

### 38. Heteronuclear Alkoxide Compounds Containing Copper and Alkaline Earth Metals

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The tetrameric Cu( $\beta$ -diketonate) alkoxide complex  $[\text{Cu}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$  (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate; **1a**) reacts with the alkaline earth metal alkoxides  $[\text{M}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$  (M = Ca, **2a**; M = Sr, **2b**; M = Ba, **2c**) to yield the heteronuclear compounds  $[\text{Cu}_2\text{M}(\text{thd})_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3]$  (M = Ca, **6a**; M = Sr, **6b**). These heterometallic complexes were also obtained in the reaction of **1a** and the mixed Ca and Sr complexes of  $\beta$ -diketonate-alkoxide  $[\text{M}_x(\text{thd})_y(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2x-y}]$  (M = Ca,  $x = 7$ ,  $y = 6$ , **3**; M = Sr,  $x = 5$ ,  $y = 3$ , **4**), respectively. In comparison, **1a** reacts with the analogous  $[\text{Ba}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]$  (**5a**) to yield a  $[\text{Ba}_2\text{Cu}_2(\text{thd})_4(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4(\text{HOCH}_2\text{CH}_2\text{OCH}_3)_2]$  species (**8a**). The *in situ* prepared mixed-ligand Ba compounds  $[\text{Ba}(\text{thd})(\text{OR})]$  (R =  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ , (**5b**); R =  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$ , (**5c**)) react with the corresponding Cu complexes  $[\text{Cu}(\text{thd})(\text{OR})_n]$  (R =  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ,  $n = 4$  (**1b**); R =  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$ ,  $n = 2$  (**1c**)) to the heteronuclear compounds  $[\text{Ba}_2\text{Cu}_2(\text{thd})_4(\text{OR})_4(\text{HOR})_2]$  (R =  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$  (**8b**); R =  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$  (**8c**)). However,  $[\text{Cu}(\text{hfd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$  (hfd = 1,1,1,5,5,5-hexafluoroacetylacetonate; **1e**) is converted in the presence of **2a–c** to the simple metathesis products  $[\text{M}(\text{hfd})_2]$  (M = Ca, Sr, Ba) and  $[\text{Cu}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ . Crystalline  $[\text{Ba}_2\text{Cu}_2(\text{hfd})_2(\text{thd})_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_4(\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_2]$  (**9**) was isolated from the reaction of **1a** with *in situ* prepared  $[\text{Ba}(\text{hfd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]$  (**5d**) in 2-methoxyethanol. X-Ray crystallographic structure determinations are reported for **6a**, **6b**, **8b**, and **8c**.

**Introduction.** – Our research group studies the synthesis and characterization of molecular compounds which might be suitable precursors for the synthesis of high-temperature superconducting materials. We attempt to synthesize heteronuclear complexes containing Y, Cu, and alkaline earth metals with alkoxides and  $\beta$ -diketonates [1–3], which tend to enhance solubility and volatility of the resulting complexes. Compounds containing these ligands are in principle good starting materials for the sol-gel process [4] and/or metalorganic chemical vapor deposition (MOCVD) [5]. Heteronuclear complexes of alkaline earth metals and Cu with oxygen-functionalized ligands are investigated by various research groups [2f] [6] [7], but there is still no systematic study of the synthetic tools and little structural understanding. The only structurally characterized alkaline earth/Cu complexes with alkoxide and  $\beta$ -diketonate ligands are  $[\text{Ba}_2\text{Cu}_2(\text{acac})_4(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4(\text{HOCH}_2\text{CH}_2\text{OCH}_3)_2]$  (acac = acetylacetonate) [7] and  $[\text{BaCu}_4(\text{thd})_4(\text{OCH}_2\text{CH}_2\text{OCH}_3)_6]$  (thd = 2,2,6,6-tetramethylheptane-3,5-dionate; **7**) [8].

We recently reported on the preparation and structural characterization of  $[\text{Cu}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$  (**1a**),  $[\text{Cu}(\text{hfd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$  (hfd = 1,1,1,5,5,5-hexafluoroacetylacetonate; **1e**), and the preparation of  $[\text{BaCu}_4(\text{thd})_4(\text{OCH}_2\text{CH}_2\text{OCH}_3)_6]$  (**7**) [8] from the reaction of **1a** with  $[\text{Ba}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$  (**2c**). In this paper, we report on the reactions of similar Cu species carrying electronically and sterically quite different  $\beta$ -diketonate groups with the alkaline-earth-metal-alkoxide complexes

$[M(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$  ( $M = \text{Ca}$ , **2a**;  $M = \text{Sr}$ , **2b**),  $[\text{Ba}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_2]$  (**2d**), and with the mixed ligand systems  $[M_x(\text{thd})_y(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2x-y}]$  ( $M = \text{Ca}$ ,  $x = 7$ ,  $y = 6$ , **3**;  $M = \text{Sr}$ ,  $x = 5$ ,  $y = 3$ , **4**;  $M = \text{Ba}$ ,  $x = y = 1$ , **5a**),  $[\text{Ba}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)]$  (**5b**), and  $[\text{Ba}(\text{thd})(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)]$  (**5c**).

**Experimental.** – *General.* All manipulations were performed under dry  $\text{N}_2$  with the use of standard *Schlenk* techniques. MeOH, 2-methoxyethanol (*Fluka*), and diethyleneglycolmonomethyl ether (*Fluka*) were dried by distillation from Mg fillings.  $[\text{Cu}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$  (**1a**); and  $[\text{Cu}(\text{thd})(i\text{-PrO})_2]$  (**1d**) were prepared as described in [8]. Bis(isopropoxy)barium and 3-methoxypropanol were prepared by literature methods [9] [10]. 2,2,6,6-Tetramethylheptane-3,5-dione (Hthd; *Fluka*), 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfd; *Lancaster*), Ba, Sr (both  $\varnothing < 0.8$  cm; *Alfa*), and Ca granules (*Fluka*) were used without further purification. All compounds mentioned in the following sections were handled and stored under  $\text{N}_2$  due to their hygroscopic nature.

1. *Preparation of  $[\text{Cu}(\text{thd})(\text{OR})]_n$*  ( $R = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ,  $n = 4$ , **1b**;  $R = \text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$ ,  $n = 2$ , **1c**).  $[\text{Cu}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)]_4$  (**1b**).  $[\text{Cu}(\text{thd})(i\text{-PrO})_2]$  (**1d**; 10.0 g, 1.36 mmol) was added to a mixture of 20 ml of diethyleneglycolmonomethyl ether and 5 ml of THF. After 2 h, the resulting dark blue soln. was slowly evaporated to dryness in a stream of  $\text{N}_2$ , yielding quantitatively 11.97 g of dark blue crystals of **1c**. M.p. 81–84°; dec.  $> 220^\circ$ ; subl.  $140^\circ/10^{-4}$  Torr. VIS (THF): 592 (118); ( $\text{CHCl}_3$ ): 607 (81), 525 (75). IR (Nujol): 1568vs, (C=O), 1553s, (C=O), 1536s, 1502s, 1396vs, 1389vs, 1361s, 1292vw, 1246w, 1223m, 1200w, 1180w, 1146m, 1117m, 1091m, 1027w, 963w, 937w, 873m, 793m, 765vw, 743w. EI-MS (rel.  $^{63}\text{Cu}$ ;  $R = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ): 795 ( $[\text{Cu}_3(\text{thd})_2(\text{OR})_2]^+$ ), 692 ( $[\text{Cu}_3(\text{thd})(\text{OR})]^+$ ), 611 ( $[\text{Cu}_2(\text{thd})_2(\text{OR})]^+$ ), 547 ( $[\text{Cu}_2(\text{thd})(\text{OR})]^+$ ), 492 ( $[\text{Cu}_2(\text{thd})_2]^+$ ), 429 ( $[\text{Cu}(\text{thd})_2]^+$ ), 428 ( $[\text{Cu}_2(\text{thd})(\text{OR})]^+$ ), 181 ( $[\text{Cu}(\text{thd})]^+$ ). Anal. calc. for  $\text{C}_{64}\text{H}_{120}\text{Cu}_4\text{O}_{20}$ : C 52.51, H 8.26, Cu 17.36; found: C 52.24, H 8.26, Cu 18.11.

$[\text{Cu}(\text{thd})(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)]_2$  (**1c**). Prepared as described for **1b** using 3-methoxypropanol. The resulting dark blue soln. was evaporated to dryness, and recrystallization from hexane at  $-30^\circ$  produced dark-blue crystals. Yield: 9.34 g (85%). M.p. 98–99°; dec.  $> 210^\circ$ ; subl.  $130^\circ/10^{-4}$  Torr. VIS (THF): 595 (106); ( $\text{CHCl}_3$ ): 605 (86), 525 (80). IR (Nujol): 1567vs, (C=O), 1554s, (C=O), 1537s, 1503s, 1398s, 1391s, 1361s, 1292vw, 1248w, 1225m, 1184m, 1148m, 1130w, 1106m, 1094m, 1040w, 961w, 937vw, 918vw, 895vw, 874m, 792m, 773vw, 745w, 636w, 559m, 510w. EI-MS (rel.  $^{63}\text{Cu}$ ;  $R = \text{CH}_2\text{CH}_2\text{OCH}_3$ ): 581 ( $[\text{Cu}_2(\text{thd})_2(\text{OR})]^+$ ), 492 ( $[\text{Cu}_2(\text{thd})_2]^+$ ), 429 ( $[\text{Cu}(\text{thd})_2]^+$ ), 389 ( $[\text{Cu}(\text{thd})(\text{OR})]^+$ ). Anal. calc. for  $\text{C}_{30}\text{H}_{56}\text{Cu}_2\text{O}_8$ : C 53.63, H 8.40, Cu 18.92; found: C 53.91, H 8.38, Cu 18.80.

2. *Preparation of  $[M_x(\text{thd})_y(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2x-y}]$*  ( $M = \text{Ca}$ ) (**3**), Sr (**4**), Ba (**5**).  $[\text{Ca}_7(\text{thd})_6(\text{OCH}_2\text{CH}_2\text{OCH}_3)_8]$  (**3**). Ca granules (0.50 g, 12.48 mmol) were stirred in 80 ml of MeOH at r.t. for 4 h in the presence of a catalytical amount of mercuric chloride (ca. 5 mg). MeOH was then removed *in vacuo* and replaced by 20 ml of 2-methoxyethanol. The resulting colorless suspension was stirred at  $50^\circ$  for 4 h, cooled to r.t., and 2.30 g (12.48 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione in 40 ml of toluene were added. After 4 h, the soln. was chilled to  $-30^\circ$ . Colorless crystals of **3** precipitated which were dried *in vacuo*. Yield: 1.24 g (35%). Dec.  $> 232^\circ$ . IR (Nujol): 1592vs (C=O), 1579s (C=O), 1536m, 1505s, 1417vs, 1357s, 1274vw, 1241m, 1225m, 1196w, 1182m, 1132m, 1110s, 1068s, 1015m, 907m, 865m, 838w, 791w, 752w, 732vw.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 5.47 (s, 3 CH); 4.12 (br. s, 4  $\text{CH}_2\text{O}$ ); 3.52 (br. s, 4  $\text{CH}_2\text{OCH}_3$ ); 3.18 (s, 4  $\text{CH}_3\text{O}$ ); 1.012 (s, 6  $(\text{CH}_3)_3\text{C}$ ).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ): 199.17 (CO); 88.73 (CH); 76.72 (br.,  $\text{CH}_2\text{O}$ ); 61.45 (br.,  $\text{C}_2\text{H}_5\text{OCH}_3$ ); 58.92 (br.,  $\text{CH}_3\text{O}$ ); 40.82 ( $(\text{CH}_3)_3\text{C}$ ); 28.79 ( $(\text{CH}_3)_3\text{C}$ ). Anal. calc. for  $\text{C}_{90}\text{H}_{170}\text{Ca}_7\text{O}_{28}$ : C 54.57, H 8.65, Ca 14.16; found: C 54.39, H 8.74, Ca 14.14.

$[\text{Sr}_5(\text{thd})_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)_7]$  (**4**). 2,2,6,6-Tetramethylheptane-3,5-dione (1.05 g, 5.71 mmol) was added dropwise at r.t. to a rapidly stirred soln. of  $[\text{Sr}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$  (prepared *in situ* from 0.50 g (5.71 mmol) Sr granules in 20 ml of 2-methoxyethanol). After 1 h, the clear mixture was slowly cooled to  $-30^\circ$ . Colorless needles were obtained and dried *in vacuo*. Yield: 0.43 g (25%). M.p. 84–86°; dec.  $> 195^\circ$ . IR (Nujol): 1596vs (C=O). 1580s (C=O), 1535m, 1503s, 1417vs, 1358s, 1272vw, 1242w, 1222w, 1187m, 1126s, 1098w, 1076m, 1069m, 1018w, 904w, 864m, 835w, 823vw, 792w, 759w, 733vw.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ): 5.76 (s, 3 CH); 3.93 (br. s, 7  $\text{CH}_2\text{O}$ ); 3.37 (br. s, 7  $\text{CH}_2\text{OCH}_3$ ); 3.31 (s, 7  $\text{CH}_3\text{O}$ ); 1.16 (s, 6  $(\text{CH}_3)_3\text{C}$ ).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ): 198.53 (CO); 90.42 (CH); 77.14 ( $\text{CH}_2\text{O}$ ); 61.68 ( $\text{CH}_2\text{OCH}_3$ ); 58.30 ( $\text{CH}_3\text{O}$ ); 44.01 ( $(\text{CH}_3)_3\text{C}$ ); 28.86 ( $(\text{CH}_3)_3\text{C}$ ).

$[\text{Ba}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]$  (**5a**). 2,2,6,6-tetramethylheptane-3,5-dione (2.68 g, 14.56 mmol) was added dropwise at r.t. to a soln. of  $[\text{Ba}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$  (prepared *in situ* from 2 g (14.56 mmol) of Ba in 25 ml of 2-methoxyethanol). After cooling of the mixture to  $4^\circ$ , colorless crystals of  $[\text{Ba}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)(\text{HOCH}_2\text{CH}_2\text{OCH}_3)]$  were obtained. They loose coordinated solvent molecules  $\text{HOCH}_2\text{CH}_2\text{OCH}_3$  upon drying *in vacuo*. Yield: 5.76 g (65%). M.p. 89–92°; dec.  $> 175^\circ$ . IR (Nujol): 1601vs (C=O), 1589s (sh, C=O), 1573s (C=O), 1531s, 1504s, 1488m, 1452s, 1428vs, 1388m, 1358s, 1267w, 1253m, 1238m,

1218w, 1197w, 1182m, 1124m, 1115m, 1106w, 1089m, 1069m, 1053s, 1020m, 953vw, 897w, 862m, 836w, 781w, 755w, 732vw. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): 5.81 (s, CH); 3.89 (br. t, J = 3.6, CH<sub>2</sub>O); 3.40 (br. t, J = 3.6, CH<sub>2</sub>OCH<sub>3</sub>); 3.22 (s, CH<sub>3</sub>O); 1.31 (s, 2(CH<sub>3</sub>)<sub>3</sub>C). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>): 198.02 (CO); 88.48 (CH); 76.30 (CH<sub>2</sub>O); 61.27 (CH<sub>2</sub>OCH<sub>3</sub>); 58.40 (CH<sub>3</sub>O); 41.01 (CH<sub>3</sub>)<sub>3</sub>C); 29.02 (CH<sub>3</sub>)<sub>3</sub>C). Anal. calc. for C<sub>14</sub>H<sub>26</sub>BaO<sub>4</sub>: Ba 34.71; found: Ba 34.19.

3. *Preparation of [CaCu<sub>2</sub>(thd)<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>] (6a).* *Method a.* A dark blue soln. of 2.50 g (1.94 mmol) of **1a** in 30 ml of 2-methoxyethanol was added dropwise at r.t. to a colorless suspension of [Ca(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**2a**) in 20 ml 2-methoxyethanol (prepared from 0.16 g (3.88 mmol) of Ca granules as described above). The resulting blue suspension was stirred overnight and then filtered off. The blue filtrate was slowly cooled to +4° affording dark blue crystals of **6a** suitable for single-crystal X-ray diffraction. Further cooling of the mother liquor to -30° produced an additional crop of crystals of **6a**, which were collected by filtration and dried *in vacuo*. Total yield: 0.91 g (25%, based on Ca). M.p. 109–116°; dec. > 200°. Compound **6a** is very soluble in THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, toluene, and slightly soluble in Et<sub>2</sub>O and hexane. VIS (CHCl<sub>3</sub>): 610 (81), 535 (76). IR (Nujol): 1590vs (C=O), 1572vs (C=O), 1552s (C=O), 1535s, 1502vs, 1422s, 1389vs, 1359vs, 1243m, 1224m, 1199w, 1180m, 1146w, 1132m, 1120m, 1088s, 1073s, 1019m, 983vw, 963vw, 914w, 872m, 837w, 791m, 763w, 744w. *M<sub>w</sub>* (osmometric): 582 (CHCl<sub>3</sub>), 639 (toluene); calc. for C<sub>42</sub>H<sub>78</sub>CaCu<sub>2</sub>O<sub>12</sub>: 942. Anal. calc. for C<sub>42</sub>H<sub>78</sub>CaCu<sub>2</sub>O<sub>12</sub>: C 53.54, H 8.34, Ca 4.25, Cu 13.49; found: C 53.80, H 8.46, Ca 4.11, Cu 12.89.

*Method b.* A colorless suspension of [Ca(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**2a**) in 15 ml of 2-methoxyethanol and 15 ml toluene (prepared *in situ* from 0.16 g (3.88 mmol) of Ca granules as described above) and 0.72 g (3.88 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione were combined as described for **3**. After 1 h, the mixture was added dropwise to a dark blue soln. of 2.50 g (1.94 mmol) of **1a** in 15 ml 2-methoxyethanol at r.t. Stirring was continued for 4 h, and the reaction mixture was then concentrated *in vacuo* to half of its original volume. Dark blue crystals of **6a** formed upon slow cooling to -30° which were collected by filtration and dried *in vacuo*. Yield: 2.74 g (75%, based on Ca). M.p. 118–121°; dec. > 205°. Anal. calc. for C<sub>42</sub>H<sub>78</sub>CaCu<sub>2</sub>O<sub>12</sub>: C 53.54, H 8.34, Ca 4.25, Cu 13.49; found: C 53.83, H 8.35, Ca 4.21, Cu 13.66.

4. *Preparation of [Cu<sub>2</sub>Sr(thd)<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>] (6b).* *Method a.* Upon slow addition of a soln. of [Sr(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**2b**) (prepared *in situ* from 0.34 g (3.88 mmol) of Sr granules and 10 ml of 2-methoxyethanol) to a dark blue soln. of 2.50 g (1.94 ml) of **1a**, a blue precipitate was formed overnight at r.t. It was filtered off and the filtrate allowed to stand at 30° for 3 d. A blue powder deposited containing some dark blue crystals of **6b** suitable for X-ray diffraction, which were isolated and dried *in vacuo*. Yield: 0.77 g (20%, based on Sr). M.p. 138–141°; dec. > 180°. Compound **6b** is somewhat better soluble in Et<sub>2</sub>O and hexane than **6a**. VIS (CHCl<sub>3</sub>): 605 (83), 530 (77). IR (Nujol): 1591s (C=O), 1571vs (C=O), 1553s (C=O), 1535s, 1504s, 1421s, 1398vs, 1359s, 1240m, 1224m, 1199w, 1181m, 1150w, 1121m, 1083s, 1074m, 1017m, 980vw, 964vw, 912w, 873m, 836w, 823vw, 792w, 765vw, 743w. Anal. calc. for C<sub>42</sub>H<sub>78</sub>Cu<sub>2</sub>O<sub>12</sub>Sr: C 50.95, H 7.94, Cu 12.84, Sr 8.85; found: C 50.89, H 8.04, Cu 12.88, Sr 8.87. *M<sub>w</sub>* (osmometric): 563 (CHCl<sub>3</sub>), 689 (toluene); calc. for C<sub>42</sub>H<sub>78</sub>Cu<sub>2</sub>O<sub>12</sub>Sr: 990.

*Method b.* As for **6a** using an *in situ* prepared solution of **4** (prepared from 0.34 g (3.88 mmol) of Sr and 0.72 g (3.88 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione in 10 ml of 2-methoxyethanol as described in **2**). Dark blue crystals of **6b** were obtained upon slow cooling to -30°. Yield: 3.07 g (80%, based on Sr). M.p. 149–151°; dec. > 210°.

5. *Preparation of [Ba<sub>2</sub>Cu<sub>2</sub>(thd)<sub>4</sub>(OR)<sub>4</sub>(HOR)<sub>2</sub>] (R = CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, **8a**; R = CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, **8b**; R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, **8c**). [Ba<sub>2</sub>Cu<sub>2</sub>(thd)<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>4</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**8a**). A soln. of 2.88 g (7.28 mmol) of **5a** in 15 ml of 2-methoxyethanol and 15 ml of toluene (**5a** might also be prepared *in situ*) was combined dropwise with a dark blue soln. of 2.35 g (1.82 mmol) of **1a** in 10 ml of 2-methoxyethanol. A purple precipitate formed instantaneously. Toluene (20 ml) was added, and the reaction mixture was heated to 100° for a short time upon which the purple precipitate dissolved. Slow cooling to +4° resulted in the formation of dark purple blue crystals of **8a**, which were collected by filtration and dried *in vacuo*. Yield: 5.49 g (95%, based on **5a**). Dec. > 190°. Compound **8a** is very soluble in THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, soluble in toluene and hexane, and very slightly in 2-methoxyethanol. VIS (CHCl<sub>3</sub>): 608 (63), 545 (59). IR (Nujol): 3245w (br., OH), 1603s (C=O), 1588vs (C=O), 1571vs (C=O), 1551m, 1534s, 1503s, 1425m, 1397vs, 1388s, 1359s, 1242w, 1221w, 1198w, 1183w, 1148w, 1119m, 1077s, 1071s, 1022m, 901w, 891w, 872w, 862w, 837w, 790w, 763w, 733w. Anal. calc. for C<sub>62</sub>H<sub>120</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>20</sub>: C 46.91, H 7.62, Ba 17.30, Cu 8.01; found: C 46.80, H 7.86, Ba 17.26, Cu 8.39. *M<sub>w</sub>* (osmometric): 750 (CHCl<sub>3</sub>), 883 (toluene); calc. for C<sub>62</sub>H<sub>120</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>20</sub>: 1587.*

[Ba<sub>2</sub>Cu<sub>2</sub>(thd)<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>4</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**8b**). A soln. of 7.28 mmol of [Ba(thd)(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)] (**5b**; prepared *in situ* from 1.00 g (7.28 mmol) of Ba granules in 25 ml of diethyleneglycolmonomethyl ether and 1.34 g (7.28 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione) was added dropwise to a dark blue soln. of 2.67 g (1.82 mmol) of **1b** in 15 ml of toluene, whereby the color changed from dark

blue to purple blue. After 2 h, the mixture was reduced to about 25% of its original volume and then chilled to +4° producing dark purple crystals of **8b**, which were filtered off and dried *in vacuo*. The filtrate was then allowed to stand for 3 d at –30°, producing an additional crop of purple crystals of **8b**, which were treated as above. Total yield: 5.74 g (85%, based on Ba). M.p. 99–102°; dec. > 135°. Compound **8b** is very soluble in THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, toluene, Et<sub>2</sub>O, diethyleneglycolmonomethyl ether, and hexane. VIS (CHCl<sub>3</sub>): 540 (as, 79). IR (Nujol): 3312w (br, OH), 1598s (sh, C=O), 1588vs (C=O), 1571s (C=O), 1551m (C=O), 1534s, 1504s, 1459s, 1430s, 1394s, 1390s, 1358s, 1259w, 1244m, 1226m, 1200m, 1183m, 1135s, 1127s, 1089s, 1075s, 1025w, 967w, 942w, 899m, 864m, 791w, 745w. Anal. calc. for C<sub>74</sub>H<sub>146</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>26</sub>: C 47.94, H 7.94, Ba 14.82, Cu 6.86; found: C 47.59, H 7.72, Ba 14.80, Cu 6.69. *M<sub>w</sub>* (osmometric): 490 (CHCl<sub>3</sub>), 385 (toluene); calc. for C<sub>74</sub>H<sub>146</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>26</sub>: 1854.

[Ba<sub>2</sub>Cu<sub>2</sub>(thd)<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**8c**). *Method a.* [Ba(i-PrO)<sub>2</sub>] (0.50 g, 1.96 mmol) was suspended in 10 ml of toluene. After addition of 2 ml of 3-methoxypropanol and 1.31 g (1.96 mmol) of **1c**, the resulting dark blue soln. was stirred at r.t. for 3 d. A blue precipitate was formed and filtered off. The filtrate was concentrated to 5 ml under a stream of N<sub>2</sub>. Purple blue crystals of **8c** precipitated from the dark blue soln. upon standing overnight at r.t. The soln. was decanted off, and the crystals of **8c** were dried *in vacuo*. By cooling the mother liquor to –30° an additional crop of crystals could be isolated as above. Total yield: 0.41 g (25%, based on Ba). M.p. 69–71°; dec. > 165°. Compound **8c** is very soluble in THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and soluble in toluene. VIS (CHCl<sub>3</sub>): 600 (143), 530 (137). IR (Nujol): 3306w (br, OH), 1590s (C=O), 1572vs (C=O), 1569vs (C=O), 1554s (C=O), 1536m, 1503s, 1422s, 1411s, 1401vs, 1391s, 1360s, 1245w, 1224m, 1185m, 1148w, 1125m, 1091m, 1027w, 962w, 872m, 865m, 792m, 733w. Anal. calc. for C<sub>68</sub>H<sub>132</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>20</sub>: C 48.87, H 7.96, Ba 16.43, Cu 7.61; found: C 48.62, H 8.16, Ba 16.25, Cu 7.71. *M<sub>w</sub>* (osmometric): 822 (CHCl<sub>3</sub>), 862 (toluene); calc. for C<sub>68</sub>H<sub>132</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>20</sub>: 1671.

*Method b.* Compound **1c** (0.66 g, 1.96 mmol) was added at once to a colorless suspension of 3.92 mmol of [Ba(thd)(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)] (**5c**; prepared *in situ* from 1.00 g (3.92 mmol) of [Ba(i-PrO)<sub>2</sub>] and 0.72 g (3.92 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione in a solvent mixture of 25 ml of toluene and 2 ml of 3-methoxypropanol). The color of the suspension changed immediately to dark green, and, after 4 h, a dark blue soln. was formed. Stirring at r.t. was continued overnight, and then the reaction mixture was chilled to –30° to produce purple blue crystals of **8c**. These were then filtered off and dried *in vacuo*. Yield: 1.80 g (55%, based on Ba). M.p. 71–72°; dec. > 165°. Anal. calc. for C<sub>68</sub>H<sub>132</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>20</sub>: C 48.87, H 7.96, Ba 16.43, Cu 7.61; found: C 48.49, H 7.70, Ba 16.34, Cu 7.28.

6. *Preparation of [Ba<sub>2</sub>Cu<sub>2</sub>(hfd)<sub>2</sub>(thd)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>4</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**9**).* 1,1,1,5,5,5-Hexafluoroacetylacetone (2.27 g, 10.92 mmol) was added dropwise at r.t. to a soln. of [Ba(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (**2**; prepared *in situ* from 1.50 g (10.92 mmol) of Ba granules in 20 ml of 2-methoxyethanol) forming *in situ* a soln. of [Ba(hfd)(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)] (**5d**). The mixture was stirred for 1 h, before it was slowly combined with a dark blue soln. of 3.52 g (2.73 mmol) of **1a** in 10 ml of 2-methoxyethanol and 5 ml of THF. A purple blue precipitate was formed which was then dissolved by warming the mixture to 80°. By slow cooling to 4° purple blue crystals of **9** suitable for X-ray diffraction were obtained, which were collected by filtration and dried *in vacuo*. Yield: 7.14 g (80%, based on Ba). M.p. 118–121°; dec. > 195°. Compound **9** is very soluble in THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, soluble in toluene and hexane, and very slightly soluble in 2-methoxyethanol. VIS (CHCl<sub>3</sub>): 625 (93), 560 (sh, 69). IR (Nujol): 3425w (br, OH), 1668s (C=O), 1573s (C=O), 1561s (C=O), 1533vs, 1506s, 1397s, 1391s, 1251vs, 1224s, 1197vs, 1187vs, 1143vs, 1134vs, 1120vs, 994vw, 966vw, 943w, 897m, 874m, 834m, 789m, 762vw, 748w, 737vw, 660m, 631vw, 591vw, 575m, 556w. Anal. calc. for C<sub>50</sub>H<sub>84</sub>Ba<sub>2</sub>Cu<sub>2</sub>F<sub>12</sub>O<sub>20</sub>: C 36.73, H 5.18, F 13.95, Ba 16.80, Cu 7.77; found: C 36.98, H 4.90, F 13.66, Ba 16.81, Cu 7.95. *M<sub>w</sub>* (osmometric): 1742 (CHCl<sub>3</sub>), 1906 (toluene); calc. for C<sub>50</sub>H<sub>84</sub>Ba<sub>2</sub>Cu<sub>2</sub>F<sub>12</sub>O<sub>20</sub>: 1635.

*X-Ray Crystal-Structure Determinations.* All data were measured on a Siemens R3m/V four-circle diffractometer with a graphite monochromator and MoK<sub>α</sub> radiation (λ = 0.71073 Å). The SHELXTL PLUS program package [11] was used for structure solution (direct methods for **6a**, **6b**, and **8c**; Patterson search for **8b**) and refinement. All non-H atoms were refined anisotropically without positional restraints; H-atoms were generally fixed at idealized positions (C–H = 0.96 Å) and given a common fixed isotropic temp. factor. In the crystal lattice of **6a**, some of the *t*-Bu groups of the thd ligands, and two C-atoms of an (OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>) ligand are two-fold disordered. They were refined with fixed site occupation factors. Crystal **9** was found to be partially twinned. By suitable choice of the scan range, it was possible to separate out those reflections which were due to the predominant twin component. Other reasons for the relatively high standard deviations of the structural parameters of **9** are considered to be a consequence of paucity of observed reflections resulting from a small crystal and of disordering in the CF<sub>3</sub> and *t*-Bu groups. Crystallographic data and details of the crystal structure determinations are summarized in the Table.

Table. Crystallographic Data of 6a, 6b, 8b, 8c, and 9

	6a	6b	8b	8c	9
Formula	$C_{40}H_{78}CaCu_2O_{12}$	$C_{40}H_{78}Cu_2O_{12}Sr$	$C_{74}H_{144}Ba_2Cu_2O_{26}$	$C_{68}H_{132}Ba_2Cu_2O_{20}$	$C_{50}H_{84}Ba_2Cu_2F_{12}O_{20}$
F. wt.	942.2	989.7	1851.7	1671.5	1634.9
$F(000)$	2016	1044	966	870	820
Crystal size [mm]	$0.60 \times 0.55 \times 0.90$	$0.40 \times 0.35 \times 0.40$	$0.80 \times 0.55 \times 0.45$	$0.70 \times 0.55 \times 0.40$	$0.20 \times 0.30 \times 0.10$
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ [Å]	24.912(8)	12.558(4)	10.533(3)	10.607(3)	9.942(2)
$b$ [Å]	10.108(3)	14.950(7)	14.693(4)	14.422(4)	13.809(7)
$c$ [Å]	21.897(7)	15.781(6)	15.920(5)	15.026(4)	14.926(9)
$\alpha$ [deg]		73.49(3)	101.55(2)	72.64(2)	66.64(4)
$\beta$ [deg]		85.69(3)	107.77(2)	70.59(2)	77.20(4)
$\gamma$ [deg]		64.93(3)	97.52(2)	76.45(2)	72.71(4)
$V$ [Å <sup>3</sup> ]	5180(3)	2569(2)	2250(1)	2046(1)	1784(2)
$Z$	4	2	1	1	1
$\rho_{calc}$ [g cm <sup>-3</sup> ]	1.208	1.279	1.367	1.357	1.520
$\mu$ [cm <sup>-1</sup> ] (MoK $\alpha$ )	9.68	18.75	13.96	15.23	17.68
$T$ [K]	236	236	221	221	231
$2\theta$ range	4 to 50°	4 to 50°	4 to 50°	4 to 50°	4 to 50°
Scan type	$Wycckoff \omega$	$Wycckoff \omega$	$Wycckoff \omega$	$Wycckoff \omega$	$Wycckoff \omega$
Scan speed	$2.0 \leq \omega \leq 14.7$	$2.5 \leq \omega \leq 14.7$	$2.5 \leq \omega \leq 14.7$	$2.3 \leq \omega \leq 14.7$	$3.0 \leq \omega \leq 14.7$
No. of independent reflections	9099	9027	7932	7209	4658
No. of observed reflections ( $F_o > 6\sigma(F_o)$ )	7343	6954	7414	6624	2012 <sup>c)</sup>
Parameters refined	678	518	473	419	259
Weighting scheme	unit weights	$w = 1/\sigma^2(F_o)$	unit weights	unit weights	$w = 1/\sigma^2(F_o)$
Absorption correction	semi-empirical	DIFABS	N/A	N/A	DIFABS
min/max Transmission	0.0311/0.0554				
$R^a)/R_w^b)$	0.058/0.056	0.087/0.054	0.028/0.032	0.037/0.043	0.083/0.10
largest dif. peak, eÅ <sup>-3</sup>	0.81	1.36	0.97	1.42	0.82

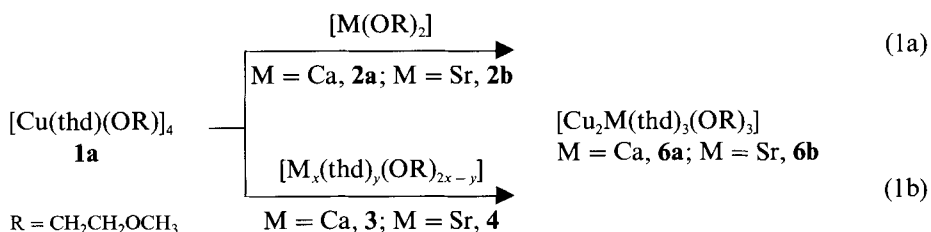
<sup>a)</sup>  $R = (\Sigma |F_o - F_c|) / \Sigma(F_o)$ .

<sup>b)</sup>  $wR = [\Sigma(w(F_o - F_c)^2) / \Sigma(w(F_o)^2)]^{1/2}$ .

<sup>c)</sup>  $F_o > 8\sigma(F_o)$ .

*Other Physical Measurements and Elemental Analyses.* M.p. were determined on a *Büchi 530* melting-point apparatus and are uncorrected. IR Spectra were recorded on a *FTS 45 BIORAD* spectrometer as nujol mulls between KBr disks. Electronic spectra in the visible region (VIS) were recorded on a *Varian Cary 2300* spectrophotometer. Absorption maxima ( $\lambda_{\text{max}}$ ) are given in nm with the molecular absorption coefficient  $\epsilon$  ( $\text{l mol}^{-1} \text{cm}^{-1}$ ) in parentheses (sh: shoulder). EI Mass spectra were recorded on a *Finnigan Mat 8320* instrument.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured on a *Varian Gemini 200* spectrometer operating at 200 and 50.3 MHz, respectively,  $^{19}\text{F}$ -NMR on a *Varian Gemini 300* spectrometer at 282.3 MHz. Molecular-weight determinations ( $M_w$ ) in  $\text{g} \cdot \text{mol}^{-1}$  were obtained with a *Knauer* vapor-pressure osmometer (type 11.00) at r.t. using  $\text{CHCl}_3$  or toluene as solvent. Elemental analyses were performed at the Microanalytical Department of the University of Zürich.

**Results and Discussion.** – Treatment of **1a** with **2a** or **2b** in 2-methoxyethanol affords, according to *Eqn. 1a*, the blue mixed-metal compounds **6a** or **6b**, which were isolated by crystallization at  $-30^\circ$  after filtration from accompanying insoluble Cu alkoxides. The yields of **6a** and **6b** were low, obviously, because the starting materials **1a** and **2a** or **2b** did not provide the amount of the required for the formation of **6a** and **6b**.



However, improving the thd/RO ratio by starting from *in situ* prepared  $[\text{M}_x(\text{thd})_y(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2x-y}]$  (M = Ca  $x = 7, y = 6, 3$ ; M = Sr,  $x = 5, y = 3, 4$ ) and **1a** raised the yield of **6a** and **6b** to 75% and 80%, respectively (*Eqn. 1b*).

The structural assignments of **6a** and **6b** were based solely on single-crystal X-ray analyses, since NMR investigations were precluded in these cases of  $\text{Cu}^{\text{II}}$ -containing compounds, and IR or UV/VIS data were not conclusive.

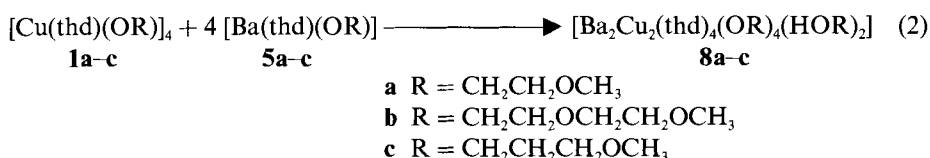
It should be noted, that the starting component **3** indeed shows a heptanuclear structure  $[\text{Ca}_7(\text{thd})_6(\text{OCH}_2\text{CH}_2\text{OCH}_3)_8]^{1)}$  which is retained in ( $D_6$ )toluene solution as indicated by  $^1\text{H}$ -NMR spectroscopy. The  $\beta$ -diketonate and alkoxide residues of **3** give rise to a single group of signals for each ligand even at  $-80^\circ$ . Therefore, it has to be assumed that we either deal with a highly symmetric solution structure – which seems to be unlikely – or with the case of a fluxional molecule in which chemically different ligand positions are equilibrated on the NMR time scale.

When changing the solvent and recording the  $^1\text{H}$ -NMR spectrum of **3** at r.t. in  $\text{CD}_2\text{Cl}_2$ , additional small resonances of a second species appear which increase in intensity upon cooling. This indicates that the integrity of the molecular structure is not retained. A partial fragmentation occurs, which is quite commonly observed in the area of polynuclear metal-alkoxide chemistry [12]. For the synthetic use of **3**, this solution behavior is beneficial, since assembly processes to form species like **6a** and **6b** normally require the rupture of polynuclear units with generation of smaller, kinetically relevant building blocks.

<sup>1)</sup> Exact solid-state structure has been determined by single-crystal X-ray diffractometry which will be published elsewhere.

For a high-yield synthesis of **6b**, it was necessary to use **4** as a starting material, the structural assignment of which is, however, not certain. Its composition was derived from the integration of the <sup>1</sup>H-NMR ligand signals (C<sub>6</sub>D<sub>6</sub>). The total <sup>1</sup>H-NMR spectrum of **4** was in agreement with the formulation of a single species which suggested, that **4** did not undergo fragmentation into smaller units at least not to a spectroscopically recognizable extent.

The Cu<sub>4</sub>Ba species **7** was reported earlier, and it was obtained by a synthetic route starting from the homoleptic [Ba(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] compound **2c** and the heteroleptic [Cu(thd)(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> system **1a** [8]. To control stoichiometry in the formation of other polynuclear Cu<sub>x</sub>Ba<sub>y</sub> compounds, we conducted experiments based on heteroleptic ether-functionalized alkoxide/β-diketonate Ba components **5a–c**. Alkoxides were varied to increase the number of ligating functionalities to change their coordination behavior *via* enlargement of the ring size in the alkoxide chelates.



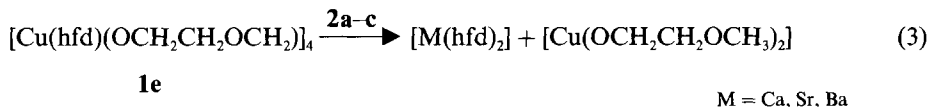
The reactions of **1a–c** with **5a–c** in 2-methoxyethanol, 3-methoxypropanol, or diethyleneglycolmonomethyl ether/toluene mixtures produced at r.t. the purple Cu<sub>2</sub>Ba<sub>2</sub> clusters **8a–c** in moderate to high yields (*Eqn. 2*). It should be noted that the starting component **5a**, a well-defined compound, was characterized structurally in the solid state<sup>2)</sup>. The structural assignment for **8b** and **8c** was based on single-crystal X-ray diffractometry, while the constitution of the core unit of **8a** was assumed to be analogous to **8b, c** because of close resemblance of the IR and UV/VIS spectroscopic data. Elemental analysis also agrees with this hypothesis.

Compounds **8a–c** are soluble in practically all organic solvents of moderate-to-high polarity. Their solution structure could, however, not be definitely assigned, since, similarly to **6a** and **6b**, there was no appropriate spectroscopic method available. Osmometric molecular-weight determinations of these heteronuclear complexes provided values which are smaller than those expected from their solid-state structures. In toluene or CHCl<sub>3</sub>, **8a** and **8c** showed a value *ca.* ½ of the solid-state molecular weight. It may, therefore, be suggested, that these compounds exist as [BaCu(thd)<sub>2</sub>(OR)<sub>2</sub>(HOR)] units in solution. But an 1:1 ratio of **8a** or **8c** in equilibrium with [Ba(thd)(OR)(HOR)] and [Cu(thd)(OR)] species would also satisfy the results of the measurements. For **8b**, we assume a total breakdown of the cluster framework into [Ba(thd)(OR)(HOR)] and [Cu(thd)(OR)] fragments, since a molecular weight of just ¼ of the value of the solid-state structure was observed.

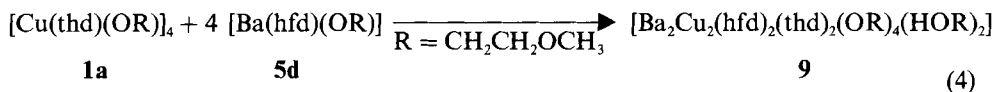
Thus, formation of Cu/alkaline earth high-nuclearity units carrying O-functionalized ligands is obviously a domain of the solid state alone. In certain cases, however, when even minor chemical variations of residues in the ligand periphery cause significant changes of the polarity of these molecules, one could expect that the size of the molecular

<sup>2)</sup> Exact solid-state structure has been determined by single-crystal X-ray diffractometry which will be published elsewhere.

aggregates will be restored in solution. By switching from the electron-donating thd to the electron-withdrawing hfd ligand, we indeed found formation of polynuclear heterometallic species that kept their integrity in solution. The preparation of them was, however, achieved only under specific obviously kinetic circumstances. Thus, if for instance **1e** is reacted with the complexes **2a–e**, simple ligand metathesis occurs (see Eqn. 3).



However, by varying the chemical conditions and using the heteroleptic component **1a** and the *in situ* prepared  $[\text{Ba}(\text{hfd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]$  complex (**5d**), the exact stoichiometry of which is not known, the formation of a blue-purple  $\text{Cu}_2\text{Ba}_2$  cluster **9** was observed (Eqn. 4).



The structure of **9** failed to be determined accurately by single-crystal X-ray diffraction. Due to crystallographic problems, the obtained data were of low quality. However, we were able to extract the connectivity and the configuration of **9** which turned out to be analogous to the structures of **8b** and **8c** and may, therefore, be taken with confidence. It is noteworthy that, in **9**, the hfd residues are bound to the Ba-centers, while the thd ligands are attached the Cu-atoms. These chemical preferences are in accord with the HSAB concept. As indicated earlier, osmometric molecular-weight determinations of **9** showed that the integrity of its molecular structure is retained in toluene or  $\text{CHCl}_3$ .

Attempts to synthesize a  $\text{Cu}_4\text{Ba}$  cluster containing thd ligands analogous to **7**, but carrying other alkoxide residues, or to obtain  $\text{Cu}_x\text{Ba}_y$  clusters with larger metal ratios  $x/y$  were unsuccessful, even though the chemical and physical reaction conditions were varied widely.

*X-Ray Crystal-Structure Determinations.* The solid-state structures of **6a** and **6b** can be conveniently discussed in comparison to the starting material

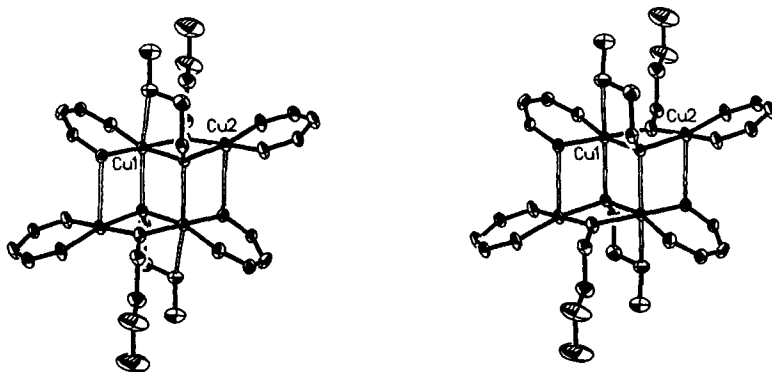


Fig. 1. ORTEP Plot of  $[\text{Cu}(\text{thd})(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_4$  (**1a**; reprinted from [8]). The thermal ellipsoids are given with 30% probability. The *t*-Bu groups of the  $\beta$ -diketonate ligands thd are omitted for clarity.



[Cu(thd)(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>4</sub>] (1a; Fig. 1) [8]. The latter consists of two dicopper units, each of which is bridged by two alkoxide ligands. The Cu–Cu distance of 2.986(2) Å is relatively long, but within the range required for a weak metal–metal interaction. The Cu–O(chelate) bond lengths vary from 1.902(5) to 1.949(4) Å, while the Cu–O(bridge) distances are between 1.896(5) and 1.985(5) Å. In addition, the dihedral angle between the Cu( $\beta$ -diketonate) rings in the dicopper units is 16.2°. This feature, along with the two bridging alkoxide functionalities, gives each Cu a nearly square-planar coordination sphere.

Compounds 6a and 6b show similar structures (Figs. 2 and 3). They are composed of a three-sided Cu–Cu–M core, where each metal is chelated by a  $\beta$ -diketonate ligand. The Ca–Cu distances are 3.155(2) Å (Ca–Cu(1)), and 3.318(2) Å (Ca–Cu(2)) and the Sr–Cu distances are 3.259(2) Å (Sr–Cu(1)) and 3.394(2) Å (Sr–Cu(2)). One alkoxide group bridges the heterometal and Cu(2), whereas the other two alkoxides link all three metals. The alkoxide moieties are all folded back such that their internal O-atoms get more strongly exposed to be heterometal. An other important structural feature of compounds 6a and 6b is that the [Cu<sub>2</sub>( $\beta$ -diketonate)<sub>2</sub>(OR)<sub>2</sub>] unit remains relatively intact in these derivatives as compared to the structure of 1a [8]. The most notable difference is found in the dihedral angle between the Cu( $\beta$ -diketonate) units, which increases from 16.2° in 1a

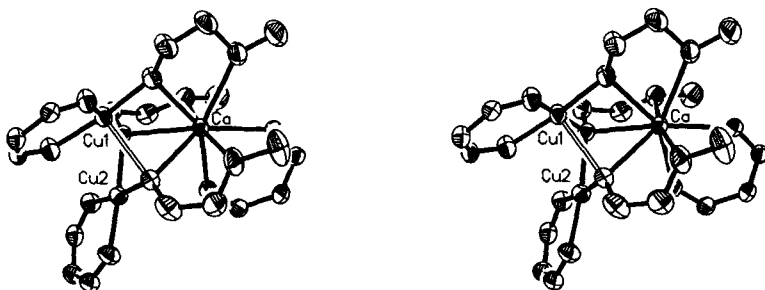


Fig. 2. ORTEP Plot of [CaCu<sub>2</sub>(thd)<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>] (6a). The thermal ellipsoids are given with 30% probability. The *t*-Bu groups of the  $\beta$ -diketonate ligands thd and the two-fold disordering of a CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O ligand are omitted for clarity. Average M–O distances: Ca–O = 2.458 Å, Cu–O = 1.925 Å. The weak Cu–O interaction (2.376(4) Å) is indicated as an open line.

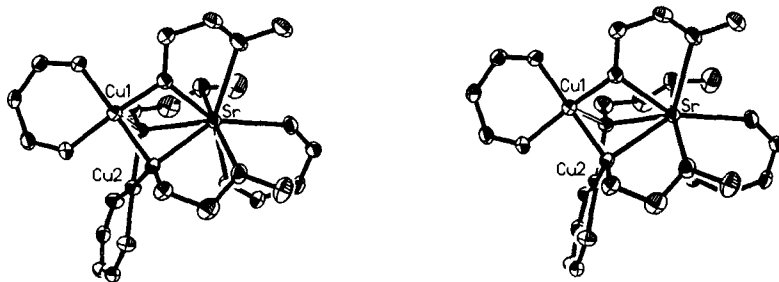


Fig. 3. ORTEP Plot of [Cu<sub>2</sub>Sr(thd)<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>] (6b). The thermal ellipsoids are given with 30% probability. The *t*-Bu groups of the  $\beta$ -diketonate ligands thd are omitted for clarity. Average M–O distances: Sr–O = 2.478 Å, Cu–O = 1.932 Å. The weak Cu–O interaction (2.323(4) Å) is indicated as an open line.

to  $62.7^\circ$  in **6a** and  $65.6^\circ$  in **6b**. Despite this large dihedral angle, both Cu-atoms retain a nearly square-planar environment. It should be noted, however, that the Cu(1)–O(7) distance in **6a** and the Cu(1)–O(9) distance in **6b** is 2.376(4) and 2.323(4) Å, respectively. They may be viewed as secondary interactions.

Compounds **8b** and **8c** are structurally very similar to each other. Both molecules consist of a four-sided  $\text{Cu}_2\text{Ba}_2$  core of alternating Ba- and Cu-atoms (Figs. 4 and 5). Both

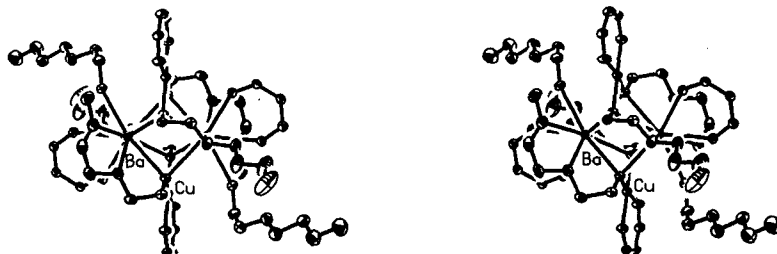


Fig. 4. ORTEP Plot of  $[\text{Ba}_2\text{Cu}_2(\text{thd})_4(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_4(\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$  (**8b**). The thermal ellipsoids are given with 30% probability. The molecule lies on a crystallographic center of inversion. The *t*-Bu groups of the  $\beta$ -diketonate ligands thd are omitted for clarity. Average M–O distances: Ba–O = 2.851 Å, Cu–O = 1.926 Å.

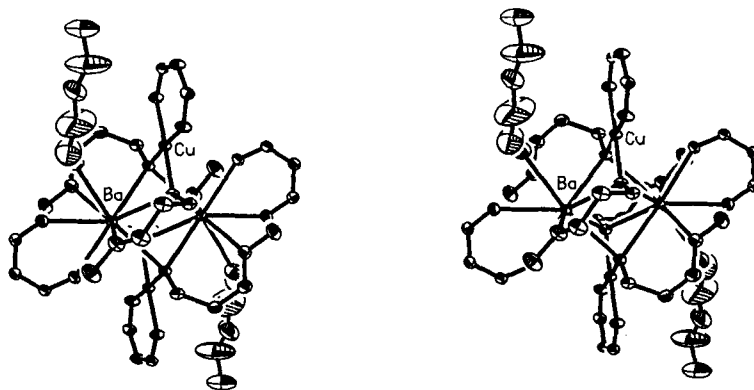


Fig. 5. ORTEP plot of  $[\text{Ba}_2\text{Cu}_2(\text{thd})_4(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_4(\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)_2]$  (**8c**). The thermal ellipsoids are given with 30% probability. The molecule lies on a crystallographic center of inversion. The *t*-Bu groups of the  $\beta$ -diketonate ligands thd are omitted for clarity. Average M–O distances: Ba–O = 2.814 Å, Cu–O = 1.932 Å.

molecules occupy crystallographic centers of inversion; hence each molecule exhibits only two unique Ba–Cu distances and the  $\text{Cu}_2\text{Ba}_2$  units are planar. The Ba–Ba distances are 3.810(1) and 3.745(1) Å in **8b** and **8c**, respectively, and the Ba–Cu distances vary between 3.612(1) and 3.719(1) Å. Each metal is bonded to one  $\beta$ -diketonate ligand; the Ba( $\beta$ -diketonate) rings are coplanar with the  $\text{Cu}_2\text{Ba}_2$  units, while the Cu( $\beta$ -diketonate) moieties are nearly perpendicular with interplanar angles of  $88.2^\circ$  (**8b**) and  $84.5^\circ$  (**8c**).

Compound **8b** contains four alkoxide functions, each of which triply bridges both Ba-atoms and the Cu-center. In two of these methoxyethoxide ligands, both ether functions also coordinate to a Ba-atom, forming a system of two five-membered rings (Fig. 4). The other two alkoxide ligands of this molecule are additionally coordinated to the Ba-atom by only one ether function. Finally, a solvent alcohol molecule is attached to each Ba-atom through the OH group.

The arrangement of the 3-methoxypropoxide ligands in **8c** is quite similar to that of **8b**. Compound **8c** contains also four alkoxides which triply bridge both Ba-atoms and the Cu-atom (Fig. 5). All of these ligands make use of ether functions for additional coordination to the Ba-atom, forming six-membered rings. As in **8b**, an alcohol molecule fills a vacant site at each Ba-center.

The coordination of Cu<sup>II</sup> is square-planar in **8b** and **8c**. In **8b**, the Cu-atom is bonded to O(3) and O(4) of the  $\beta$ -diketonate ligand, as well as to the triply bridging O-atoms O(8) and O(11) (Fig. 4). The mean absolute deviation from the Cu–O(3)–O(4)–O(8)–O(11) least-squares plane is 0.043 Å. In **8c**, the Cu-atom is fixed to O(3) and O(4) of the  $\beta$ -diketonate ligand and to the triply bridging O-atoms O(5) and O(7) (Fig. 5). In this instance, the mean absolute deviation from the Cu–O(3)–O(4)–O(5)–O(7) least-squares plane amounts to only 0.007 Å.

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