

# REACTIVITY OF MIXED-METAL BaCu and BaY $\beta$ -DIKETONATOALKOXIDES WITH LEWIS BASES: MOLECULAR STRUCTURES OF $[Ba_2Cu(\mu_3,\eta^2-OCHMeCH_2NMe_2)_2(\mu,\eta^2-thd)_2(\eta^2-thd)_2(Pr^iOH)_2],$ $[Cu_3(\mu_3-OBu^t)_2(\mu-OBu^t)(\eta^2-thd)_3]$ AND $[Ba(\eta^2-thd)_2(TMEDA)_2]$

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Abstract—Reactions involving Y(thd)<sub>3</sub> and Cu(thd)<sub>2</sub> with barium tert-butoxide or 2-dimethylamino-2-proposide were investigated. The mixed-metal complexes  $[YBa_3(OBu')_6(thd)_3]$ (1) and  $[BaCu(OBu^1)_2(thd)_2]_m$  (3) (thdH = 2,2,6,6-tetramethylheptane-3,5-dione) were isolated in hexane. Dissolution of 3 in  $Et_2O$  or THF afforded  $[Cu_3(OBu^1)_3(thd)_3]$  (4) and [Cu(thd)<sub>2</sub>(OBu<sup>1</sup>)<sub>2</sub>(THF)<sub>2</sub>] (5), respectively, while [Ba(thd)<sub>2</sub>(TMEDA)<sub>2</sub>] (2) was obtained in the presence of N', N'-tetramethylenediamine. Dissolution of 1 in THF afforded a THF adduct (1a) giving 1 by sublimation at  $190^{\circ}$  C/10<sup>-3</sup> Torr. By contrast, the reaction between the barium aminoalkoxide and  $Y(thd)_3$  in hexane proceeded directly to the formation of homometallic compounds, whereas with Cu(thd)<sub>2</sub> the mixed-metal compound {Ba<sub>2</sub>Cu  $[OCHMeCH_2NMe_2]_2(thd)_4(Pr^iOH)_2$  (6) was obtained by crystallization from Pr<sup>i</sup>OH. All compounds were characterized by elemental analysis, IR, <sup>1</sup>H NMR, ESR and TGA for the copper species. Compounds 2, 4 and 6 were characterized by single-crystal X-ray diffraction. The  $[Ba(thd)_2(TMEDA)_2]$  adduct is monomeric. The structures of 4 and 6 consist of triangular aggregates with  $Cu_3(\mu_3-OBu^t)_2(\mu-OBu^t)(thd)_3$  and  $Ba_2Cu(\mu_3,\eta^2-OCHMe$  $CH_2NMe_2_2(\mu,\eta^2-thd)_2(\eta^2-thd)_2(Pr^iOH)_2$  cores, respectively. Compound 4 exhibits one square planar and two square pyramidal copper centres. The Cu-O bond lengths range from 1.90(2) to 2.27(2) Å, the order of variation being Cu-O(thd) < Cu- $\mu$ - $OR < Cu - \mu_3 - OR$ . For compound 6, the thd, OR and Pr'OH ligands are bonded asymmetrically to the three metallic centres. Each barium atom bears a chelating thd ligand, two other thd are bridging-chelating, linking the two barium atoms, and one barium, Ba(2), to the copper atom, respectively. The nitrogen-donor sites of the two  $\mu_3$ -aminoalkoxide ligands interact with the copper and Ba(2) centres. The two isopropanol molecules are bonded to the other barium, Ba(1); the solvate is stabilized by intramolecular hydrogen bonds. This allows the barium atoms to reach high coordination numbers, seven and eight, and the copper atom to be pentacoordinated. The Ba-O bond lengths range from 2.59(1) to 2.87(1) Å. The Ba—N bond distance is 2.85(1) Å. Compounds 4 and 5 are volatile; 5 loses its THF upon sublimation to yield 4.

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Superconducting  $YBa_2Cu_3O_{7-x^3}$  as well as copper metal films<sup>1b</sup> produced by Metal-Organic Chemical Vapour Deposition (MOCVD) at low temperatures are of interest for microelectronic applications, in particular for use in integrated circuits, and provide advantages over other methods such as better purity and quality of the films. Volatile precursors are required for both materials. For the deposition of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7, x</sub>, only barium  $\beta$ -diketonates<sup>2</sup> and  $\beta$ -ketoimines<sup>3</sup> have to date proven useful due to the lack of volatility of barium compounds as a general feature. Copper(II)  $\beta$ -diketonates and Lewis base adducts of copper(I)  $\beta$ -diketonates are currently used as volatile precursors of copper.<sup>4</sup> Heterometallic compounds containing barium, yttriumbarium or barium-copper may be a means to improve the transport of barium in the vapour phase. We have recently succeeded in the synthesis, in high yield, of volatile mixed-metal  $\beta$ -diketonatofluoroalkoxides,<sup>5</sup> [Y<sub>2</sub>Ba[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>(thd)<sub>4</sub>],  $[BaCu_2[OCH(CF_3)_2]_4(thd)_2]$ and [YCu[OCH  $(CF_3)_2]_2(thd)_3].$  $[Y_2Ba[OCH(CF_3)_2]_4(thd)_4]$ is monomeric in the solid state and is the only volatile yttrium-barium compound known to date. A nonvolatile yttrium barium  $\beta$ -diketonatooxoalkoxide,  $[Y_4Ba_2O(OEt)_8(thd)_6]$ , has also been reported.<sup>6</sup> Barium-copper compounds of different stoichiometries have been published.7 9 Non-volatile yttrium-copper(II)  $\beta$ -diketonatoalkoxides<sup>10</sup> and a Y-Cu<sup>1</sup> siloxide have also been synthethized.<sup>11</sup>

We report here our attempts to build up mixedmetal  $\beta$ -diketonatoalkoxides by using bulky alcohols such as tert-butanol or bidentate ones such as 2-dimethylamino-2-propanol. Buhro et al. have shown that aminoalcohols are able to form volatile copper species,<sup>12</sup> and we have reported the synthesis of the volatile barium derivative [Ba<sub>5</sub>(OH)]  $(OCHMeCH_2NMe_2)_4(thd)_5$ .<sup>13</sup> The production of an oxo- or hydroxo-free barium tert-butoxide  $[Ba(OBu^{1})_{2}(BuOH)_{2}]_{4}^{14}$  shows that the nuclearity of barium alkoxides, generally five or more, can be reduced by bulky ligands. Reactions between metal alkoxides and  $\beta$ -diketonates can give access to mixed-metal species, Ba-Ti for instance, by spontaneous self-assembly.<sup>15</sup> An alternative is, however, the formation of heteroleptic homometallic derivatives via unstable mixed-metal intermediates as observed with  $Y(OC_2H_4OR)_3$  and  $Cu(acac)_3$ , giving  $[Cu(OC_2H_4OR)(acac)]_4$  and  $[Y_3(OC_2H_4OR)_5]$  $(acac)_4$ ] (R = Me, Pr<sup>i</sup>).<sup>16</sup> We have investigated the reaction between barium alkoxides and yttrium or copper tetramethylheptanedionates as a one-pot synthetic route to heterometallic compounds. This strategy has allowed the isolation of [YBa<sub>3</sub>  $(OBu^{1})_{6}(thd)_{3}$ ] (1), a THF adduct (1a), [BaCu  $(OBu^{t})_{2}(thd)_{2}m$  (3) and  $\{Ba_{2}Cu[OCHMeCH_{2}$  NMe<sub>2</sub>]<sub>2</sub>(thd)<sub>4</sub>(Pr<sup>i</sup>OH)<sub>2</sub>] (6), the YBa butoxide adduct **1a** being volatile. The reaction between the barium aminoalkoxide and Y(thd)<sub>3</sub> afforded homometallic β-diketonatoalkoxides, namely [Ba<sub>5</sub>(OH) (OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>4</sub>(thd)<sub>5</sub>], illustrating the difference of reactivity of copper and yttrium βdiketonates toward the barium aminoalkoxide. The poor stability of **3** in polar solvents led to the formation of Cu<sub>3</sub>(OBu<sup>1</sup>)<sub>3</sub>(thd)<sub>3</sub> (**4**) and [Cu(thd) (OBu<sup>1</sup>)(THF)]<sub>2</sub> (**5**) in diethyl ether and THF, respectively. All compounds were characterized by elemental analysis, NMR (<sup>1</sup>H and <sup>13</sup>C), FT-IR and ESR for the copper species. Compounds **2**, **4** and **6** have been characterized by single-crystal X-ray diffraction.

#### EXPERIMENTAL

All manipulations were performed under dry nitrogen using Schlenk tubes and vacuum line techniques. Solvents were purified by standard methods. Tert-butanol was distilled over sodium. The aminoalcohol and  $\beta$ -diketone were dried over 3 Å molecular sieves prior to use. Ba<sub>5</sub>(OH) [OCHMeCH<sub>2</sub>NMe<sub>2</sub>]<sub>9</sub><sup>13</sup> and Ba(OBu<sup>t</sup>)<sub>2</sub><sup>14</sup> were prepared according to the literature. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-200. IR spectra were recorded as Nujol mulls on an IR-FTS 45 spectrometer. ESR spectra were recorded using a Bruker E-200 spectrometer. Melting points were determined in capillaries and are given uncorrected. TGA measurements were done with a Shimadzu system TGA-50H at a heating rate of 5°C min<sup>-1</sup>. Microanalyses were performed at the Centre de Microanalyses du CNRS.

### Synthesis of $[YBa_3(OBu^t)_6(thd)_3]$ (1)

A solution of  $Y(thd)_3$  (1.55 g, 2.43 mmol) in 30 cm<sup>3</sup> of hexane was added to a suspension of barium tert-butoxide (2.06 g, 7.29 mmol) in 50 cm<sup>3</sup> of hexane. Progressive solubilization was observed; after 2 h, the solution was stripped to dryness leaving a white powder. Addition of 50 cm<sup>3</sup> of hexane and cooling the solution to  $-20^{\circ}$ C gave crystals of 1 (2.8 g, 77%), m.p. =  $250^{\circ}$ C. Found : Y, 5.4; Ba, 27.6. Calc. for  $C_{57}H_{111}O_{12}Ba_3Y : Y, 6.0$ ; Ba, 27.6%. IR (cm<sup>-1</sup>): 1595 vs, 1578 vs, 1555 w, 1538 w, 1506 m [v(C=C), v(C=O)]; 1273 w, 1244 m, 1222 s, 1197 s, 1188 s, 1141 m, 1127 m, 1021 m, 962 s, 935 s, 918 m, 868 m, 799 m, 790 m, 756 m, 731 m; 607 w, 594 w, 518 m, 507 m, 499 m, 474 s, 380 s [v(Ba-O), v(Y - O)]. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 5.83 (s, 1H, CH); 1.3 (br, 18H, OBu<sup>t</sup>); 1.1 [s, 18H, Bu<sup>t</sup>(thd)].

Dissolution of 1 in THF, evaporation to dryness and crystallization in hexane gave 1a. Its IR spectrum is similar to that of 1, with an additional band at 1047 cm<sup>-1</sup> [ $\nu$ (C—O) THF]. Sublimation of 1a at 190°C/10<sup>-3</sup> Torr gave 1 in 70% yield.

### Synthesis of [Ba(thd)<sub>2</sub>(TMEDA)<sub>2</sub>] (2)

Dissolution of 1 in hexane, addition of TMEDA (1:6 molar) and cooling gave 2 as the first crop of crystals, m.p. = 95–105°C. Found : C, 55.9; H, 9.0; N, 7.6. Calc. for  $C_{34}H_{70}N_4O_4Ba$ : C, 55.5; H, 8.5; N, 7.4%. IR (cm<sup>-1</sup>): 1595 s, 1587 s, 1577 s, 1533 m, 1503 s [v(C=C), v(C=O)]; 1296 s, 1265 w, 1242 w, 1224 m, 1124 m, 1184 s, 1157 m, 1134 m, 1075 m, 1038 s, 1028 s, 958 s, 928 w, 890 w, 861 m, 818 w, 788 s, 783 s, 751 m, 730 m, 588 w, 571 w, 470 s, 459 w, 424 m, 382 m, 375 m [v(Ba—O), v(Ba—N)]. <sup>1</sup>H NMR ( $C_6D_6$ , >0.1 M): 5.84 s (1H, CH); 2.25 s (12H, NMe<sub>2</sub>); 2.18 s (4H, CH<sub>2</sub>); 1.32 s (36H, Bu<sup>t</sup>).  ${}^{13}C{}^{1}H{}(C_6D_6)$  : 197 (C==O) ; 88.7 (CH) ; 57.6 (CH<sub>2</sub>); 45.3 (CH<sub>3</sub>); 41.3 (Cquat); 29.4 (Bu<sup>t</sup>). MS (IE, m/z, %): M (1), Ba(thd)<sub>2</sub>(TMEDA)Me (1), Ba(thd)(BuCOCHCO) (2), Ba(thd)(TMEDA) (2),  $Ba(thd)NMe_2$  (2), Ba(thd) (9), TMEDA (15), Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub> (30), Me<sub>3</sub>N (45), BuH (100). TGA  $(N_2, 1 \text{ atm})$ : 100–200°C, -32% (-2TMEDA); -58% (sublimation and slight 315–500°C, decomposition). TGA (N<sub>2</sub>, 5 Torr): 90–115 $^{\circ}$ C, -32% (-2TMEDA); 200–250°C, -58% (sublimation). Sublimation is quantitative at 160-180°C/10<sup>-3</sup> Torr with loss of TMEDA giving  $[Ba(thd)_2]_4$ . Compound 2 is soluble in hydrocarbons and ethers.

Crystals of **2** were obtained by recrystallization in petroleum ether. Unit cell parameters: a = 14.790(2), b = 16.078(2), c = 18.267(2) Å,  $\alpha = 90, \beta = 91.25, \gamma = 90^{\circ}$ , space group C2/c.

#### Synthesis of $[BaCu(OBu^{t})_{2}(thd)_{2}]_{m}$ (3)

A procedure similar as for 1 was applied to Cu(thd)<sub>2</sub> (2.16 g, 5.03 mmol) and barium tertbutoxide (1.42 g, 5.03 mmol) in 70 cm<sup>3</sup> of hexane. The resulting dark green solution was concentrated and cooled to 4°C, affording 3.17 g of green crystals of 3, yield 88%. Sublimation of 3 occurred at 160°C under  $10^{-3}$  Torr with intensive decomposition, m.p. = 230°C. Found: C, 48.4; H, 7.6; Ba, 19.3; Cu; 8.4 Calc. for C<sub>30</sub>H<sub>56</sub>O<sub>6</sub>BaCu: C, 50.5; H, 7.9; Ba, 19.3; Cu, 8.9%. IR (cm<sup>-1</sup>): 1589 vs, 1576 vs, 1569 vs, 1556 vs, 1536 vs, 1505 vs [v(C=O), v(C=C); 1286 w, 1274 w, 1245 m, 1225 s, 1185 s, 1143 m, 1130 m, 1024 w, 953 m, 936 w, 909 m, 870 m, 865 m, 798 w, 791 w, 753 w, 747 w; 628 w, 591 m, 554 w, 491 m, 469 m, 392 m [v(Ba-O), v(Cu-O)].  $\mu = 1.67$  B.M. ESR (hexane, RT):  $\langle q \rangle = 2.13.$ 

Crystals of **3** decomposed during X-ray data collection; lattice parameters  $(-100^{\circ}\text{C})$ : a = 14.038(3), b = 15.739(6), c = 18.621(6) Å,  $\alpha = 68.66(3), \beta = 80.93(2), \gamma = 89.08(2)^{\circ}$ , triclinic.

Compounds 1, 1a and 3 are soluble in hydrocarbons and very air-sensitive. They rapidly decomposed in Ba(thd)<sub>2</sub>, yttrium oxide or hydroxide or Cu(thd)<sub>2</sub> and tert-butanol, as shown by IR.

### Synthesis of $[Cu_3(OBu^i)_3(thd)_3]$ (4)

Dissolution of 1.8 g of 2 in 30 cm<sup>3</sup> of  $Et_2O$  led to a green solution; by cooling to 4°C, 0.77 g of green crystals of 4 were obtained, yield 43% based on 3 (95.9% based on copper). Further crystallization led to Ba(thd)<sub>2</sub>. Compound 4 was purified by sublimation at  $140^{\circ}C/10^{-3}$  Torr, yield 78% (of the sublimation). Compound 4 also crystallized from hexane-DME solutions but did not form in pure hexane, m.p. =  $195^{\circ}$ C. Found: C, 56.7; H, 4.9; Cu, 19.3. Calc. for C<sub>45</sub>H<sub>84</sub>O<sub>9</sub>Cu<sub>3</sub>: C, 56.3; H, 4.8; Cu, 19.9%. IR (cm<sup>-1</sup>): 1590 s, 1567 vs, 1554 vs, 1536 vs, 1504 vs [v(C=C) v(C=O)]; 1290 w, 1247 m, 1226 s, 1187 s, 1149 s, 1025 w, 963 m, 956 sh, 944 m, 935 sh, 874 s, 823 w, 794 s, 766 m, 744 w; 631 m, 608 sh, 598 m, 579 w, 503 sh, 493 m, 470 sh, 426 w, 393 m [ $\nu$ (Cu—O)]. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 6.05 (br, 1H, CH); 5.9 (br, 6H,  $\mu_3$ -OBu<sup>t</sup>); 2.75 (br, 3H,  $\mu$ -OBu<sup>t</sup>); 1.2 [s, 9H, Bu<sup>t</sup> (thd)].  $\mu$  = 1.91 B.M. ESR (hexane, RT):  $\langle g \rangle = 2.11$ ,  $\langle A \rangle = 85.1$  G. TGA (N<sub>2</sub>, 1 atm) :  $90-250^{\circ}C$  (-85%, sublimation).

### Synthesis of [Cu(thd)(OBu<sup>t</sup>)(THF)]<sub>2</sub> (5)

Dissolution of 2 g of 2 in 30 cm<sup>3</sup> of THF led to an olive green solution which progressively turned to brown. On cooling to 4°C, blue crystals of 5 were formed, yield 48% based on 3 (87.4% based on copper). Sublimation of 5 at 135°C/10<sup>-3</sup> Torr gave 5, yield 69% (of the sublimation). Found : C, 58.5; H, 5.0; Cu, 16.9. Calc. for C<sub>38</sub>H<sub>72</sub>O<sub>8</sub>Cu<sub>2</sub>: C, 58.2; H, 4.9; Cu, 16.2%. IR  $(cm^{-1})$ : 1591 s, 1568 vs, 1556 vs, 1536 vs, 1504 vs [v(C=C), v(C=O)]; 1290w, 1246 m, 1225 s, 1204 sh, 1187 s, 1175 sh 1148 s; 1058 m [v(C-O) THF]; 1026 w, 971 sh, 962 m, 939 s, 915 w, 899 m, 873 s, 824 w, 794 s, 770 w, 763 w, 744 w; 633 m, 609 m, 503 sh, 493 m, 471 sh, 426 sh, 398 m [v(Cu-O)].  $\mu = 1.59$  B.M. ESR (hexane, RT):  $\langle q \rangle = 2.10$ ,  $\langle A \rangle = 84$  G. TGA (N<sub>2</sub>, 1 atm): 50-130°C (-18%, -THF); 130-250°C (-69%, sublimation).

### Synthesis of $[Ba_2Cu(OCHMeCH_2NMe_2)_2(thd)_4$ (Pr<sup>i</sup>OH)<sub>2</sub>] (6)

A solution of  $Cu(thd)_2$  (1.93 g, 4.49 mmol) in 40 cm<sup>3</sup> of hexane was added to a suspension of

Ba<sub>5</sub>(OH)(OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>9</sub> (1.45 g, 4.49 mmol) in 20 cm<sup>3</sup> of hexane. The precipitate dissolved progressively, giving a turquoise blue solution. After 2 h, filtration was achieved and the filtrate was evaporated to dryness giving a turquoise blue solid. IR (cm<sup>-1</sup>): 1587 s, 1572 s, 1551 w, 1532 s, 1502 s [ $\nu$ (C=O),  $\nu$ (C=C)]; 1313 w, 1276 sh, 1259 m, 1243 m, 1224 s, 1185 s, 1139 s, 1129 s, 1083 s, 1042 m, 1029 s, 1009 sh, 948 m, 865 s, 833 w, 790 s, 778 w, 744 w, 732 w, 644 w, 592 w, 515 w, 751, 732; 618, 592, 525, 493 w, 475 w, 421 [ $\nu$ (M-O)].

Addition of Pr'OH to a hexane solution of this material led to the precipitation of blue crystals of 6, while the colour of the solution changed from turquoise blue to purple. Yield 89%. Evaporation of the filtrate gave a purple solid identified as Cu  $(OCHMeCH_2NMe_2)_2$  (IR). Found: C,51.8; H, 8.5; N, 2.1; Ba, 18.8; Cu, 4.9. Calc. for  $C_{60}H_{116}$ N<sub>2</sub>O<sub>12</sub>Ba<sub>2</sub>Cu: C, 51.6; H, 8.4; N, 2.0; Ba, 19.7; Cu, 4.6%. IR  $(cm^{-1})$ : 3354 [v(O-H)]; 1588 vs, 1573 vs, 1554 w, 1533 s, 1503 s [v(C==O), v(C==C)]; 1320 w, 1311 w, 1287 m, 1275 sh 1270 m, 1260 m, 1240 m, 1224 m, 1189 s, 1160 w, 1136 sh, 1127 s, 1083 s, 1042 w, 1028 m, 1009 w, 948 s, 864 s, 837 m, 816 w, 790 m, 751 w, 732; 618 w, 590 m, 576 w, 536 sh, 525 w, 493 sh, 475 m, 421 sh [v(M-O)]. ESR (hexane, RT):  $\langle q \rangle = 2.10$ ;  $\langle A \rangle = 86.8$  G.

### *Reaction between* [Ba<sub>5</sub>(OH)(OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>9</sub>] and Y(thd)<sub>3</sub>

A solution of  $Y(thd)_3$  (2.54 g, 3.98 mmol) in 60 cm<sup>3</sup> of hexane was added to a suspension of  $[Ba_5(OH)(OCHMeCH_2NMe_2)_9]$  (1.3 g, 0.79 mmol) in 40 cm<sup>3</sup> of hexane. Solubilization was observed and the reaction medium was stirred for 2 h. After filtration, the filtrate was cooled to 4°C, giving crystals of 7 (0.96 g). The second crop of crystals was a mixture of 7 and of  $[Ba_{5}(OH)(OCHMeCH)]$  $NMe_{2}_{4}(thd)_{5}$ , m.p. 280°C; subl. 200 C/10<sup>-2</sup> Torr. Found: C, 49.5; H, 7.7; N, 2.1. Calc. for  $C_{108}H_{196}N_4O_{23}Y_6$ : C, 52.1; H, 7.9; N, 2.3%. IR  $(cm^{-1})$ : 1595 vs, 1576 vs, 1558 w, 1539 s, 1506 vs [v(C=C), v(C=O)]; 1309 w, 1286 w, 1248 w, 1226m, 1186 m, 1142 m, 1103 w, 1093 w, 1080 m, 1039 w, 1022 m, 960 w, 945 m, 866 m, 837 w, 795 m, 758 w, 735 w; 598 m, 511 w, 474 m, 426 sh, 408 m, 397 sh [v(Y - O)]. <sup>1</sup>H NMR  $(C_6 D_6)$ : 5.95 [s. 2H, CH(thd); 4.6 (m, 1H, OCHMeCH<sub>2</sub>NMe<sub>2</sub>); 3.18 (t, 1H,  $CH_2$  in  $\alpha$  position of an asymmetric carbon, ABX,  $A^2J = {}^{3}J = 11.6 \text{ Hz}$ ; 2.43 (s, 3H, NMe<sub>3</sub>); 2.3 (s, 3H, NMe<sub>2</sub>); 1.86 (dd, 1H, CH<sub>2</sub> in  $\alpha$  position of an asymmetric carbon, ABX, B  $^{2}J = 11.6$  Hz,  ${}^{3}J = 2Hz$ ; 1.3 (s, 36H, Bu<sup>t</sup>); 1.29 (s, 3H, CH<sub>3</sub>).  $^{13}C{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>): 199.2 (C=O); 91.2

[CH(thd)]; 71 (CH); 67.6 (NMe<sub>2</sub>); 66.7 (CH<sub>2</sub>); 41 [ $C(CH_3)_3$ ]; 29.1 [ $C(CH_3)_3$ ]; 24 (CH<sub>3</sub>).

Compounds 4 and 5 are soluble in hydrocarbons and ethers and are quite air stable. Compound 7 displays comparable solubility properties but is slightly air-sensitive.

Crystal structure determination of  $[Ba_2Cu (OCHMeCH_2NMe_2)_2(thd)_4(Pr^iOH)_2]$  (6) and of  $[Cu_3(OBu^i)_3(thd)_3]$  (4)

X-ray quality crystals of **4** and of **6** grown from hexane and hexane–Pr<sup>i</sup>OH solutions, respectively, were mounted onto an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo- $K_z$  radiation at  $-100^{\circ}$ C. The unit cell parameters and basic information about data collection and structure refinement are given in Table 1.

Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (DIFABS)<sup>17</sup> were applied. Computations were performed by using CRYSTALS<sup>18</sup> adapted on a Micro Vax II. Atomic form factors for neutral Ba, Cu, O, N, C and H were used.<sup>19</sup> Anomalous dispersion was taken into account. The structures were solved by direct methods (SHELXS)<sup>20</sup> and standard Fourier techniques. The asymmetric unit of 4 presents two independent molecules; the parameters of 114 atoms had thus to be refined with only 2353 reflections  $[I > 3\sigma(I)]$ . As a result, all atoms were left isotropic. Hydrogen atoms were located on successive difference Fourier maps; they were included in the refinement as fixed contributors. The asymmetric unit of 6 contains 77 non-hydrogen atoms and only 3227 reflections  $[I > 3\sigma(I)]$  were available for structure refinement. All atoms were thus left isotropic. Hydrogen atoms were introduced in calculated positions as fixed contributors and recalculated after each refinement. One of the tert-butyl groups [on C(40)] is disordered; this disorder is well resolved by introduction of two sets of carbon atoms [C(41), C(42), C(43) and C(41'), C(43'), respectively] in half occupation. Least-square refinements with approximations in three blocks to the normal matrix were carried out to minimize the function  $\Sigma w(|F_0| - |F_c|)^2$ , where  $F_0$  and  $F_c$  are the observed and calculated structure factors. Unit weight was used. Models reached convergence with  $R = \Sigma(|F_{o}| - |F_{c}|)/\Sigma|F_{o}|$  and  $R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma|F_{o}|]$  $\Sigma w(F_{o})^{2}$  having the values listed in Table 1. Criteria for a satisfactory complete analysis were the ratios of r.m.s. shift to standard deviation being less than 0.1 and no significant feature in the final difference map.

Atomic coordinates for hydrogen and nonhydrogen atoms, thermal parameters and non-

Chemical formula	$C_{45}H_{84}O_9Cu_3$ (4)	$C_{60}H_{114}O_{12}N_2Ba_2Cu$ (6)
Formula weight	959.81	1393.8
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Z	4	2
<i>a</i> (Å)	11.672(4)	10.364(6)
$b(\mathbf{A})$	20.321(7)	14.213(3)
c (Å)	22.958(9)	26.570(5)
α()	92.95(3)	97.05(1)
$\beta$ ( )	104.81(3)	97.96(3)
7 ()	106.67(3)	108.95(3)
$V(\hat{A}^3)$	4997(3)	3607(3)
F(000)	2052	1282
$\rho$ (calc.) (g cm <sup>-3</sup> )	1.27	1.28
$\mu$ (Mo- $K_r$ ) (cm <sup>-1</sup> )	13.15	14.2
Diffractometer	CAD4	CAD4
Monochromator	graphite	graphite
Radiation	Mo-K, (0.71070)	$Mo-K_{x}$ (0.71070)
Scan type	ω-20	$\omega$ -2 $\theta$
Scan range $\theta$ ( )	$1.2 \pm 0.34 \tan \theta$	$1.2 \pm 0.34 \tan \theta$
$2\theta$ range ()	4-32	4-34
Reflections collected	4839	4188
Reflections used (criteria)	2353 $[l > 3\sigma(l)]$	$3227 [l > 3\sigma (l)]$
R	0.059	0.060
$R_{w}^{a}$	0.068	0.065
Weighting scheme	unit weights	unit weights
l.s. parameters	458	322

Table 1. Crystallographic data for  $Cu_3(thd)_3(OBu^1)_3$  and  $Ba_2Cu(thd)_4(OCHMeCH_2NMe_2)_2(Pr^iOH)_2$ (data collection at -100 C)

 ${}^{a}R_{w} = [\Sigma_{i}w_{i}(F_{o} - F_{c})^{2}/\Sigma_{i}w_{i}F_{o}^{2}]^{1/2}.$ 

essential bond lengths and angles are given as supplementary material.

#### **RESULTS AND DISCUSSION**

#### Synthesis and characterization

Several routes to BaCu and YBa mixed-metal species have been investigated previously. Metathesis reactions between copper or yttrium chlorides and barium fluoroalkoxides<sup>11</sup> have afforded  ${BaCu_2[OCMe(CF_3)_2]_6}^{21}, {YBa_2[OCH(CF_3)_2]_7}$  $(THF)_3$  and  $\{BaCu[OCH(CF_3)_2]_4(DME)_2\}$ .<sup>5</sup> The reaction between NaCu(OtBu)<sub>3</sub> and BaBr<sub>2</sub> led to the isolation of  $Ba[Cu(OBu^{t})_{3}]_{2}^{22}$  but in modest yield (31%). Lewis acid-base reactions between metal alkoxides have been less studied in the Y/Ba/Cu system, the high solubility of the heterometallic species often precluding their isolation, although BaCu(C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>)<sub>n</sub>(C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub> (n = 3, 6) has been obtained from barium and copper ethyleneglycolates in the parent glycol.9 The most largely investigated routes to YBa and BaCu species have been those involving alkoxide and  $\beta$ -diketonate ligands. Incorporation of the thd ligand has been achieved by reaction of thdH with YBa and BaCu alkoxides isolated or *in situ*,<sup>5,6</sup> affording  $\{Y_2Ba[OCH(CF_3)_2]_4(thd)_4\}$ ,  $\{BaCu_2[OCH(CF_3)_2]_4$  $(thd)_2\}^5$  and  $\{Y_4Ba_2O(OEt)_8(thd)_6\}$ ,<sup>6</sup> or by the reaction of copper  $\beta$ -diketonatoalkoxides with barium alkoxides or  $\beta$ -diketonatoalkoxides, giving  $[Ba_2Cu_2(OR)_4(\beta$ -dik)\_4(ROH)\_2]^7 and  $[BaCu_4(OR)_6$  $(thd)_4]^8$  (R = C<sub>2</sub>H<sub>4</sub>OMe). This latter route is so far limited to BaCu species and to alkoxyalkoxide ligands.

Self-assembly between metal alkoxides and  $\beta$ diketonates is another potential strategy.<sup>15</sup> Thus barium tert-butoxide and 2-dimethylamino-2propoxide have been allowed to react with yttrium and copper tetramethylheptanedionates in hexane; solubilization of the barium alkoxides was observed at room temperature. The reactions are summarized in Scheme 1. The various compounds were characterized by elemental analysis, IR, NMR (<sup>1</sup>H or <sup>13</sup>C), ESR for the paramagnetic derivatives and TGA for the homometallic copper derivatives.

The reaction between  $Y(thd)_3$  and barium tertbutoxide (1:3 stoichiometry) afforded [YBa<sub>3</sub>



 $R_N OH = Me_2 NCH_2 CHMeOH$ 

Scheme 1.

 $(OtBu)_6(thd)_3$ ] (1) in good yield. The heterometallic nature of 1 was suggested by elemental analysis, 'H NMR and IR. The IR spectra show v(C==O) and v(C==C) vibrations (two intense absorption bands at 1595 and 1578  $cm^{-1}$ , two weaker ones at 1543 and 1538  $cm^{-1}$ ) different from these of  $Ba(thd)_2$  and  $Y(thd)_3$ . The strong absorption bands of the C-O and C-C bonds of the OBu<sup>t</sup> group are split into two bands, one at higher frequency, one at lower frequency with respect to  $Ba(OBu^{t})_{2}$ . The frequencies of the M—O (thd and/or R) vibrations are also different from those of the starting materials. However, the strongest evidence for 1 being a mixed-metal species is given by its sublimation as a THF adduct (1a). Indeed, while 1 is non-volatile, its THF adduct, obtained by dissolution in THF and characterized by a v(C-O-C) vibration at 1047 cm<sup>-1</sup> in the IR, sublimes at  $190^{\circ}/10^{-3}$  Torr. Since volatility could be achieved, most efforts were directed toward the quest for Lewis bases that would stabilize compound 1. By contrast to the easy formation of an adduct with THF, attempts to form stable complexes with ligands such as Et<sub>2</sub>O, DME or Bu'OH were unsuccessful. Addition of a nitrogen donor, TMEDA, led to segregation and crystallization of a compound analysing as  $[Ba(thd)_2(TMEDA)_2]$  (2). The identity of this product was established by comparison with the IR spectrum of an authentic sample [obtained by reacting Ba(thd), and TMEDA in 1:2 stoichiometry] and by X-ray diffraction. <sup>1</sup>H NMR data indicate that the molecular constitution of the solutions of  $[Ba(thd)_2(TMEDA)_2]$  in C<sub>6</sub>D<sub>6</sub> is a function of the dilution. For concentrated media

(>0.1 M), the solid state structure—monomeric adduct—is retained, the signals of the NMe<sub>2</sub> groups being shifted to low field with respect to those of the free ligand. For more diluted solutions, dissociation reactions of the adduct are observed.

A similar approach offered a compound analysing as  $[BaCu(OBu^{t})_{2}(thd)_{2}]_{m}$  (3). As observed for 1, its IR spectrum accounts for v(C==O), v(C==C)and v(C-O), v(C-C) absorptions at frequencies different from these observed for Cu(thd)<sub>2</sub> and  $Ba(OBu^{t})_{2}$ , respectively. Moreover, the frequencies of the v(M - O) vibrations suggest that the thd ligands are linked to barium centres. Compound 3 is stable in hexane but displays a poor stability in polar solvents. Trinuclear or dinuclear compounds  $[Cu_3(OBu^{t})_3(thd)_3]$  (4) and  $[Cu_2(thd)_2(OBu^{t})_2]$  $(THF)_{2}$  (5) are obtained in diethyl ether and THF respectively, together with barium tert-butoxide and barium tetramethylheptanedionate [eqs (1) and (2)]. Thus, **3** appears as a kinetic intermediate on the route to copper  $\beta$ -diketonatotert-butoxide derivatives. The YBa<sub>3</sub> tert-butoxide derivative 1 is more stable than the BaCu one with respect to oxygen-donor solvents, but segregation is observed with TMEDA. All mixed-metal tert-butoxide derivatives 1, 1a and 3 are highly air-sensitive, giving  $\beta$ -diketonates and oxides or hydroxides, as shown by FT-IR. The IR spectra of the copper(II) tetramethylheptanedionatobutoxides 4 and 5 differ mainly by the presence, for the latter, of an additional v(C-O) vibration characteristic of the THF ligand. This Lewis base reduces the nuclearity of compound 5-in the solid state and in solutionwith respect to compound 4, a possible structure

$$x \operatorname{BaCu}(\operatorname{OBu}^{t})_{2}(\operatorname{thd})_{2} \xrightarrow{\operatorname{Et_{2}O}} \operatorname{Cu}_{3}(\operatorname{OBu}^{t})_{3}(\operatorname{thd})_{3} + 3/2 \operatorname{``Ba}(\operatorname{OBu}^{t})_{2} \operatorname{''} + 3/2[\operatorname{Ba}(\operatorname{thd})_{2}(\operatorname{Et_{2}O})]_{2}$$

$$\xrightarrow{x \operatorname{BaCu}(\operatorname{OBu}^{t})_{2}(\operatorname{thd})_{2}} (4)$$

$$\xrightarrow{\operatorname{THF}}_{x=2} \operatorname{Cu}_{2}(\operatorname{OBu}^{t})_{2}(\operatorname{thd})_{2}(\operatorname{THF})_{2} + \operatorname{``Ba}(\operatorname{OBu}^{t})_{2} \operatorname{''} + \operatorname{Ba}(\operatorname{thd})_{2}$$

$$(5)$$

being A. These observations are consistent with the solid-state structure of  $[Cu(tfd)(OC_6F_5)(THF)]_2$  (tfdH = 1,1,1-trifluoro-2,4-pentanedione).<sup>8b</sup> However, their volatility is comparable since  $[Cu(thd)_2(OBu')_2(THF)_2]$  loses its THF molecules, thus being converted into  $[Cu_3(thd)_3(OBu')_3]$  (see thermal behaviour).

The instability of BaCu compounds in the presence of Lewis bases has already been observed, the mixed-metal BaCu<sub>2</sub>(hftb)<sub>6</sub> species dissociating in Cu(hftb)<sub>2</sub>(TMEDA) and insoluble Ba(hftb)<sub>2</sub> by addition of TMEDA for instance [hftb = OCMe  $(CF_3)_2$ ].<sup>23</sup> In addition to the formation of thermodynamically more stable copper species, the driving force of these dissociation reactions might also be the precipitation of insoluble barium species. No dissociation reactions have been reported for mixed-metal species such as  $[Ba_2Cu_2(OR)_4(thd)_4(HOR)_2]^7$  and  $[BaCu_4(OR)_6]^7$ (thd)<sub>4</sub>]<sup>8</sup> supported by 2-methoxyethoxide ligands. The nature of the BaCu species based on ethyleneglycol was, however, dependent on the crystallization, namely solvent conditions.<sup>9</sup>

The stability of the YBa and BaCu species is also a function of the alkoxide ligands. Thus, in the case of the 2-dimethylamino-2-propoxide ligand, the mixed-metal YBa species was no longer isolable from hexane and the reaction proceeds directly to the formation of homometallic heteroleptic derivatives  $[Ba_5(OH)(OCHMeCH_2NMe_2)_4(thd)_5]^{13}$  and an yttrium  $\beta$ -diketonatoalkoxide (7). IR spectra, especially the region of the v(C==O) and v(C==C)vibrations. suggest that the tetramethylheptanedionate ligands are in terminal-chelating as well as in bridging-chelating positions. <sup>1</sup>H NMR data account for an integration ratio of 2:1 between the thd and aminoalkoxide ligands OCH MeCH<sub>2</sub>NMe<sub>2</sub>, in addition to magnetically different surroundings of the NMe<sub>2</sub> groups. Analytical data are consistent with compound 7 being an oxo species. It is quite volatile, thus suggesting a small nuclearity or a closo structure. Compound 7 remains to be fully characterized, especially since such derivatives might be active as catalysts in the polymerization of lactones.<sup>24</sup>

Redistribution reactions were observed pre-

viously for the  $[Y(OC_2H_4OR)_3]_{10}/Cu(acac)_2$  system.<sup>16</sup> By contrast to the YBa system, a stable BaCu species has been obtained by the reaction between [Ba<sub>5</sub>(OH)(OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>9</sub>] and  $Cu(thd)_2$  (5:4.5 stoichiometry) in hexane. The turquoise product, obtained after evaporation to dryness of the reaction medium, is highly soluble in non-polar and polar aprotic solvents, precluding its crystallization. We postulate that this compound is a BaCu mixed-metal species of 1:1 stoichiometry, probably [Ba<sub>2</sub>Cu<sub>2</sub>(OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>4</sub>(thd)<sub>4</sub>]. This is evidenced by the fact that by addition of Pr'OH to a hexane solution, the precipitation of blue crystals of [Ba<sub>2</sub>Cu(OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(thd)<sub>4</sub>  $(Pr^{i}OH)_{2}$  (6) was observed, while Cu(OCH MeCH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>, identified by its IR spectrum,<sup>12</sup> was formed as by-product [eqs (3) and (4)]. FT-IR spectra of the crude product and of compound 6differ essentially by the presence of the isopropanol molecules, as shown by an absorption band at 3354  $cm^{-1}$ . The difference of reactivity of copper and yttrium tetramethylheptanedionates toward the barium aminoalkoxide, i.e. formation of a BaCu species in the first case, whereas homometallic yttrium and barium  $\beta$ -diketonatoalkoxides are obtained in the second case, is surprising. It may be explained by a difference of reactivity of the amino functionality toward copper and yttrium or lanthanides,<sup>25</sup> the strong Cu-N interaction being responsible for the stabilization of the mixed-metal compound 6.

$$Ba_5(OH)(OCHMeCH_2NMe_2)_9 + 4.5 Cu(thd)_2$$

$$\xrightarrow{\text{hexane}} 9/4'' \text{Ba}_2 \text{Cu}_2(\text{OCHMeCH}_2\text{NMe}_2)_4(\text{thd})_4'' + 1/2 \text{Ba}(\text{OH})_2 \quad (3)$$

$$\xrightarrow{\text{Pr}^{i}\text{OH}} \text{Ba}_{2}\text{Cu}(\text{OCHMeCH}_{2}\text{NMe}_{2})_{2}(\text{thd})_{4}(\text{Pr}^{i}\text{OH})_{2} + \text{Cu}(\text{OCHMeCH}_{2}\text{NMe}_{2})_{2} \quad (4)$$

The ESR spectra of 4, 5 and 6 in hexane at room temperature show a four-line pattern [<sup>63</sup>Cu: I = 3/2] with  $\langle g \rangle$  values of 2.11, 2.10 and 2.12, respectively, and coupling constants of 85.1, 84 and 86.8 G. The hyperfine coupling is not discernible at room temperature in the ESR spectrum of 3, the  $\langle g \rangle$  value being 2.13. The magnetic susceptibilities are in agreement with one unpaired electron for copper, but no detailed study of the magnetic behaviour has been achieved.

The preceding observations indicate that mixedmetal  $\beta$ -diketonatoalkoxides might undergo quite facile modifications in the presence of a variety of Lewis bases. The choice of a solvent and/or ligand thus becomes crucial for the formation and/or retention of a heteronuclear moiety.

Molecular structures of  $[Cu_3(\mu_3-OBu^1)_2(\mu-OBu^1)(\eta^2-thd)_3$  (4)  $[Ba_2Cu(OCHMeCH_2NMe_2)_2(thd)_4$ (Pr<sup>i</sup>OH)<sub>2</sub>] (6) and of  $[Ba(thd)_2(TMEDA)_2]$  (2)

As established by X-ray diffraction, compound 4 corresponds to a trinuclear copper heteroleptic species,  $[Cu_3(\mu_3-OBu')_2(\mu-OBu')(thd)_3]$ . Its molecular structure is represented in Fig. 1. Selected bond lengths and angles are collected in Table 2. The compound crystallizes as two independent trinuclear molecules, which differ slightly in their bond distances and angles. No intermolecular short contacts are observed in the asymmetric unit. The three metal atoms form nearly regular isosceles triangles with two Cu $\cdots$ Cu distances of 3.017(5) and a third one of 2.788(5) Å. These non-bonding distances are rather short in comparison to those present in the  $[Cu(OC_2H_4OR)(\beta-dik)]_4^{16,26}$  tetramers (2.98-3.36 Å). The triangles are capped by two triply bridging tert-butoxide groups while the third OBu' is doubly bridging. Each copper centre bears a terminal chelating thd ligand. Two types of coordination numbers are observed: Cu(2) and Cu(3)[Cu(52) and Cu(53)] are five-coordinate with a distorted square pyramidal surrounding and O(2) [O(52)] in apical positions, while Cu(1) [Cu(51)] is tetracoordinated and has a distorted square planar geometry. The molecules present a pseudo-symmetry mirror which is based on the plan of the square planar copper ligands and which also contains the oxygen of the alkoxide ligands. The Cu—O bond lengths range from 1.90(2) to 2.27(2)Å, the order of variation being Cu-O(thd) (av.  $1.92 \text{ Å} < \text{Cu}-\mu-\text{OR}$  (av. 1.99 Å)  $< \text{Cu}-\mu_3-\text{OR}$ (av. 2.15 Å). For the square pyramidal copper atoms, the apical Cu-O bond distances [av. 2.26(2) Å] are longer than the basal ones (1.9– 2.08 Å). These values are typical of Jahn-Teller distorted five- and six-coordinated copper(II) complexes. As a result, the Cu— $\mu_3$ -OBu<sup>t</sup> bond distances range from 1.98(2) to 2.27(2) Å. The overall



Fig. 1. Molecular structure of  $[Cu_3(\mu_3-OBu^1)_2(\mu-OBu^1)(\eta^2-thd)_3]$  showing the atom labelling scheme (one of the trinuclear units). The carbons of the methyl groups have been omitted for clarity.

	1.00/0		
Cu(1) = O(1)	1.98(2)	Cu(51) - O(51)	1.98(2)
$Cu(1) \rightarrow O(2)$	1.94(2)	Cu(51)O(52)	1.90(2)
Cu(1)—O(4)	1.92(2)	Cu(51)—O(54)	1.92(2)
Cu(1)—O(5)	1.93(2)	Cu(51)—O(55)	1.96(2)
Cu(2)—O(1)	2.04(1)	Cu(52)O(51)	2.06(2)
Cu(2) - O(2)	2.27(2)	Cu(52)O(52)	2.27(2)
Cu(2) - O(3)	1.90(2)	Cu(52)O(53)	1.95(1)
Cu(2) - O(6)	1.93(2)	Cu(52) - O(56)	1.90(2)
Cu(2) - O(7)	1.94(2)	Cu(52) - O(57)	1.94(2)
$C_{1}(3) = O(1)$	2.08(2)	Cu(53) - O(51)	2.11(2)
Cu(3) = O(2)	2.00(2)	Cu(53) = O(57)	2.71(2)
Cu(3) = O(2)	2.23(2)	Cu(53) = O(52)	2.27(2)
Cu(3) = O(3)	1.94(2)	Cu(53) = O(53)	1.09(2)
Cu(3) = O(8)	1.94(2)	Cu(53) = O(58)	1.89(2)
Cu(3) = O(9)	1.89(2)	Cu(53) - O(59)	1.89(2)
Cu(1)— $Cu(2)$	3.011(5)	Cu(51) $Cu(52)$	3.021(5)
Cu(2) $Cu(3)$	2.788(5)	Cu(52)— $Cu(53)$	2.788(5)
Cu(1)— $Cu(3)$	3.013(5)	Cu(51)Cu(53)	3.013(5)
O(2)—Cu(1)—O(1)	75.9(7)	O(52)Cu(51)-O(51)	76.8(7)
O(4) - Cu(1) - O(1)	94.8(7)	O(54)Cu(51)O(51)	95.4(7)
O(4) - Cu(1) - O(2)	168.2(6)	O(54)-Cu(51)-O(52)	169.2(7)
O(5) - Cu(1) - O(1)	170.8(6)	O(55) - Cu(51) - O(51)	170.7(7)
O(5) - Cu(1) - O(4)	91.4(7)	O(55)— $Cu(51)$ — $O(54)$	89.8(7)
Q(5) - Cu(1) - Q(2)	98.7(7)	O(55)Cu(51)O(52)	99.0(7)
O(2) - Cu(2) - O(1)	67.6(6)	O(52) - Cu(52) - O(51)	67.6(6)
O(3) - Cu(2) - O(1)	81.3(6)	O(53) - Cu(52) - O(51)	80.6(6)
O(3) - Cu(2) - O(2)	87.2(6)	O(53) - Cu(52) - O(52)	87.1(6)
O(5) = Cu(2) = O(2)	88.8(7)	O(55) = O(52) = O(52)	176 5(7)
O(0) = Cu(2) = O(1)	160.0(7)	O(56) = Cu(52) = O(51)	170.3(7)
O(6) = Cu(2) = O(3)	109.0(7)	O(50) - Cu(52) - O(53)	90.3(7)
O(6) = Cu(2) = O(2)	93.3(6)	O(56) - Cu(52) - O(52)	115.8(6)
O(7) = Cu(2) = O(2)	115.0(6)	O(57) - Cu(52) - O(52)	91.8(6)
O(7) - Cu(2) - O(1)	176.9(7)	O(57) - Cu(52) - O(51)	87.1(7)
O(7) - Cu(2) - O(6)	92.7(7)	O(57) - Cu(52) - O(56)	93.6(7)
O(7) - Cu(2) - O(3)	97.0(7)	O(57) - Cu(52) - O(53)	167.2(7)
O(2) - Cu(3) - O(1)	67.4(6)	O(52) - Cu(53) - O(51)	66.9(6)
O(3) - Cu(3) - O(1)	79.5(6)	O(53)—Cu(53)—O(51)	80.7(6)
O(3)—Cu(3)—O(2)	86.6(6)	O(53)Cu(53)O(52)	88.7(6)
O(8) - Cu(3) - O(1)	170.3(7)	O(58)Cu(53)O(51)	87.3(7)
O(8) - Cu(3) - O(3)	100.6(7)	O(58)Cu(53)-O(53)	168.0(7)
O(8) - Cu(3) - O(2)	122.3(7)	O(58) - Cu(53) - O(52)	87.2(7)
$O(9) - C_{II}(3) - O(2)$	88.0(6)	O(59) - Cu(53) - O(52)	122.7(6)
O(9) - Cu(3) - O(1)	87 4(6)	O(59) - Cu(53) - O(51)	170.2(7)
O(9) - Cu(3) - O(8)	92 5(7)	O(59) - Cu(53) - O(58)	91.0(7)
O(9) - Cu(3) - O(3)	166.8(7)	O(59) - Cu(53) - O(53)	100.7(7)
$C_{1}(2) = O(1) = C_{1}(1)$	07.1(6)	$C_{\mu}(52) = O(51) = C_{\mu}(51)$	96.6(7)
Cu(2) = O(1) = Cu(1)	97.1(0)	Cu(52) = O(51) = Cu(51)	90.0(7)
Cu(3) = O(1) = Cu(1)	90.1(0)	Cu(33) - O(31) - Cu(31)	93.1(/)
Cu(3) - O(1) - Cu(2)	83.2(0)	Cu(55) = O(51) = Cu(52)	83.8(0) 02.2(7)
Cu(2) = O(2) = Cu(1)	91.1(6)	Cu(52) - O(52) - Cu(51)	92.3(7)
Cu(3) - O(2) - Cu(1)	91.6(6)	Cu(53) - O(52) - Cu(51)	92.6(6)
Cu(3) - O(2) - Cu(2)	76.1(5)	Cu(53) - O(52) - Cu(52)	75.8(5)
Cu(3) - O(3) - Cu(2)	93.2(6)	Cu(53)—O(53)—Cu(52)	93.0(7)

Table 2. Selected bond lengths (Å) and angles (<sup>\*</sup>) for Cu<sub>3</sub>(OBu<sup>1</sup>)<sub>3</sub>(thd)<sub>3</sub>

metallic core ressembles that of the recently characterized  $MCu_2(OC_2H_4OMe)_3(thd)_3$  species (M = Ca, Sr).<sup>8a</sup>

Copper(II) alkoxides are generally polymeric and insoluble. This observation is valid for classical

alkoxide ligands such as tert-butoxides, but also for functional alkoxides such as 2-methoxyethoxides. Polyfunctional alcoxy- or aminoalcohols are required in order to break down the extensive aggregation with formation of soluble  $Cu(OR)_2$  oligomers or monomers.<sup>12</sup> Another strategy to impart solubility is the formation of heteroleptic copper (11) alkoxides. Ancillary ligands have been  $\beta$ -diketonates<sup>16</sup> and more recently fluoroalkoxides.<sup>27</sup> acetates<sup>28</sup> or various nitrogen donor anions.<sup>29</sup> Copper (11)  $\beta$ -diketonatoalkoxides exist in the solid state mostly as tetramers with cubane or pseudocubane structures,<sup>16,26</sup> or as dimers.<sup>8</sup> Trinuclear units are less common and are essentially represented by {Cu<sub>3</sub>[OCH(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Cl<sub>4</sub>},<sup>30</sup> [Cu<sub>3</sub>(OMe)<sub>4</sub>(Et<sub>2</sub>N-N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]<sup>29</sup> and {Cu<sub>3</sub>( $\mu$ -OBu<sup>1</sup>)<sub>4</sub> [OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}.<sup>27</sup> Triangular<sup>30</sup> and open-shell polyhedral structures<sup>27,29</sup> have been observed.

The heterometallic character of **6** has been confirmed by X-ray diffraction. The compound corresponds to  $BaCu_2(\mu_3,\eta^2-OCHMeCH_2NMe_2)_2$  $(\mu,\eta^2-thd)_2(\eta^2-thd)_2(iPrOH)_2$ ; its molecular structure is represented in Fig. 2. Selected bond lengths and angles are collected in Table 3. The Ba<sub>2</sub>Cu framework is based on a triangular unit capped by two triply bridging aminoalkoxide ligands whose NMe<sub>2</sub> functionalities are linked to Ba(2) and Cu(1), respectively. The most salient feature is the disymmetry of the molecule. The two isopropanol molecules are linked to the same barium centre Ba(1), which is eight-coordinate with an environment of oxygen-donor ligands only. Ba(2) is sevencoordinate with a capped octahedral surrounding, one coordination site being occupied by a nitrogen atom; Cu(1) is five-coordinate. The tetramethylheptanedionate ligands are of three types: two chelate the Ba(1) and Ba(2) atoms, the other displays a bridging-chelating coordination mode and connect Ba(1) and Ba(2), and Ba(2) and Cu(1), respectively. The Ba-O bond lengths range from 2.59(1) to 2.87(1) Å; these values are consistent with the data reported in the literature.<sup>2,31</sup> The isopropanol solvate is stabilized by intramolecular hydrogen with oxygens of bonds tetramethylheptadionate ligands borne by the same metal  $[O(12)-H\cdots O(8)]$  and  $O(11)-H\cdots O(10)$ distances of 2.59(3) and 2.57(2) Å, respectively]. This strong hydrogen bonding appears to be responsible for the asymmetric coordination of the thd ligands on Ba(1) with respect to that on Ba(2). The Cu-O bond lengths range from 1.92(1) to 2.28(1) Å, the longest distance corresponding to the apical bond, Cu(1)—O(4), of the square pyramidal copper atom and thus probably reflects Jahn-Teller distorsion. The Cu-N distance of 2.05(1) Å is in agreement with the values found for coordination bonds in compounds such as  $[Cu_6(dmap)_3Cl_6]$ 



Fig. 2. Molecular structure of [Ba<sub>2</sub>Cu(OCHMeCH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(thd)<sub>4</sub>(Pr'OH)<sub>2</sub>] showing the atom labelling. Intramolecular hydrogen bonds are represented by dotted lines. The carbons (Me groups of the thd ligand and of the isopropanol molecules) have been omitted for clarity.

		2/3((((()))))	
Ba(1) - O(1)	2.73(1)	Ba(1)O(2)	2.70(1)
Ba(1)O(7)	2.87(1)	Ba(1) - O(8)	2.70(1)
Ba(1)-O(9)	2.68(1)	Ba(1) - O(10)	2.74(1)
Ba(1)O(11)	2.81(2)	Ba(1) - O(12)	2.78(2)
Ba(2)O(1)	2.75(1)	Ba(2) - O(2)	2.73(1)
Ba(2)O(4)	2.74(1)	Ba(2)O(5)	2.61(1)
Ba(2)O(6)	2.59(1)	Ba(2) - O(7)	2.67(1)
Ba(2) - N(1)	2.85(1)		
Cu(1)-O(1)	1.93(1)	Cu(1)O(2)	1.92(1)
Cu(1)-O(3)	1.92(1)	Cu(1)O(4)	2.28(1)
Cu(1)—N(2)	2.05(1)		
Ba(2)— $Ba(1)$	4.074(2)		
Ba(1)— $Cu(1)$	3.520(2)		
Ba(2)—Cu(1)	3.325(2)		
O(2) - Ba(1) - O(1)	55.4(3)	O(7) - Ba(1) - O(1)	78.2(3)
O(7) - Ba(1) - O(2)	72.6(3)	O(8) - Ba(1) - O(1)	90.5(3)
O(8) - Ba(1) - O(2)	128.1(3)	O(8) - Ba(1) - O(7)	61.9(3)
O(9) - Ba(1) - O(1)	78.6(3)	O(9) - Ba(1) - O(2)	85.9(3)
O(9) - Ba(1) - O(7)	154.6(4)	O(9) - Ba(1) - O(8)	128.2(4)
O(10)— $Ba(1)$ — $O(1)$	134.4(3)	O(10)—Ba(1)—O(2)	96.2(3)
O(10) - Ba(1) - O(7)	131.2(3)	O(10) - Ba(1) - O(8)	132.1(4)
O(10)Ba(1)-O(9)	63.1(4)	O(11) - Ba(1) - O(1)	151.6(4)
O(11)—Ba(1)—O(2)	100.7(4)	O(11) - Ba(1) - O(7)	79.7(4)
O(11) - Ba(1) - O(8)	94.7(4)	O(11) - Ba(1) - O(9)	118.4(4)
O(11) - Ba(1) - O(10)	55.3(4)	O(12)-Ba(1)-O(1)	111.1(5)
O(12)—Ba(1)—O(2)	162.7(5)	O(12)—Ba(1)—O(7)	117.9(5)
O(12)Ba(1)-O(8)	56.9(5)	O(12)—-Ba(1)—O(9)	80.2(5)
O(12)-Ba(1)-O(10)	86.8(5)	O(12)—Ba(1)—O(11)	95.0(6)
O(2) - Ba(2) - O(1)	54.8(3)	O(4) - Ba(2) - O(1)	67.2(3)
O(4)-Ba(2)-O(2)	70.6(3)	O(5) - Ba(2) - O(1)	137.9(3)
O(5)—Ba(2)—O(2)	164.6(3)	O(5)— $Ba(2)$ — $O(4)$	104.5(3)
O(6)Ba(2)O(1)	150.3(3)	O(6) - Ba(2) - O(2)	98.6(3)
O(6)-Ba(2)-O(4)	93.2(3)	O(6) - Ba(2) - O(5)	66.7(3)
O(7)—Ba(2)—O(1)	81.3(3)	O(7) - Ba(2) - O(2)	75.4(3)
O(7) - Ba(2) - O(4)	142.9(3)	O(7) - Ba(2) - O(5)	112.2(3)
N(7)—Ba(2)—O(6)	106.3(3)	N(1)—Ba(2)—O(1)	62.4(3)
N(1)— $Ba(2)$ — $O(2)$	117.0(3)	N(1)—Ba(2)—O(4)	91.0(3)
N(1)— $Ba(2)$ — $O(5)$	77.1(4)	N(1)—Ba(2)—O(6)	143.4(4)
N(1)— $Ba(2)$ — $O(7)$	91.4(4)		
O(2) - Cu(1) - O(1)	81.9(4)	O(3) - Cu(1) - O(1)	99.6(4)
O(3)—Cu(1)—O(2)	175.1(5)	O(4) - Cu(1) - O(1)	91.9(4)
O(4) - Cu(1) - O(2)	97.2(4)	O(4) - Cu(1) - O(3)	87.5(4)
N(2) - Cu(1) - O(1)	165.4(5)	N(2) - Cu(1) - O(2)	85.1(5)
N(2)-Cu(1)-O(3)	92.9(5)	N(2) - Cu(1) - O(4)	96.3(5)
Ba(2) - O(7) - Ba(1)	94.5(4)	Cu(1) - O(4) - Ba(2)	82.5(3)
Ba(1) - O(2) - Ba(2)	97.3(3)	Cu(1) - O(2) - Ba(1)	97.9(4)
Ba(1) - O(1) - Cu(1)	96.5(4)	Cu(1)-O(2)-Ba(2)	89.5(4)
Ba(1) - O(1) - Ba(2)	85.9(3)		
Ba(2) - O(1) - Cu(1)	88.5(4)		

Table 3. Selected bond lengths (Å) and angles (") for  $Ba_2Cu(OCHMe\ CH_2NMe_2)_2(thd)_4(Pr^iOH)_2$ 

(O)(OH)],  $[Cu_2(dmapH)_2Cl_4]$   $[dmapH = 1,3-bis-(dimethylamino)-2-propanol^{32}]$  or  $[Cu(teaH)]_4$  (teaH<sub>3</sub> = triethanolamine).<sup>33</sup> One may notice that these values are shorter that those observed in the case of the 2,6-bis[(dimethylamino)methyl]-4-

methylphenol ligand.<sup>34</sup> The Ba—N bond distance [(2.85(1) Å] is also quite short with respect to the values observed, for instance, for [Ba(thd)<sub>2</sub> (OHCHMeCH<sub>2</sub>NMe<sub>2</sub>)]<sub>2</sub> [2.962(6) Å] or for Ba[N(C<sub>2</sub>H<sub>4</sub>O)(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>]<sub>2</sub>•2EtOH [3.009(3) Å].<sup>35</sup>

This might result from a lower coordination number, Ba(2) being only seven-coordinate.

The barium tetramethylheptanedionate adduct, [Ba(thd)<sub>2</sub>(TMEDA)<sub>2</sub>] (2), is monomeric in the solid state, as observed for the recently reported adducts with polydentate amines.<sup>36</sup> The centrosymmetric molecular structure is represented in Fig. 3, but no suitable refinement model could be found for all carbons. The structure is reasonable by all chemical criteria, but distances and angles are not precise and/or reliable and are deposited only as supplementary material. Barium is eight-coordinate with Ba—O bond distances around 2.67 Å, while the Ba—N coordination bonds have values around 3.04 Å. Despite the poor resolution of the structure. these values are in agreement with the data reported in the literature.<sup>2,31</sup>

#### Thermal behaviour

Thermogravimetric analyses of the volatile compounds  $[Cu_3(OBu')_3(thd)_3]$  and [Cu(thd)(OBu') $(THF)]_2$  have been made under nitrogen at a pressure of 1 atm. The TGA curve of 5 shows a two-step process: an initial weight loss of 18% in the range 35–130°C corresponding to the elimination of two THF molecules, and then a rapid weight loss of 69.1% in the range 180–238 C which can be attributed to sublimation of the Cu(OBu<sup>t</sup>)(thd) moiety with some decomposition. TGA data of Cu<sub>3</sub>(OBu<sup>t</sup>)<sub>3</sub>(thd)<sub>3</sub> indicate a smooth sublimation in the range  $80-250^{\circ}$ C.

The  $Ba(thd)_2$  adduct (2) is volatile but its sublimation proceeds with loss of TMEDA. As observed for other Ba(thd)<sub>2</sub> adducts,<sup>27</sup> complexation leads to a decrease in the melting point from 210 to 105°C. Thermogravimetric analyses were achieved under normal pressure and under vacuum (5 Torr). The first weight loss, around  $150^\circ C$  under normal pressure and  $100^\circ C$  under vacuum, corresponds to the elimination of the two TMEDA ligands. The second weight loss accounts for the sublimation of  $[Ba(thd)_2]m$ . One may notice that the TGA data account for a lower stability of the  $[Ba(thd)_2(TMEDA)_2]$  adduct as compared to  $[Ba(thd)_2(Me_2NCH_2CHMeOH)]_2$ .<sup>13</sup> These data are also in agreement with the facile dissociation of  $[Ba(thd)_2(TMEDA)_2]$  in solution.

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Fig. 3. Molecular structure of [Ba(η²-thd)₂(TMEDA)₂] (the atoms labelled with a prime are related to the atom having the same numbering by a C₂ symmetry axis). Selected bond lengths (Å) and angles (°): Ba—O 2.67(2); Ba—N: 3.03(2) Å; ∠O—Ba—O (bite): 64.8(6)°.

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