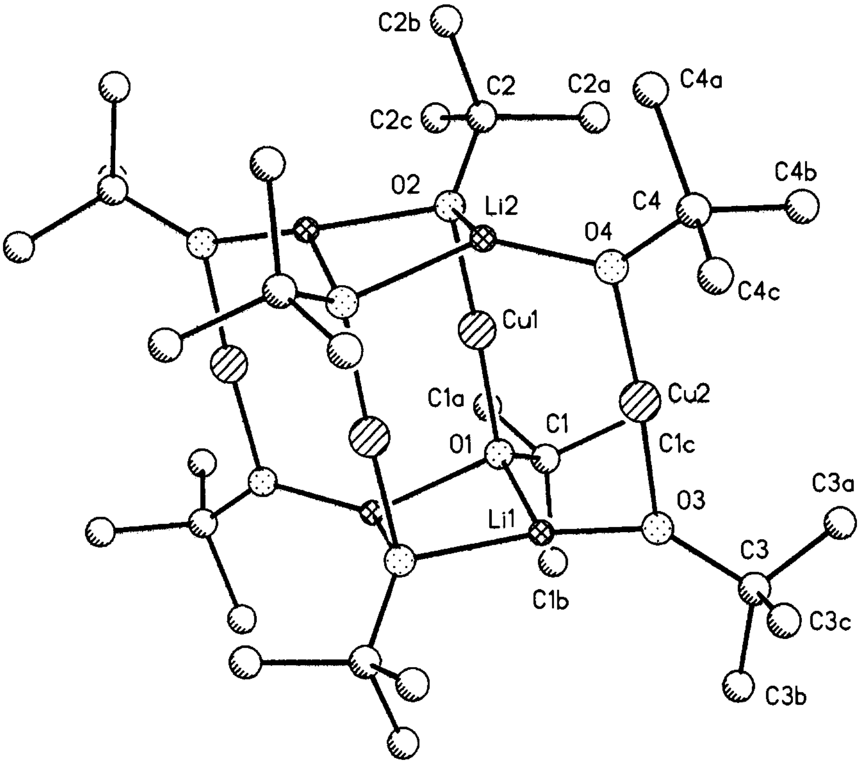

Fig. 1. Structure of $Li_4Cu_4(OCMe_3)_8$ (1).

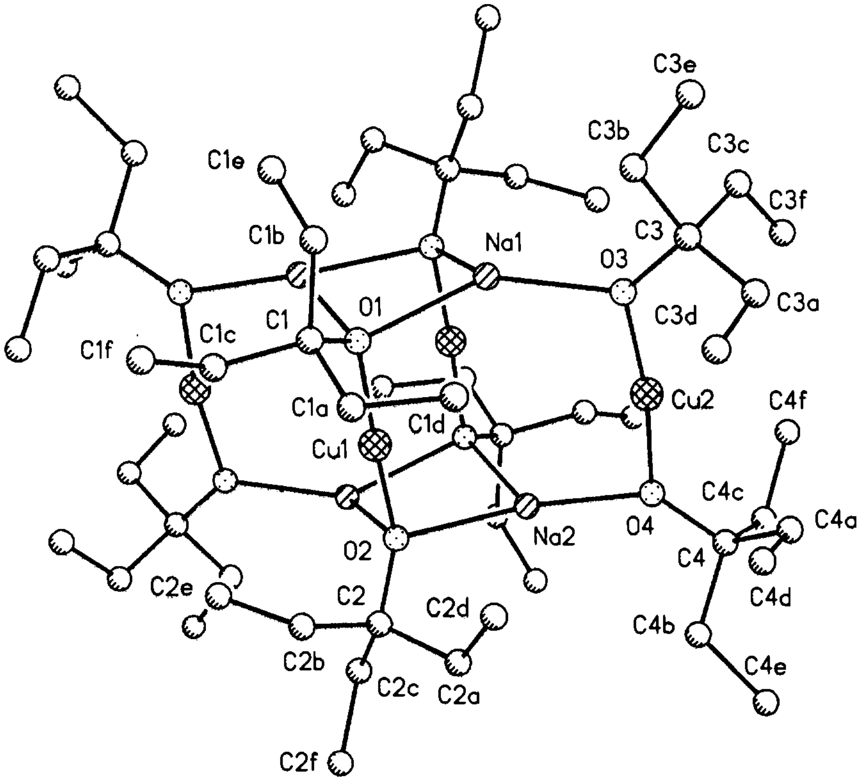

Fig. 2. Structure of $Na_4Cu_4(OCEt_3)_8$ (2).

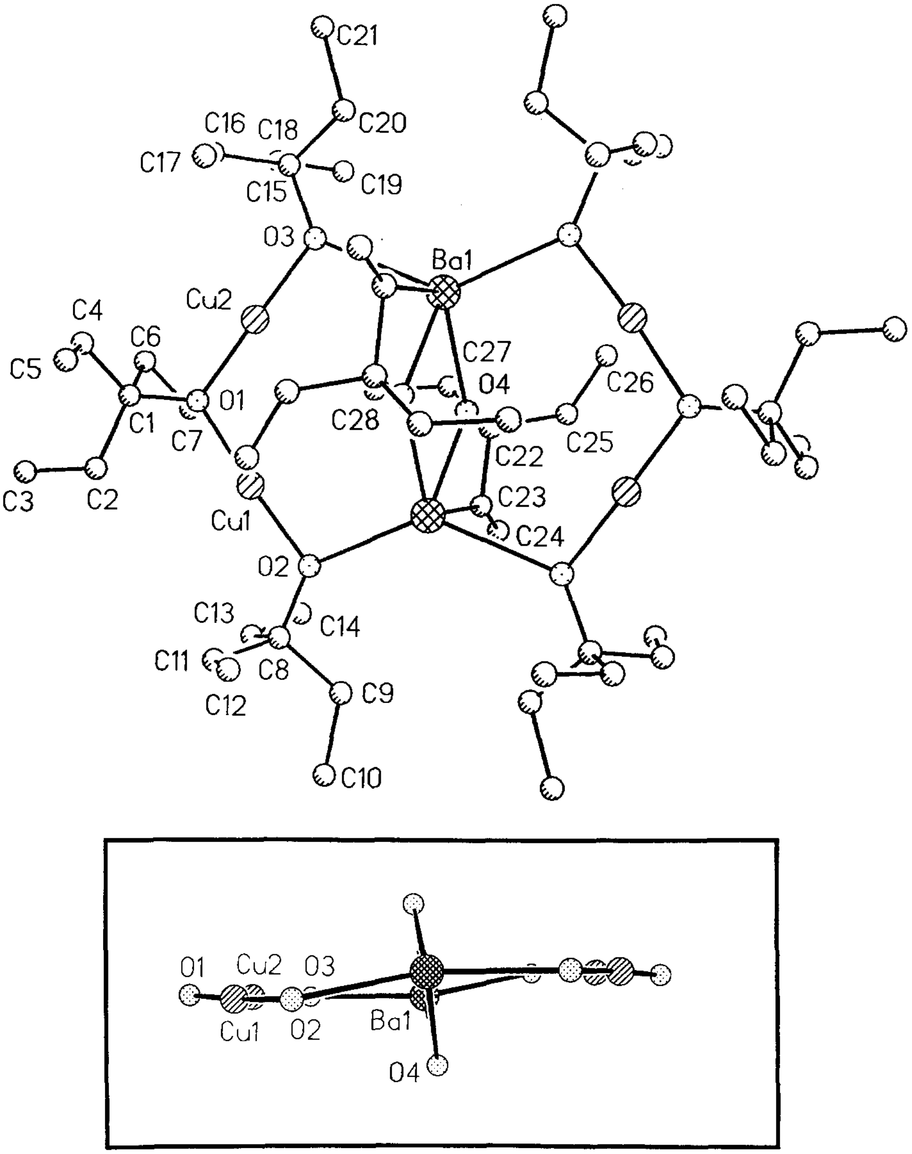

Fig. 3. Structure of $Ba_2Cu_4(OCEt_3)_8$ (3) (top). Inset (bottom) shows a side view of the $Ba_2Cu_4O_8$ core with the $\{BaCu_2O_3\}$ planes oriented perpendicular to the plane of the paper.

the literature.[8] The reason for Cu_2O formation is uncertain, but the copper metal was undoubtedly produced from thermal decomposition of Cu_2O *in vacuo*.

Crystal structures

The geometry of complexes **1** and **2** are very similar for the metal and oxygen framework with differences due mainly to lithium and sodium ion size (Figs 1 and 2). These two complexes are clearly dominated by the preference of Cu^I atoms for two-coordinate linear geometry in homoleptic complexes of simple monodentate ligands such as R, OR and NR_2. Exceptions to the latter only occur when extreme steric bulk or additional ligands are present.[9] The O—Cu—O angles, which range from 171.2 to 175.6°, are in the normal range observed for copper(I) alkoxides, for example O—Cu—O angles range from 172.1 to 176.8° in $(CuOCMe_3)_4$ and from 172.3 to 173.9° in $Cu_4Zr_4O(OCHMe_2)_{18}$.[2] These $\{CuO_2\}$ moieties are arranged parallel to one another in a diamond shape about a crystallographic inversion centre. The copper atoms are exactly planar, and the oxygens are in two nearly planar and parallel layers with respect to the copper plane (mean deviation from a least squares plane is 0.012 Å for **1** and 0.008 Å for **2**). The three-coordinate lithium and sodium atoms are also planar and approximately normal to the copper plane

Table 3. Physical properties of compounds

	NMR[a]										
	^{1}H		^{13}C				Solubility[b]				
Compound	CH_3	CH_2	CH_3	CH_2	C		H	B	T	Sub.[c] (dec.)	Ref.
$Li_4Cu_4(OCMe_3)_8$[d]	1.45		35.0		69.4	4 OR	—	sl	sl	150	
	1.50		35.9		71.0	4 OR					
$Na_4Cu_4(OCEt_3)_8$[e]	1.05	1.55	9.74	35.5	75.0	4 OR	v	v	v	185 (220)	3
	1.13	1.61	9.22	35.3	74.0	4 OR					
$Ba_2Cu_4(OCEt_3)_8$[e]	0.99	1.52	8.90	34.6	76.9	4 OR	v	v	v	N (170)	
	1.07	1.67	8.78	35.0	78.1	2 OR					
	1.34	1.81	10.7	35.1	76.4	2 OR					
$(CuOCMe_3)_4$	1.30		35.7		72.6			v	s		4
$(LiOCMe_3)_6$	1.26		35.7		65.0			v	v	170[f] (250)	10c
$(CuOCEt_3)_4$	1.00	1.47	8.70	34.7	77.2		v	v	v	110 (135)	3
$(LiOCEt_3)_n$[g]	0.86	1.37	9.36	34.4	72.5		v	v	v	122	
$(NaOCEt_3)_n$	0.88	1.23	9.50	35.9	71.3		v	v	v	130 (135)	3
$[Ba(OCEt_3)_2]_n$[d]	0.81	1.37	—	—	—		i	i	sl	265 (350)	3

[a] C_6D_6 solvent unless indicated otherwise.
[b] H, hydrocarbon; B, benzene; T, THF.
[c] Dynamic vacuum unless indicated otherwise.
[d] D-8 THF NMR solvent.
[e] Correlation between ^{1}H and ^{13}C NMR verified by 2-D NMR.
[f] 1 atm. pressure.
[g] Minor oligomer also present, δ 0.99 and 1.57.

(dihedral angle between planes is 90.2° for **1** and 88.3° for **2**). Lithium atoms are positioned an average of 0.28 Å outside the oxygen planes in **1** and sodium atoms are on average 0.31 Å outside the oxygen planes in **2**, such that the Li—O and Na—O bonding is slightly pyramidal. The Li_2O_2 and Na_2O_2 rings are puckered with a dihedral angle between the LiO_2 ring planes of 157.8° and between the NaO_2 ring planes of 159.2°. Alkali metals in most organometallic complexes are at least four-coordinate and lower coordination is relatively rare. While there have been a number of three-coordinate $\{LiO_3\}$ complexes reported,[10] a literature search found only $(NaOCMe_3)_6$ with a similar three-coordinate $\{NaO_3\}$ geometry for sodium.[11] The Li—O distances average 1.94 Å to the μ_3-$OCMe_3$ within the Li_2O_2 ring and 1.80 Å to the μ_2-$OCMe_3$ [in **1** and **2**, O(3) and O(4) are planar with angles that sum to $>359.7°$]. These distances are comparable to Li—O distances in other three-coordinate complexes, i.e. $LiOCBu_3(THF)$,[10a] $LiOAr(OEt_2)$[10d] and $LiOCMe_2Ph$[10c] range from 1.84 to 1.91 Å; in two-coordinate $LiOC(CMe_3)_3$,[12] Li—O = 1.75 Å. In **2** the average Na—μ_3O and Na—μ_2O distances are 2.314 and 2.185 Å, respectively. In $(NaOCMe_3)_6$, Na—O distances[11b] range from 2.14 to 2.39 Å and average 2.25 Å.

Complex **3** has C_i molecular symmetry and the metal oxygen framework consists of three planes, two symmetry-related $\{BaCu_2O_3\}$ parallel planes about 0.48 Å apart and an intersecting planar $\{Ba_2O_2\}$ ring (see inset in Fig. 3). The geometric arrangement around the Cu^{I} atoms is two-coordinate and linear (O—Cu—O = 174.9 and 177.5° respectively for the two crystallographically unique coppers). Both Cu(1) and Cu(2) share a common μ_2 oxygen, O(1), which may be extended to include Ba(1) to form a plane that passes *ca* 0.24 Å from the inversion centre (average deviation from a least squares plane $\{BaCu_2O_3\}$ is 0.02 Å). The four-coordinate barium, bridged by μ_2 oxygen O(4), forms a planar Ba_2O_2 ring that is centred on the inversion centre and is near normal to the $\{BaCu_2O_3\}$ plane. The dihedral angle between the respective planes is 80.0°. Within **3**, average Cu—O distances are 1.83 Å, the expected values for two-coordinate Cu^{I}. Values of 1.84 Å have been observed in $BaCu_2O_2$,[8b] $Cu—O_{av} = 1.85$ Å in $Cu_2Zr_2(OCHMe_2)_{10}$,[2] and are 1.83 and 1.84 Å in **1** and **2**. The Cu—O—Cu angle is 110.4° in **3**. In the two previously cited complexes Cu—O—Cu = 102° in $BaCu_2O_2$, which has $(Cu—O)_\infty$ chains, and 92.0° in $Cu_2Zr_2(OCHMe_2)_{10}$, whose geometry has some similarity to **3** with a (O—Cu—O—Cu—O) unit bridging a (Zr2(OCH

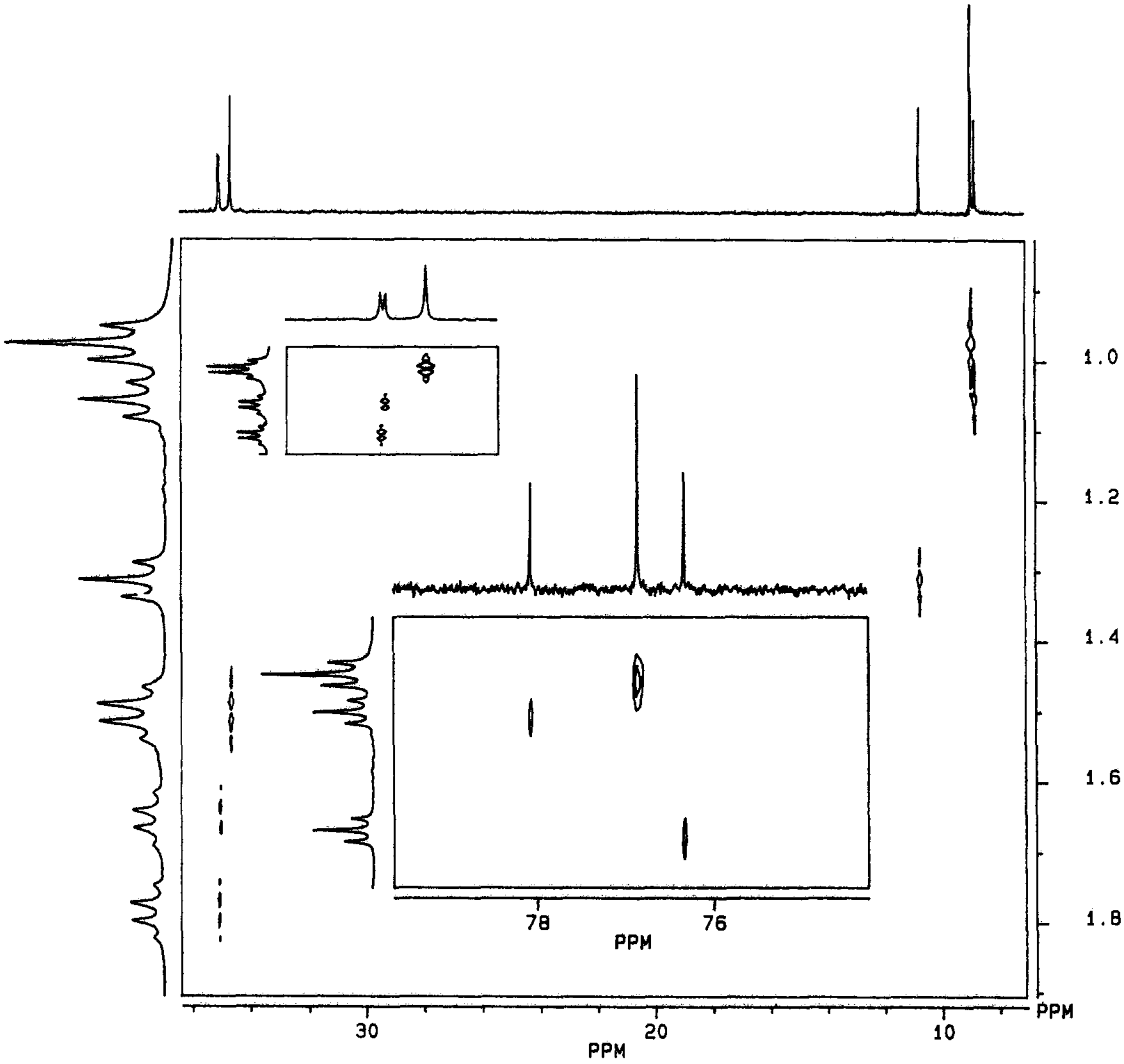

Fig. 4. H,C-COSY (HETCOR) contour plot for $Ba_2Cu_4(OCEt_3)_8$ (3). Upper inset is an expanded view of the CH_2 region and the lower inset depicts a COLOC contour plot between the quaternary carbons and the CH_3 protons in 3.

$Me_2)_3$) cluster. In $Cu_2Zr_2(OCHMe_2)_{10}$, however, the $OCHMe_2$ bridged zirconiums are 3.227 Å apart, much less than the Ba---Ba = 3.963(3) Å for 3. The Ba—O distances within the Ba_2O_2 ring average 2.59 Å and are the same as those observed in the Ba_2O_2 ring of $[BaZr_2(OCHMe_2)_{10}]_2$[13] and within the range of 2.46–2.83 Å observed for four-coordinate Ba—O distances in $Ba_2(OSiBu_3)_4(THF)$.[14] The unusually low coordination observed for lithium and sodium in **1** and **2**, as well as for barium[15] in **3**, is attributable to the steric effects imposed by the bulky alkoxide ligands.

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