Synthesis and Characterization of Novel Yttrium–Copper Alkoxide Clusters

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On reaction of $[Y(OCH_2CH_2OMe)_3]_{10}$ (**2**) with $[(thd)Cu(OCH_2CH_2OMe)]_4$ (**1a**) and $[(hfd)Cu(OCH_2CH_2OMe)]_4$ (**1b**) (thd = 2,2,6,6-tetramethyl-3,5-heptanedione; hfd = 1,1,1,5,5,5-hexafluoroacetylacetone), the mixed-metal clusters $(thd)_4Cu_3Y(OCH_2CH_2OMe)_5$ (**3**), $[(hfd)_2CuY(OCH_2CH_2OMe)_3]_2$ (**4**), and $(hfd)_2(thd)_2Cu_2Y(OCH_2CH_2OMe)_3$ (**5**) are formed. Their elemental analyses and IR and vis spectroscopic data are reported. **3**–**5** were studied by X-ray diffractive methods: **3**, space group *Cc*, $a = 33.084(5)$ Å, $b = 13.980(2)$ Å, $c = 18.789(3)$ Å, $Z = 4$, $R = 0.086$, $R_w = 0.056$ for 6163 reflections with $F > 8\sigma(F)$; **4**, space group $P2_1/n$, $a = 10.800(4)$ Å, $b = 20.067(7)$ Å, $c = 13.703(5)$ Å, $Z = 2$, $R = 0.078$, $R_w = 0.072$ for 2609 reflections with $F > 10\sigma(F)$; **5**, space group $P\bar{1}$, $a = 14.179(4)$ Å, $b = 14.425(4)$ Å, $c = 14.489(4)$ Å, $Z = 2$, $R = 0.088$, $R_w = 0.073$ for 7509 reflections with $F > 4\sigma(F)$.

Introduction

Recent efforts in our research group have addressed the synthesis and characterization of molecular compounds which might be suitable precursors to high-T_c superconductors in various chemical deposition processes. We have attempted to incorporate Y, Cu, and alkaline earth metals into the desired compounds, since these combinations of elements are found in the more recently discovered high-T_c superconducting ceramics.[1] The ligand systems of choice have been alkoxides[2] and β-diketonates,[3] which tend to enhance solubility and volatility and could be expected to make the target complexes good candidates for sol–gel processes[4] and MOCVD.[5] We recently reported on the preparation and structural characterization of $[(thd)Cu(OCH_2CH_2OMe)]_4$ (**1a**) and $[(hfd)Cu(OCH_2CH_2OMe)]_4$ (**1b**).[6] In this paper we wish to show the results of our studies on the reactions of $[Y(OCH_2CH_2OMe)_3]_{10}$ (**2**) with these species.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. 2-Methoxyethanol (Fluka AG) was dried by distillation from Mg turnings. Bis(μ-2-methoxyethoxy)bis(μ_3-2-methoxyethoxy)tetrakis[(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II)] ($[(thd)Cu(OCH_2CH_2OMe)]_4$, **1a**) and tetrakis($\mu_3$-2-methoxyethoxy)tetrakis[(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II)] ($[(hfd)Cu(OCH_2CH_2OMe)]_4$, **1b**) were prepared as described earlier.[6] Decakis[tris(2-methoxyethoxy)yttrium(III)], $[Y(OCH_2CH_2OMe)_3]_{10}$ (**2**), and bis(2-methoxyethoxy)copper(II), $Cu(OCH_2CH_2OMe)_2$, were prepared by literature methods.[7,8] 2,2,6,6-Tetramethyl-3,5-heptanedione (Fluka AG) and 1,1,1,5,5,5-hexafluoroacetylacetone (Lancaster) were used without further purification. All compounds carrying alkoxide residues are hygroscopic and were therefore stored under nitrogen.

Synthesis of $(thd)_4Cu_3Y(OCH_2CH_2OMe)_5$ (3). A solution of $[Y(OCH_2CH_2OMe)_3]_{10}$ (0.5 g, 0.2 mmol) in 2-methoxyethanol (15 mL) was added dropwise to **1a** (1.5 g, 1.2 mmol) dissolved in 2-methoxyethanol (25 mL). The resulting dark blue solution was stirred at room temperature for 3 days and was then allowed to stand for 2 weeks at +4 °C to form dark blue crystals of **3** suitable for single-crystal X-ray diffraction. The crystals were collected by filtration and dried in vacuo: yield 7%; mp 98–101 °C (dec >185 °C). Compound **3** is soluble in THF, $CHCl_3$, CH_2Cl_2, toluene, hexane, and 2-methoxyethanol. Anal. Calc for $C_{59}H_{111}O_{18}Cu_3Y$: Cu, 13.74; Y, 6.41. Found: Cu, 14.30; Y, 6.88. Vis ($CHCl_3$): 605 nm (ϵ 120), 525 (114). IR (Nujol): ν(C═O) 1590 (s), 1571 (vs), 1553 cm^{-1} (s). Osmometric MW ($CHCl_3$): 594, calc 1388.

Synthesis of $[(hfd)_2CuY(OCH_2CH_2OMe)_3]_2$ (4). Method a. A solution of $[Y(OCH_2CH_2OMe)_3]_{10}$ (1.0 g, 0.3 mmol) in toluene (25 mL) was added dropwise to a green suspension of **1b** (1.1 g, 0.7 mmol) in a solvent mixture of 2-methoxyethanol (10 mL) and THF (5 mL) at room temperature. After addition, the green suspension became a clear dark green solution. The reaction mixture was allowed to stir overnight and then cooled slowly to −30 °C for 2 days. The color of the solution changed from dark green to light green with formation of green crystals of **1b**. The light green solution was decanted and allowed to stand for another week at −30 °C, leading to formation of light blue crystals of **4** suitable for single-crystal X-ray diffraction. These were then filtered off and dried in vacuo: yield 65%; mp 148–152 °C (dec >160 °C). Anal. Calc for $C_{38}H_{46}F_{24}O_{20}Cu_2Y_2$: C, 28.87; H, 2.93; F, 28.79; Cu, 8.03; Y, 11.23. Found: C, 29.05; H, 3.20; F, 28.61, Cu, 8.06; Y, 11.26. Compound **4** is very slightly soluble in THF, $CHCl_3$, and toluene, giving light green solutions. Vis: (THF) 680 nm (ϵ 77); ($CHCl_3$) 665 (84); (toluene) 675 (30). IR (Nujol): ν(C═O) 1666 (vs), 1655 cm^{-1} (vs). Osmometric MW ($CHCl_3$): 1727, calc 1584.

Method b. A solution of $[Y(OCH_2CH_2OMe)_3]_{10}$ (1.0 g, 0.3 mmol) in toluene (15 mL) was cooled to −10 °C. 1,1,1,5,5,5-Hexafluoroacetylacetone (1.3 g, 6.3 mmol) was added to this very slowly, forming a solution of "$[(hfd)_2Y(OCH_2CH_2OMe)]_n$" in situ. The reaction mixture was warmed to room temperature and stirred for 1 h before it was added dropwise to a dark blue suspension of $Cu(OCH_2CH_2OMe)_2$ (0.7 g, 3.2

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Table I. Crystallographic Data for **3**–**5**

	3	**4**	**5**
formula	$C_{59}H_{111}Cu_3O_{18}Y$	$C_{38}H_{46}Cu_2F_{24}O_{20}Y_2$	$C_{41}H_{61}Cu_2F_{12}O_{14}Y$
fw	1388.0	1583.6	1221.9
cryst system	monoclinic	monoclinic	triclinic
space group	*Cc*	$P2_1/n$	$P\bar{1}$
a, Å	33.084(5)	10.800(4)	14.179(4)
b, Å	13.980(2)	20.067(7)	14.425(4)
c, Å	18.789(3)	13.703(5)	14.489(4)
α, deg			88.95(2)
β, deg	121.70(10)	96.42(3)	71.45(2)
γ, deg			77.56(2)
V, Å^3	7394(2)	2951(2)	2740(1)
Z	4	2	2
T, K	238	238	238
λ, Å	0.710 73	0.710 73	0.710 73
ρ_{calc}, g cm^3	1.247	1.782	1.448
μ, cm^{-1}	16.9	28.1	19.2
no. of indep reflsn	8643	5187	13289
no. of obsd reflns	6163 (>8σ)	2609 (<10σ)	7509 (<4σ)
R	0.086	0.078	0.088
R_w	0.056	0.072	0.073

[a] $R = \sum(|F_o - F_c|)/\sum(F_o)$. [b] $R_w = [\sum(w(F_o - F_c)^2/\sum(w(F_o)^2)]^{1/2}$.

mmol) in 2-methoxyethanol (15 mL). The dark blue suspension changed in 1 h to a dark green solution, which was slowly cooled to −30 °C. After 1 day, green crystals of **1b** were formned and the color of the dark green solution changed to light green. The solution was decanted and allowed to stand for another 5 d at −30 °C, leading to formation of light blue crystals of **4**. These were isolated and dried *in vacuo*: yield 55%; mp 147–150 °C (dec >160 °C). Anal. Calc for $C_{38}H_{46}F_{24}O_{20}Cu_2Y_2$: Cu, 8.03; Y, 11.23. Found: Cu, 8.16; Y, 11.32.

Table III. Selected Bond Lengths (Å) for **3**

Y(1)–Cu(1)	3.204(2)	Cu(1)–O(11)	1.916(7)
Y(1)–Cu(2)	3.246(2)	Cu(1)–O(101)	1.904(9)
Y(1)–Cu(3)	3.377(2)	Cu(1)–O(102)	1.947(7)
Y(1)–O(1)	2.305(6)	Cu(2)–O(5)	2.407(8)
Y(1)–O(2)	2.349(7)	Cu(2)–O(7)	1.977(9)
Y(1)–O(3)	2.294(7)	Cu(2)–O(9)	1.956(6)
Y(1)–O(5)	2.425(8)	Cu(2)–O(201)	1.897(10)
Y(1)–O(6)	2.530(11)	Cu(2)–O(202)	1.920(7)
Y(1)–O(7)	2.464(7)	Cu(3)–O(3)	1.943(9)
Y(1)–O(9)	2.315(8)	Cu(3)–O(5)	1.912(8)
Y(1)–O(11)	2.265(10)	CU(3)–O(4)	2.588(11)
Cu(1)–O(7)	1.988(8)	Cu(3)–O(301)	1.940(9)
Cu(1)–O(8)	2.484(11)	Cu(3)–O(302)	1.934(11)
Cu(1)–O(9)	2.664(8)		

Synthesis of [(hfd)$_2$(thd)$_2$Cu$_2$Y(OCH$_2$CH$_2$OMe)$_3$] (5). To a solution of $[Y(OCH_2CH_2OMe)_3]_{10}$ (1.5 g, 0.5 mmol) in toluene (20 mL) was added very slowly (−10 °C) 1,1,1,5,5,5-hexafluoroacetylacetone (2.0 g, 9.6 mmol), forming a solution of "$[(hfd)_2Y(OCH_2CH_2OMe)]_n$" in situ. The reaction mixture was warmed to room temperature and stirred for 1 h before it was added dropwise to a dark blue solution of **1a** (3.1 g, 2.4 mmol) in a solvent mixture of 2-methoxyethanol (25 mL) and THF (5 mL) at room temperature. After 4 h, the resulting dark blue solution was evaporated to half its original volume and chilled to +4 °C, producing dark blue crystals of **5** suitable for single-crystal X-ray diffraction. These were filtered off and dried in vacuo. The filtrate was allowed to stand 5 d at −30 °C, producing an additional crop of dark blue crystals of **5**: total yield 50%; mp 96–97 °C (dec >185 °C). Anal. Calc for $C_{41}H_{61}F_{12}O_{14}Cu_2Y$: C, 40.30; H, 5.03; F, 18.66; Cu, 10.40; Y, 7.28. Found: C, 42.77; H, 5.31; F, 18.10, Cu, 10.05; Y, 7.55. Compound **5** is very soluble in THF, CHCl$_3$, and toluene and is soluble in diethyl ether and hexane. Vis (THF): 625 nm (ε 55). IR (Nujol): ν(C=O) 1664

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **3**

	x	*y*	*z*	*U*(eq)[a]
Y(1)	0	1059(1)	0	31(1)
Cu(1)	129(1)	2731(1)	−1031(1)	36(1)
Cu(2)	−815(1)	2653(1)	−1050(1)	36(1)
Cu(3)	−1085(1)	59(1)	−1188(1)	46(1)
O(1)	615(3)	1522(5)	1303(5)	37(4)
O(2)	559(3)	−188(5)	548(5)	43(4)
C(1)	1035(4)	1232(8)	1842(7)	38(3)
C(2)	1229(4)	383(9)	1783(8)	46(3)
C(3)	995(5)	−282(10)	1143(8)	50(4)
C(4)	1306(5)	1920(10)	2596(9)	62(4)
C(5)	1817(6)	1634(13)	3189(10)	105(6)
C(6)	1324(6)	2896(11)	2296(10)	93(5)
C(7)	1027(5)	1950(11)	3027(9)	88(5)
C(8)	1232(5)	−1219(9)	1092(8)	48(3)
C(9)	1189(6)	−1255(13)	273(10)	106(6)
C(10)	1747(5)	−1262(13)	1778(9)	101(6)
C(11)	981(6)	−2036(12)	1225(10)	98(6)
O(3)	−435(3)	−163(6)	−891(5)	44(4)
C(21)	−341(5)	−1138(9)	−917(9)	65(4)
C(22)	−398(6)	−1702(12)	−333(11)	92(5)
O(4)	−852(5)	−1594(10)	−460(14)	226(10)
C(23)	−1062(6)	−2233(12)	−422(10)	96(5)
O(5)	−834(2)	1140(5)	−458(5)	39(4)
C(31)	−915(5)	1273(9)	231(8)	52(4)
C(32)	−680(4)	487(9)	862(8)	50(3)
O(6)	−196(3)	476(6)	1059(5)	54(4)
C(33)	99(5)	−119(11)	1776(9)	78(5)
O(7)	−427(3)	1890(5)	−1358(4)	34(4)
C(41)	−599(4)	1411(9)	−2134(7)	42(3)
C(42)	−604(4)	2056(9)	−2791(8)	55(4)
O(8)	−121(3)	2277(6)	−2484(5)	56(5)
C(43)	−66(6)	2926(11)	−2969(10)	87(5)
O(9)	−197(2)	2649(5)	−3(4)	36(4)
C(51)	−76(4)	3274(8)	672(7)	38(3)
C(52)	155(5)	4148(10)	597(8)	62(4)
O(10)	303(4)	4739(8)	1328(7)	88(6)
C(53)	593(7)	5497(13)	1397(12)	121(7)
O(11)	470(2)	1596(5)	−459(5)	37(4)
C(61)	963(4)	1490(9)	−159(7)	43(3)
C(62)	1033(5)	1342(11)	−873(9)	70(4)
O(12)	1522(3)	1249(10)	−551(7)	114(6)
C(63)	1602(7)	1233(15)	−1194(12)	137(7)
O(101)	685(3)	3478(6)	−674(5)	52(4)
O(102)	−283(3)	3833(5)	−1552(5)	44(4)
C(101)	717(5)	4342(9)	−819(8)	46(3)
C(102)	310(5)	4956(10)	−1280(8)	55(4)
C(103)	−151(4)	4644(9)	−1594(7)	40(3)
C(104)	1216(5)	4720(10)	−453(9)	61(4)
C(105)	1260(8)	5633(14)	−756(14)	165(9)
C(106)	1468(7)	4057(14)	−744(13)	151(8)
C(107)	1483(6)	4659(14)	472(11)	127(7)
C(108)	−560(5)	5401(10)	−2064(8)	54(4)
C(109)	−464(7)	6132(13)	−2515(11)	132(7)
C(110)	−1016(6)	4907(12)	−2693(10)	101(6)
C(111)	−645(7)	5769(15)	−1456(12)	150(8)
O(201)	−1106(3)	3539(6)	−692(5)	42(4)
O(202)	−1378(3)	2561(6)	−2144(5)	50(4)
C(201)	−1529(4)	3848(9)	−1101(7)	40(3)
C(202)	−1863(5)	3600(9)	−1918(8)	51(3)
C(203)	−1775(5)	2965(9)	−2388(8)	46(3)
C(204)	−1663(5)	4569(10)	−627(8)	55(4)
C(205)	−2066(6)	5179(13)	−1222(11)	115(6)
C(206)	−1781(6)	3943(11)	−100(10)	93(5)
C(207)	−1234(5)	5159(10)	−43(8)	65(4)
C(208)	−2153(6)	2714(12)	−3292(10)	74(4)
C(209)	−2645(7)	2980(15)	−3559(14)	170(9)
C(210)	−2176(8)	1621(14)	−3448(14)	162(9)
C(211)	−2029(7)	3018(15)	−3846(12)	155(8)
O(301)	−1374(3)	−629(7)	−2240(6)	59(5)
O(302)	−1675(3)	68(7)	−1204(5)	58(5)
C(301)	−1780(4)	−1027(9)	−2632(8)	46(3)
C(302)	−2105(5)	−912(10)	−2382(8)	58(4)
C(303)	−2043(5)	−428(10)	−1723(8)	53(4)
C(304)	−1896(4)	−1616(9)	−3389(8)	46(3)
C(305)	−2367(6)	−1342(12)	−4099(10)	108(6)
C(306)	−1906(6)	−2643(12)	−3180(11)	115(6)
C(307)	−1555(6)	−1480(13)	−3660(10)	107(6)
C(308)	−2437(5)	−348(11)	−1470(9)	65(4)
C(309)	−2241(6)	−876(13)	−660(11)	120(7)
C(310)	−2514(6)	665(12)	−1368(11)	111(6)
C(311)	−2901(7)	−726(15)	−2117(12)	161(8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Angles (deg) for 3

O(1)–Y(1)–O(3)	148.1(3)	O(11)–Cu(1)–O(102)	171.1(5)
O(2)–Y(1)–O(3)	79.3(2)	Y(1)–Cu(2)–O(5)	48.0(2)
O(1)–Y(1)–O(5)	124.6(3)	Y(1)–Cu(2)–O(7)	49.3(2)
O(2)–Y(1)–O(5)	132.7(3)	O(5)–Cu(2)–O(7)	80.8(3)
O(3)–Y(1)–O(5)	67.3(3)	Y(1)–Cu(2)–O(9)	44.9(2)
O(1)–Y(1)–O(6)	72.7(3)	O(5)–Cu(2)–O(9)	78.5(3)
O(2)–Y(1)–O(6)	83.3(3)	O(7)–Cu(2)–O(9)	78.2(3)
O(3)–Y(1)–O(6)	90.7(3)	O(5)–Cu(2)–O(201)	105.5(4)
O(5)–Y(1)–O(6)	65.2(3)	O(7)–Cu(2)–O(201)	170.5(3)
O(1)–Y(1)–O(7)	132.3(3)	O(9)–Cu(2)–O(201)	95.9(3)
O(2)–Y(1)–O(7)	134.0(3)	O(5)–Cu(2)–O(202)	100.9(3)
O(3)–Y(1)–O(7)	78.3(3)	O(7)–Cu(2)–O(202)	93.7(4)
O(5)–Y(1)–O(7)	71.6(3)	O(9)–Cu(2)–O(202)	171.9(4)
O(6)–Y(1)–O(7)	136.3(3)	O(3)–Cu(3)–O(5)	85.6(3)
O(1)–Y(1)–O(9)	79.8(2)	O(3)–Cu(3)–O(301)	95.2(4)
O(2)–Y(1)–O(9)	150.3(2)	O(5)–Cu(3)–O(301)	156.7(4)
O(3)–Y(1)–O(9)	130.2(2)	O(3)–Cu(3)–O(302)	163.9(4)
O(5)–Y(1)–O(9)	71.8(3)	O(5)–Cu(3)–O(302)	93.5(4)
O(6)–Y(1)–O(9)	97.1(3)	O(301)–Cu(3)–O(302)	92.1(4)
O(7)–Y(1)–O(9)	62.5(3)	Y(1)–O(3)–Cu(3)	105.4(4)
O(1)–Y(1)–O(11)	85.0(3)	Y(1)–O(5)–Cu(2)	84.4(3)
O(2)–Y(1)–O(11)	82.7(3)	Y(1)–O(5)–Cu(3)	101.6(4)
O(3)–Y(1)–O(11)	105.2(3)	Cu(2)–O(5)–Cu(3)	118.0(4)
O(5)–Y(1)–O(11)	136.9(3)	Y(1)–O(7)–Cu(1)	91.4(2)
O(6)–Y(1)–O(11)	156.5(2)	Y(1)–O(7)–Cu(2)	93.3(4)
O(7)–Y(1)–O(11)	65.4(3)	Cu(1)–O(7)–Cu(2)	103.2(3)
O(9)–Y(1)–O(11)	86.0(3)	Y(1)–O(9)–Cu(2)	98.6(3)
O(7)–Cu(1)–O(11)	81.9(3)	Y(1)–O(11)–Cu(1)	99.7(4)
O(7)–Cu(1)–O(101)	176.6(3)	O(201)–Cu(2)–O(202)	92.1(4)
O(11)–Cu(1)–O(101)	94.7(3)	O(101)–Cu(1)–O(102)	92.0(3)
O(7)–Cu(1)–O(102)	91.3(3)		

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 4

	x	*y*	*z*	*U*(eq)[a]
Y	–99(1)	990(1)	1603(1)	53(1)
Cu	–1211(2)	321(1)	–662(1)	55(1)
O(1)	–1670(9)	1744(5)	2076(7)	74(5)
O(2)	136(9)	2069(5)	912(7)	70(4)
C(1)	–1783(14)	2366(9)	2127(10)	64(6)
C(2)	–1064(14)	2836(7)	1691(10)	67(7)
C(3)	–172(14)	2655(7)	1084(11)	63(6)
C(4)	–2775(7)	2599(4)	2733(5)	93(9)
F(1)	–3864	2307	2451	176(8)
F(2)	–2451	2448	3674	190(8)
F(3)	–2940	3256	2668	156(7)
C(5)	535(8)	3181(3)	585(6)	84(8)
F(4)	1760	3085	759	164(7)
F(5)	287	3795	876	154(7)
F(6)	219	3146	–382	136(6)
O(3)	–1372(9)	439(5)	2689(7)	66(4)
O(4)	574(10)	1345(5)	3193(7)	78(5)
C(6)	–1562(14)	535(7)	3549(11)	60(6)
C(7)	–875(17)	967(9)	4216(10)	85(8)
C(8)	119(16)	1336(8)	3987(12)	71(7)
C(9)	–2664(8)	156(5)	3865(6)	96(10)
F(7)	–2587	105	4839	208(9)
F(8)	–3717	476	3558	203(10)
F(9)	–2740	–457	3490	177(8)
C(10)	764(9)	1802(5)	4755(6)	115(11)
F(10)	438	1687	5649	257(11)
F(11)	1997	1741	4798	214(10)
F(12)	468	2429	4514	211(10)
O(5)	728(8)	605(4)	212(6)	56(4)
C(11)	1634(14)	1040(8)	–131(11)	74(7)
C(12)	2689(14)	1162(8)	641(11)	73(7)
O(6)	2169(10)	1283(5)	1561(8)	81(5)
C(13)	3100(17)	1374(11)	2344(14)	148(12)
O(7)	–778(9)	9(4)	–1895(7)	63(4)
C(14)	–901(23)	471(10)	–2649(13)	166(14)
C(15)	–1120(16)	1128(8)	–2400(12)	90(8)
O(8)	–1393(11)	1222(5)	–1471(8)	89(5)
C(16)	–1653(15)	1851(8)	–1179(11)	89(8)
O(9)	–1720(8)	684(4)	530(6)	56(4)
C(17)	–2977(14)	594(8)	704(10)	68(7)
C(18)	–3899(15)	789(8)	–117(13)	79(8)
O(10)	–3653(10)	417(6)	–934(9)	86(5)
C(19)	–4457(16)	584(10)	–1789(14)	124(11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Selected Bond Lengths (Å) for 4

Y–Cu	3.471(2)	Y–O(9)	2.243(8)
Y–Cu(A)	3.317(3)	Y–O(7A)	2.235(9)
Y–O(1)	2.415(11)	Cu–O(5)	2.362(9)
Y–O(2)	2.387(10)	Cu–O(7)	1.909(9)
Y–O(3)	2.405(10)	Cu–O(8)	2.119(11)
Y–O(4)	2.329(10)	Cu–O(9)	1.923(9)
Y–O(5)	2.327(9)	Cu–O(5A)	2.008(8)
Y–O(6)	2.526(11)		

(vs), 1658 (vs), 1595 (s), 1571 (vs), 1556 cm^{-1} (vs). Osmometric MW ($CHCl_3$): 1083, calc 1222.

X-ray Crystal Structure Determinations. All data were obtained at ca. –35 °C on a Siemens R3m/V four-circle diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.710 73 Å). Empirical absorption corrections were applied for 4 (φ-scan), and the SHELXTL PLUS program package[9] was used for structure solution (Patterson search for 3 and 4; direct methodes for 5 and refinement). Hydrogen atoms were generally fixed at idealized positions (C–H = 0.96 Å) and assigned common refined isotropic temperature factors. In the crystal lattice of 5 some of the *tert*-butyl groups of the "thd" ligands located at the Cu centers are 2-fold disordered (disordered C atoms are indicated with an A). They were refined as regular tetrahedrons with refined site occupation factors. Crystallographic data and details of the crystal structure determinations are summarized in Table I. Atomic coordinates as well as selected bond lengths and angles are given in Tables II–X.

Other Physical Measurements. Melting points were determined on a Büchi 530 melting point apparatus and are uncorrected. Infrared 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 (λ_{max}) are given in nm with the molecular absorption coefficient ε (L mol^{-1} cm^{-1}) in parentheses (sh = shoulder). Elemental analysis was performed at the Microanalytical Department of the University of Zurich. The Cu and Y contents were determined by AAS. The fluoride assay was performed by dissolving the residue of the combustion analysis and subsequent titration with lanthanum perchlorate. The molecular weights were determined on a Knauer Dampfdurck osmometer, Type 11.00.

Results and Discussion

According to eq 1 treatment of **1a** with $[Y(OCH_2CH_2OCH_3)_3]_{10}$ (**2**) in toluene affords the novel dark blue bimetallic complex **3**. The formation of the YCu_3 unit is accompanied by

$$\underset{\mathbf{1a}}{[(thd)Cu(OR)]_4} \xrightarrow{[Y(OCH_2CH_2OCH_3)_3]_{10}\,(2)} \underset{\mathbf{3}}{(thd)_4YCu_3(OR)_5} \qquad (1)$$

exchange of one β-diketonate ligand which is binding to the Y center in **3**. **3** has been isolated by fractional crystallization. It was not possible to improve the relatively low yield of **3** (7%) by major variations of the physical and chemical reaction conditions. Therefore we suggest that eq 1 may actually represent an equilibrium situation.

In contrast to the formation of YCu_3 unit of **3**, reaction of **1b** with **2** in toluene/THF/2-methoxyethanol affords the light blue Y_2Cu_2 complex **4** in moderate yield (55%). The constitution of **4** indicates complete transfer of the β-diketonate ligands from Cu to Y (eq 2). The bimetallic cluster **4** is formally composed

$$\underset{\mathbf{1b}}{[(hfd)Cu(OR)]_4} \xrightarrow{[Y(OCH_2CH_2OCH_3)_3]_{10}\,(2)} \underset{\mathbf{4}}{[(hfd)_4YCu(OR)_3]_2} \qquad (2)$$

of one "$[(hfd)_2Y(OCH_2CH_2OCH_3)]$" and one "$Cu(OCH_2CH_2$-

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(9) SHELXTL PLUS, Release 4.2, Siemens Analytical X-Ray Intruments, 1990.

(10) Poncelet, O.; Hubert-Pfalzgraf, L. G.; Daran, J.-C. *Inorg. Chem.* **1990**, *29*, 2883.

Table VII. Selected Bond Angles (deg) for **4**

O(1)–Y–O(2)	69.3(4)	O(2)–Y–O(7a)	145.4(4)
O(1)–Y–O(3)	69.8(3)	O(3)–Y–O(7A)	74.7(3)
O(2)–Y–O(3)	139.1(3)	O(4)–Y–O(7A)	91.4(3)
O(1)–Y–O(4)	73.3(3)	O(5)–Y–O(7A)	69.8(3)
O(2)–Y–O(4)	93.4(3)	O(6)–Y–O(7A)	79.7(4)
O(3)–Y–O(4)	72.7(3)	O(9)–Y–(7A)	99.0(3)
O(1)–Y–O(5)	140.7(3)	O(5)–Cu–O(7)	103.7(4)
O(2)–Y–O(5)	84.8(3)	O(5)–Cu–O(8)	94.9(4)
O(3)–Y–O(5)	130.7(3)	O(7)–Cu–O(8)	80.4(4)
O(4)–Y–O(5)	139.5(3)	O(5)–Cu–O(9)	78.5(3)
O(1)–Y–O(6)	124.9(4)	O(7)–Cu–O(9)	175.9(4)
O(2)–Y–O(6)	68.5(3)	O(8)–Cu–O(9)	95.9(4)
O(3)–Y–O(6)	138.1(3)	O(5)–Cu–O(5A)	83.2(3)
O(4)–Y–O(6)	75.4(4)	O(7)–Cu–O(5A)	83.5(4)
O(5)–Y–O(6)	66.2(3)	O(8)–Cu–O(5A)	162.9(4)
O(1)–Y–O(9)	80.1(3)	O(9)–Cu–O(5A)	100.3(4)
O(2)–Y–O(9)	95.6(3)	Y–O(5)–Cu	95.5(3)
O(3)–Y–O(9)	79.7(3)	Y–O(5)–Cu(A)	99.6(4)
O(4)–Y–O(9)	146.7(4)	Cu–O(5)–Cu(A)	96.8(3)
O(5)–Y–O(9)	73.4(3)	Cu–O(7)–Y(A)	106.1(4)
O(6)–Y–O(9)	137.4(4)	Y–O(9)–Cu	112.6(4)
O(1)–Y–O(7A)	144.2(4)		

OCH$_3$)$_2$" unit. **4** can also be obtained by in situ preparation starting from "[(hfd)$_2$Y(OCH$_2$CH$_2$OCH$_3$)]$_n$" in toluene and reacting this mixed-ligand material with the insoluble Cu(OCH$_2$CH$_2$OCH$_3$)$_2$ compound (eq 3).

$$[\mathrm{Cu(OR)_2}]_n \xrightarrow[\mathrm{R\,=\,CH_2CH_2OCH_3}]{\text{“}[(\mathrm{hfd})_2\mathrm{Y(OR)}]_n\text{”}} \underset{\mathbf{4}}{[(\mathrm{hfd})_2\mathrm{YCu(OR)_3}]_2} \qquad (3)$$

Table IX. Selected Bond Lengths (Å) for **5**

Y–Cu(1)	3.265(2)	Y–O(13)	2.505(6)
Y–Cu(2)	3.286(2)	Cu(1)–O(1)	1.911(6)
Y–O(5)	2.337(6)	Cu(1)–O(2)	1.903(5)
Y–O(6)	2.359(5)	Cu(1)–O(11)	1.897(6)
Y–O(7)	2.389(5)	Cu(1)–O(13)	2.006(4)
Y–O(8)	2.346(4)	Cu(1)–O(14)	2.439(5)
Y–O(9)	2.258(5)	Cu(2)–O(3)	1.888(5)
Y–O(10)	2.789(5)	Cu(2)–O(4)	1.893(5)
Y–O(11)	2.218(5)	Cu(2)–O(9)	1.925(5)
Y–O(12)	2.687(6)	Cu(2)–O(13)	1.963(5)

The reaction of **1a** with in situ prepared "[(hfd)$_2$Y(OCH$_2$CH$_2$OCH$_3$)]$_n$" in a solvent mixture of toluene/THF/2-methoxyethanol at room temperature results in the formation of the YCu$_2$ compound **5** (eq 4). **5** was isolated in moderate yield (50%)

$$\underset{\mathbf{1a}}{[(\mathrm{thd})\mathrm{Cu(OR)}]_4} \xrightarrow[\mathrm{R\,=\,CH_2CH_2OCH_3}]{\text{“}[(\mathrm{hfd})_2\mathrm{Y(OR)}]_n\text{”}} \underset{\mathbf{5}}{[(\mathrm{hfd})_2(\mathrm{thd})_2\mathrm{YCu_2(OR)_3}]} \qquad (4)$$

as dark blue crystals directly from the reaction mixture after standing at 4 °C for 4 d.

It should be mentioned that the compounds **3**–**5** show good solubility in various organic solvents but decompose before they are volatilized.

The methoxyethoxide ligand obviously represents an appropriate candidate for the construction of heteronuclear oxometal cluster compounds by providing distinct oxygen donor functionalities. But it should be clear, that the self-assembly of the β-diketonate/alkoxide Cu–Y cluster compounds with different

Table VIII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **5**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Y	3684(1)	2406(1)	2909(1)	44(1)	C(23)	5373(6)	3544(6)	3190(6)	54(4)
Cu(1)	2540(1)	641(1)	3102(1)	50(1)	C(24)	6141(6)	2769(6)	3170(6)	65(4)
Cu(2)	2279(1)	2087(1)	1574(1)	44(1)	C(25)	6080(6)	1844(6)	2912(6)	52(3)
O(1)	1867(4)	352(3)	2226(4)	55(2)	C(26)	5547(8)	4550(7)	3353(9)	83(6)
O(2)	2947(4)	–654(3)	3369(4)	67(3)	C(27)	6985(7)	1050(7)	2862(8)	72(5)
C(1)	1767(5)	–487(5)	2058(5)	53(4)	F(1)	5798(7)	4965(5)	2538(6)	163(5)
C(2)	2129(6)	–1293(5)	2453(6)	62(4)	F(2)	6301(5)	4507(4)	3723(6)	139(4)
C(3)	2697(5)	–1352(4)	3065(6)	58(4)	F(3)	4752(5)	5085(4)	3951(5)	108(3)
C(4)	1180(4)	–479(4)	1304(4)	67(4)	F(4)	7664(4)	1268(4)	3210(5)	118(4)
C(5)	3082(4)	–2324(4)	3435(4)	73(4)	F(5)	6703(4)	328(4)	3359(5)	118(3)
C(6)[b]	1241(18)	–1526(5)	979(15)	74(9)	F(6)	7482(5)	718(5)	1985(5)	135(4)
C(7)[b]	1679(14)	61(17)	391(10)	74(9)	O(7)	2938(4)	3643(4)	2069(4)	56(2)
C(8)[b]	35(7)	40(17)	1788(8)	83(9)	O(8)	2478(4)	3531(3)	4083(3)	51(2)
C(6A)[c]	718(14)	–1384(9)	1403(12)	89(7)	C(28)	2346(7)	4424(6)	2317(6)	57(4)
C(7A)[c]	1938(7)	–479(15)	245(5)	113(8)	C(29)	1849(7)	4831(6)	3257(7)	66(4)
C(8A)[c]	299(11)	436(9)	1510(11)	88(6)	C(30)	1964(6)	4355(6)	4058(6)	53(4)
C(9)[d]	3606(9)	–3058(6)	2563(7)	116(7)	C(31)	2197(11)	5031(8)	1487(9)	97(7)
C(10)[d]	3853(8)	–2229(6)	3957(8)	70(5)	C(32)	1474(7)	4851(7)	5067(8)	72(5)
C(11)[d]	2171(7)	–2658(8)	4154(9)	124(8)	F(7)	2048(6)	4549(4)	817(5)	133(4)
C(9A)[e]	4254(6)	–2621(9)	2988(13)	111(12)	F(8)	1473(7)	5797(5)	1738(6)	169(5)
C(10A)[e]	2784(15)	–2245(8)	4557(6)	151(16)	F(9)	3007(7)	5355(6)	1038(6)	163(5)
C(11A)[e]	2595(14)	–3076(7)	3132(14)	93(10)	F(10)	1011(5)	4300(4)	5717(4)	101(3)
O(3)	930(4)	2744(4)	1725(3)	56(2)	F(11)	771(4)	5634(4)	5099(4)	100(3)
O(4)	2572(4)	2031(4)	196(3)	56(2)	F(12)	2158(4)	5089(4)	5399(4)	104(3)
C(12)	549(5)	2997(5)	1027(6)	57(4)	O(9)	3621(3)	1558(3)	1644(3)	45(2)
C(13)	1093(7)	2816(6)	54(6)	61(4)	O(10)	5061(4)	2600(4)	1089(4)	76(3)
C(14)	2114(7)	2358(6)	–318(5)	53(4)	C(33)	4489(6)	1247(6)	818(6)	62(4)
C(15)	–578(4)	3555(4)	1422(4)	76(5)	C(34)	4900(6)	2066(7)	340(6)	73(4)
C(16)	2641(7)	2268(7)	–1415(6)	67(4)	C(35)	5408(9)	3419(8)	716(7)	120(7)
C(17)[f]	–948(7)	3926(9)	555(7)	89(6)	O(11)	3414(4)	1087(3)	3658(3)	56(2)
C(18)[f]	–1254(7)	2889(7)	2007(10)	152(10)	O(12)	4009(4)	2215(3)	4638(3)	53(2)
C(19)[f]	–659(7)	4411(7)	2100(9)	102(7)	C(36)	3924(6)	641(5)	4289(6)	61(4)
C(17A)[g]	–620(7)	4639(6)	1363(14)	223(24)	C(37)	3780(7)	1371(6)	5075(6)	65(4)
C(18A)[g]	–1188(7)	3262(13)	799(11)	165(17)	C(38)	3809(6)	2975(6)	5346(6)	67(4)
C(19A)[g]	–1054(8)	3324(11)	2499(7)	47(7)	O(13)	2017(4)	2031(3)	2986(3)	45(2)
C(20)	3541(8)	1451(7)	–1664(6)	94(5)	O(14)	1039(5)	1002(4)	4556(4)	79(3)
C(21)	3027(8)	3177(7)	–1678(7)	103(6)	C(39)	1017(6)	2381(5)	3642(5)	51(3)
C(22)	1947(8)	2114(9)	–1984(7)	120(7)	C(40)	888(7)	2021(7)	4624(6)	73(4)
O(5)	4541(4)	3581(3)	3056(3)	50(2)	C(41)	916(8)	581(7)	5419(7)	108(6)
O(6)	5373(4)	1601(3)	2725(3)	53(2)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Site occupation factor: 0.4688. [c] Site occupation factor: 0.5312. [d] Site occupation factor: 0.6295. [e] Site occupation factor: 0.3705. [f] Site occupation factor: 0.5920. [g] Site occupation factor: 0.4080.

Table X. Selected Bond Angles (deg) for **5**

O(5)–Y–O(6)	74.2(2)	O(6)–Y–O(13)	139.1(2)
O(5)–Y–O(7)	79.8(2)	O(7)–Y–O(13)	75.5(2)
O(6)–Y–O(7)	134.0(2)	O(12)–Y–O(13)	111.5(2)
O(5)–Y–O(8)	74.8(2)	O(1)–Cu(1)–O(2)	93.8(3)
O(6)–Y–O(8)	132.9(2)	O(1)–Cu(1)–O(11)	163.8(2)
O(7)–Y–O(8)	72.2(2)	O(2)–Cu(1)–O(11)	95.0(3)
O(5)–Y–O(9)	134.5(2)	O(1)–Cu(1)–O(13)	89.4(2)
O(6)–Y–O(9)	92.8(2)	O(2)–Cu(1)–O(13)	173.3(2)
O(7)–Y–O(9)	79.3(2)	O(11)–Cu(1)–O(13)	83.3(2)
O(8)–Y–O(9)	133.9(2)	O(1)–Cu(1)–O(14)	97.2(2)
O(5)–Y–O(10)	71.1(2)	O(2)–Cu(1)–O(14)	95.0(2)
O(6)–Y–O(10)	66.8(2)	O(11)–Cu(1)–O(14)	95.5(2)
O(7)–Y–O(10)	69.2(2)	O(13)–Cu(1)–O(14)	78.7(2)
O(8)–Y–O(10)	131.9(2)	O(3)–Cu(2)–O(4)	93.4(2)
O(9)–Y–O(10)	63.8(2)	O(3)–Cu(2)–O(9)	168.9(2)
O(5)–Y–O(11)	135.2(2)	O(4)–Cu(2)–O(9)	95.8(2)
O(6)–Y–O(11)	79.4(2)	O(3)–Cu(2)–O(13)	93.0(2)
O(7)–Y–O(11)	141.8(2)	O(4)–Cu(2)–O(13)	173.3(2)
O(8)–Y–O(11)	99.3(2)	O(9)–Cu(2)–O(13)	78.0(2)
O(9)–Y–O(11)	81.5(2)	Y–O(9)–Cu(2)	103.2(2)
O(10)–Y–O(11)	128.7(2)	Y–O(9)–C(33)	121.7(5)
O(5)–Y–O(12)	73.4(2)	Y–O(11)–Cu(1)	104.8(2)
O(6)–Y–O(12)	68.6(2)	Y–O(13)–Cu(1)	92.1(2)
O(7)–Y–O(12)	137.4(2)	Y–O(13)–Cu(2)	93.9(2)
O(8)–Y–O(12)	69.2(2)	Cu(1)–O(13)–Cu(2)	101.2(2)
O(9)–Y–O(12)	142.3(2)	O(8)–Y–O(13)	76.5(2)
O(10)–Y–O(12)	128.6(2)	O(9)–Y–O(13)	61.6(2)
O(11)–Y–O(12)	63.5(2)	O(10)–Y–O(13)	118.7(2)
O(5)–Y–O(13)	146.6(1)	O(11)–Y–O(13)	66.4(2)

Y:Cu stoichiometries 1:1, 1:2, and 1:3 is a consequence of the variation of the β-diketonate component. Obviously, the oxo cluster formation is rather sensitive to the stereoelectronic properties of these ligand residues.

The determination of the molecular weights of **3**–**5** in $CHCl_3$ solution led for **4** and **5** to values in approximate agreement with the molecular unit in the solid state. This may imply that **4** and **5** retain their molecular integrity in solution, while **3** certainly breaks down to smaller units. However, when the light blue compound **4** is dissolved in THF, $CHCl_3$, or toluene, green solutions appear with λ_{max} at 680, 670, or 675 nm, respectively. The same vis spectral data are observed for **1b** in the corresponding solvents. When **2** is added to solutions of **4**, a new band at 575 nm and a blue color are generated, which are now probably due to the presence of **4**. Thus, it may be concluded that in solutions of lower concentration **4** reassembles almost completely homometallic units with molecular weights similar to that of **4**. The vis spectrum of **3** also supports the presence of homometallic Cu agglomerates, but obviously of lower molecular weight than **3**. **5** displays only one broad vis band at λ_{max} = 625 nm in $CHCl_3$. Since this band can be identified with neither **1a** or **1b**, this indicates the existence of a distinct species, which probably is molecule **5**. The solution behavior of compounds **3**–**5** seems to be rather complicated and not uniform. Depending on the stereoelectronic influences of the organic periphery, we can induce not only different metal compositions of the molecular units but obviously also different stabilities of these in solution.

The solid-state structure of **3** consists of a four-metal atom core with one Y and three Cu atoms (Figure 1), having Y–Cu distances of 3.204(2) (Y–Cu(1)), 3.246(2) (Y–Cu(2)), and 3.377(2) (Y–Cu(3)) Å and Cu–Cu contacts of 3.107(2) (Cu(1)–Cu(2)) and 3.711(2) (Cu(2)–Cu(3)) Å. Each metal atom is bonded to the O atoms of one β-diketonate ligand. The linkage of the metal cores is established by five 2-methoxyethoxide units. The alkoxide O atoms of the 2-methoxyethoxide can function as μ_2 (O(3), O(9), O(11)) or μ_3 bridges (O(5), O(7)) while the methoxy oxygen atoms are not (O(10), O(12) or only weakly linked (O(4), O(6), O(8)) to the metal centers. The Y center is surrounded by eight O atoms with bond lengths of 2.265(10)–2.530(11) Å (see Table III). The average Y–O distance in this crystal structure is 2.39 Å. The Cu atom environments are square pyramidal, with four Cu–O bond distances ranging from 1.897(10) to 1.988(8) Å (average 1.94 Å); in addition, each Cu atom has a weak interaction with a fifth oxygen atom: Cu(1)–O(8) = 2.484(9), Cu(2)–O(5) = 2.407(8), Cu(3)–O(4) = 2.588(9) Å.

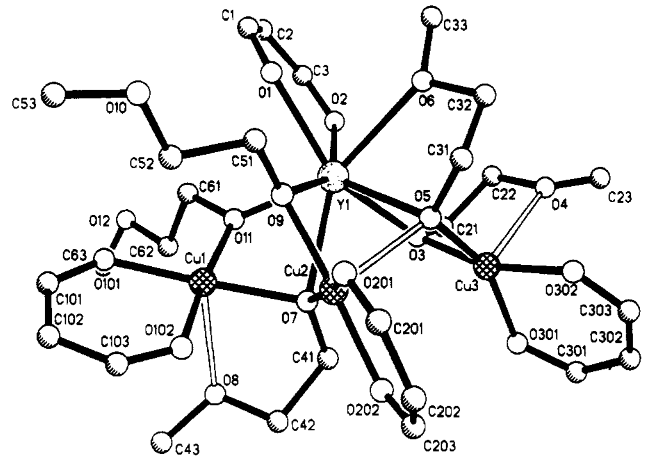

Figure 1. Structure of $(thd)_4Cu_3Y(OCH_2CH_2OMe)_5$ (**3**) (Y = dotted, Cu = cross-hatched, O = white, C = shaded; without H atoms). The *tert*-butyl groups of the β-diketonate ligands "thd" are omitted for clarity. The weak Cu–O interactions (>2.40 Å) are indicated as open lines.

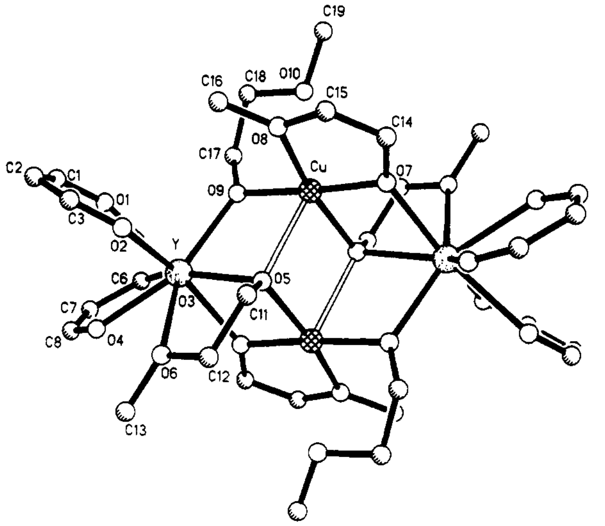

Figure 2. Structure of $[(hfd)_2CuY(OCH_2CH_2OMe)_3]_2$ (**4**) (Y = dotted, Cu = cross-hatched, O = white, C = shaded; without H atoms). The molecule lies over a crystallographic center of inversion. The trifluoromethyl groups of the "hfd" ligands are omitted for clarity in this representation. The weak Cu–O interactions (>2.36 Å) are indicated as open lines.

The crystal structure of compound **4** (Figure 2) consists of a four-sided Y_2Cu_2 unit having Y–Cu distances of 3.471(2) and 3.317(3) Å. The Cu–Cu distance is 3.276(3) Å. The molecule lies over a crystallographic center of inversion. Each of the yttrium atoms carry two β-diketonate ligands ("hfd"), whereas the coordination spheres of both Cu centers contain alkoxide units only. Yttrium and copper centers are glued together by 2-methoxyethoxide moieties, and the internal oxygens of these ligands seek additional coordination to a neighboring Cu center. There are also two alkoxides which triply bridge a Y and two Cu atoms and further bind to yttrium through their methoxy functions. The Y atom is, as in the previous structure, surrounded by eight O atoms (Y–O = 2.235(9)–2.526(11) Å; average 2.36 Å; see Table VI). The Cu environment is square pyramidal, with four Cu–O bond lengths ranging from 1.909(9) to 2.119(11) Å (average 1.99 Å) and an additional weak Cu–C(5) interaction (2.362(9) Å).

The structure of **5** is composed of one Y and two Cu centers and two "thd" and two "hfd" units, as well as three 2-methoxyethaoxides (Figure 3). The Y–Cu distances are 3.265(2) and

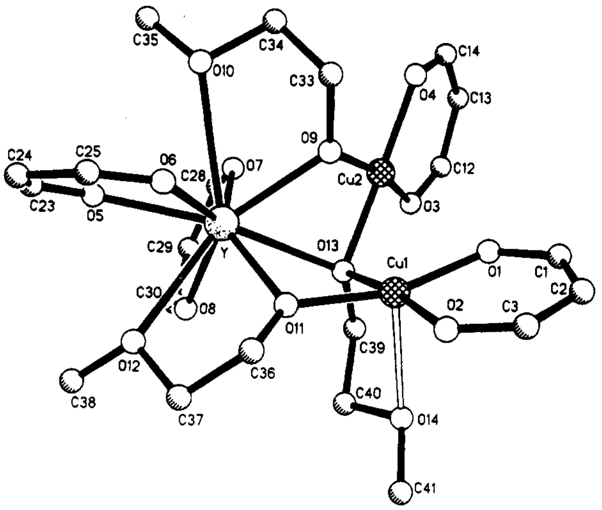

Figure 3. Structure $(hfd)_2(thd)_2Cu_2Y(OCH_2CH_2OMe)_3$ (**5**) (Y = dotted, Cu = cross-hatched, O = white, C = shaded; without H atoms). The *tert*-butyl groups of the "thd" ligands, located at the Cu centers, and the trifluoromethyl groups of the "hfd" ligands, located at the Y center, are omitted for clarity. The weak Cu–O interaction (>2.43 Å) is indicated as an open line.

3.286(2) Å; the Cu–Cu distance is 3.071(2) Å and thus beyond the limits of a covalent M–M contact. The "hfd" ligands are connected to the Y center, whereas the "thd" moieties are bound to the Cu atoms, in accord with a supposed tendency to prefer ionic ("hfd", Y) and covalent ("thd", Cu) binding. The ethoxy O atoms of the 2-methoxyethoxides connect the Cu and Y centers, whereby two μ_2 (O(9), O(11) and one μ_3 bridge (O(13)) exist. The methoxy O atoms of the μ_2-bridging ligands are attached to the Y center, completing its 8-fold oxygen environment (Y–O = 2.218(5)–2.687(6) Å; average 2.39 Å; see Table IX), with an additional secondary contact to O(10) (2.789(5) Å). The geometry of the CuO polyhedron is approximately square pyramidal ($(Cu–O)_{eq}$ = 1.888(5)–2.006(4) Å; average 1.92 Å); Cu(1) exhibits an additional weak interaction with O(14) (2.439(5) Å).

Remarkably, there is an apparent structural relation between the Cu/Y/O cores in compounds **3**–**5** and the well-known prototype superconductor $YBa_2Cu_3O_{7-x}$. In the orthorhombic $YBa_2Cu_3O_{7-x}$,[11] two different Cu sites with square planar and square pyramidal oxygen coordinations are observed. The Y centers are surrounded by eight O atoms in an approximate antiprismatic environment. Complexes **3**–**5** show great resemblance in coordination number, connectivity, and M–O distances to the described structural features of the $YBa_2Cu_3O_{7-x}$ ceramics.

Although there are a few recent bimetallic lanthanoid–copper compounds described in which the Ln and Cu atoms are bridged either by hydroxy ligands,[12] PyO$^-$ (deprotonated 2-hydroxypyridine) ligands,[13] or by O^{2-},[14] there are no known bimetallic Y–Cu clusters with μ_2-OR and μ_3-OR bridging. The YCu_3 (**3**), Y_2Cu_2 (**4**), and YCu_2 (**5**) compounds described here are the first examples of Y–Cu heterometal alkoxides with participation of the β-diketonate ligands "thd" and "hfd". The syntheses of bimetallic clusters with still other ratios of Y and Cu and trimetallic clusters containing Ba, Y, and Cu are the next chemical steps to approach the goal of stoichiometry control in soluble or volatile molecular precursors for the generation of high-T_c superconducting films.

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Supplementary Material Available: Tables giving crystal data and details of the crystal structure determinations, atom coordinates, thermal parameters, bond lengths and angles, and hydrogen atom locations for **3**, **4**, and **5** (32 pages). Ordering information is given on any current masthead page.

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