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# Synthesis and Characterization of the First Group 2 Mixed $\beta$-Diketonate Alkoxide Complexes. X-ray Crystal Structures of $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$, $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$, and $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$

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The reaction of the ethanol-solvated metal ethoxides $[M(OEt)_2(EtOH)_4]_\infty$ (M = Ca, Sr, Ba) in *n*-hexane suspensions/solutions with 1 equiv of a $\beta$-diketone, H-tmhd {H-tmhd is $Bu^tCOCH_2COBu^t$}, yields the compounds $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ (**1**), $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ (**2**), and $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ (**3**); further reaction of these complexes with a bifunctional alcohol yields the complexes $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ (**4**), $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ (**5**), $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$ (**6**), $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ (**7**), $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ (**8**), and $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ (**9**) {the values of *n* are as yet unknown}. **1**, **4**, and **8** have also been characterized by X-ray crystallography. Crystal data: for **1**, monoclinic space group $P2_1/c$, $a = 14.781(2)$ Å, $b = 26.959(7)$ Å, $c = 20.443(2)$ Å, $\beta = 110.60(2)°$, $Z = 4$; for **4**, monoclinic space group $P2_1/n$, $a = 14.1803(7)$ Å, $b = 12.047(3)$ Å, $c = 25.114(5)$ Å, $\beta = 100.64(1)°$, $Z = 2$; for **8**, monoclinic space group $C2/c$, $a = 30.899(7)$ Å, $b = 11.395(2)$ Å, $c = 29.782(5)$ Å, $\beta = 103.08(1)°$, $Z = 4$. Complexes **1**, **4**, and **8** are all tetrameric with a $M_4O_4$ structural motif; **1** has a cubane type structure while **4** and **8** are built from a ladder-like framework. All Ca atoms in **1** have very similar six-coordinate octahedral symmetry. The two unique Ca atoms in **4**, which is centrosymmetric, are also six-coordinate, but one is octahedral and the other is trigonal prismatic. In complex **8**, which is also centrosymmetric, the environments of the two unique Ba atoms are again different, one showing an eight-coordinate, bicapped trigonal prismatic and the other a nine-coordinate, monocapped square prismatic geometry. Compounds **1**−**9** may have properties pertinent for application as sol−gel precursors.

## Introduction

In continuation of our studies on alkaline earth metal complexes with oxygen-based ligands,[2,3] we report here on the synthesis and characterization of some mixed $\beta$-diketonate and alkoxide complexes of Ca, Sr, and Ba.

The structures and properties of the deceptively simple group 2 metal alkoxides (Mg, Ca[4]) $[M(OR)_2]_\infty$ (R = Me, Et) have been known since the late nineteenth century, but to date, there have been few key studies to elucidate not only their reproducible synthesis but also more importantly their solution and solid state spectroscopic characterization. Early research suggested these materials were polymeric insoluble solids with $CdI_2$ type structures.[5] More recently, however, other researchers showed that these metals have a pronounced tendency to form a large range of molecular aggregates, stabilized by either oxo, hydroxo, water, or other suitable Lewis bases, e.g. $[Ca_6(O)_2(OEt)_8(EtOH)_{14}]$,[6] $[HBa_5(O)(OPh)_9(thf)_8]$,[7] $[H_4Ba_6(O)(OCH_2CH_2OMe)_{14}]$,[8] and $[Ca_3(OPh)_5(HMPA)_6][(OPh)(PhOH)_2]$.[9]

The alkaline earth metal $\beta$-diketonates have also attracted attention, the complex $Ba_5(tmhd)_9(H_2O)_3(OH)$ being obtained from aqueous media,[10] while from methanol the compound $[Ba(tmhd)_2(MeOH)_3]\cdot MeOH$ is obtained.[11] The widely used hydrated alkaline earth precursors $[Ca_2(hfpd)_4(H_2O)_4]$ and $[Ba(hfpd)_2(H_2O)]_\infty$ (hfpd is 1,1,1,5,5,5-hexafluoro-2,4-propanedionate) were also structurally characterized recently.[12] However, if more rigorous anaerobic conditions (e.g. Schlenk techniques) are used, then it is possible to obtain products of consistently high purity, e.g. the Lewis base-adducted dimeric barium complexes $[Ba_2(tmhd)_4(L)_2]$ (L = $NH_3$,[13] $Et_2O$[14]). Lewis base-free complexes have also been reported exhibiting a range of

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(2) (a) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Otway, D. J. *Polyhedron* **1992**, *11*, 1995. (b) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A.; Otway, D. J. *Inorg. Chem.* **1993**, *32*, 4464.

(3) (a) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A. *Polyhedron* **1993**, *12*, 1621. (b) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A. *J. Chem. Soc., Chem. Commun.* **1993**, 478.

(4) (a) Cahours, A. *Liebigs Ann. Chem.* **1860**, *114*, 227. (b) Cahours, A.; Wankyln, J. A. *Liebigs Ann. Chem.* **1866**, *140*, 353. (c) Szarvasy, E. *Chem. Ber.* **1897**, *30*, 806.

(5) (a) Turova, N. Y.; Popovkin, B. A.; Novoselova, A. N. *Izv. Akad. Nauk SSSR, Neorg. Mater*, **1967**, *3*, 1435 and references therein. (b) Lutz, H. D. *Z. Anorg. Allg. Chem.* **1967**, *353*, 207; **1968**, *356*, 132.

(6) Turova, N. Y.; Turevskaya, E. P.; Kessler, V. G.; Yanovsky, A. I.; Struchkov, Y. T. *J. Chem. Soc.,Chem. Commun.* **1993**, 21.

(7) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Folting, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1349.

(8) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1498.

(9) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Folting, K.; Huffman, J. C.; Streib, W. E. *Inorg. Chem.* **1993**, *32*, 1970.

(10) (a) Turnipseed, S. B.; Barkley, R. M.; Sievers, R. E. *Inorg. Chem.* **1991**, *30*, 1164. (b) Turnipseed, S. B.; Barkley, R. M.; Sievers, R. E. *Inorg. Chem.* **1994**, *33*, 798.

(11) Gleizes, A.; Sans-Lenain, S.; Medus, D. *C. R. Acad. Sci., Ser. II* **1991**, *312*, 983.

(12) Bradley, D. C.; Hasan, M.; Hursthouse, M. B.; Motevalli, M.; Khan, O. F. Z.; Pritchard, R. G.; Williams, J. O. *J. Chem. Soc., Chem. Commun.* **1992**, 575.

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aggregation, i.e. $[Ca_3(tmhd)_6]$,[15] $[Sr_3(Htmhd)_6(tmhd)]$,[16] and $[Ba_4(tmhd)_8]$.[16,17] More recent studies reported the stabilization of such complexes by the addition of either closed or open oligoethers,[18] e.g. $[Ba(hfpd)_2(18\text{-crown-}6)]$[19] or $[Ca(tmhd)_2(triglyme)]$.[20] Similarly, other workers have isolated the monomeric barium complexes $[Ba(diki)_2]$, $[Ba(triki)_2]$ (diki = $Bu^tCOCHCN(R)Me$ {R = $(CH_2CH_2O)_2Me$}, triki = $Bu^tCOCHCN(R)Bu^t$ {R = $(CH_2CH_2O)_3Me$}), and $[Ba(dmmod)_2]$ (H-dmmod = $Bu^tCOCH_2COCH_2CH_2CH_2OMe$) by saturating the metal center with multifunctionalized ligands.[21] Hovnanian *et al.*[22] recently reported the synthesis of a barium mixed aryl alcohol/$\beta$-diketonate complex of formulation $[Ba(tmhd)_2(HOC_6H_3Bu^t{}_2\text{-}3,5)_2(thf)_2]$. This compound contains only neutral aryl alcohol ligands and is probably held together *via* electrostatic rather than direct bonding metal−oxygen interactions. However, to date there is still no precedent for an alkaline earth metal complex supported by both alkoxide and $\beta$-diketonate ligands. [After the submission of this paper Hubert-Pfalzgraf *et al.*[23] reported the synthesis of the barium complexes $[Ba_5(OH)(OCH(Me)CH_2NMe_2)_4(tmhd)_5]$ and $[Ba(tmhd)_2(OCH(Me)CH_2NMe_2)]_2$. The first of these is a true mixed-ligand complex with a pentanuclear, square pyramidal framework, while the second is a centrosymmetric dimer, similar to that reported by Hovnanian[22] above.]

Thus, by using a 1:1 ligand combination of $\beta$-diketone and functionalized alcohol around the metal center, we have attempted to achieve a better tailoring of not only the ligand to metal sets but also control of the degree of oligomerization of the complexes. Herein, we describe our synthesis and spectroscopic analyses of a series of alkaline earth metal $\beta$-diketonate alkoxide complexes, **1**−**9** which may have interesting sol−gel properties. Compounds **1**, **4**, **and 8** have been further characterized by single-crystal X-ray analysis.

## Experimental Section

**General Methods.** All manipulations were carried out under an atmosphere of dry (molecular sieves) nitrogen using standard glovebox (Miller-Howe FF 160 with double-recirculator system) and Schlenk techniques. All hydrocarbon solvents were rigorously predried, distilled over calcium oxide, and redistilled over sodium metal by standard techniques. Elemental analyses were performed by the microanalytical department of Imperial College. Microanalyses for **2** and **3** are consistent with the desolvated solids. The melting points were measured under argon in sealed capillaries and are uncorrected.

**Physical Techniques.** Infrared spectra were recorded on a Perkin-Elmer FTIR 1720 spectrometer as either Nujol or hexachlorobutadiene mulls between 25 × 4 mm CsI plates. The Nujol and hexachlorobutadiene were both predried with 4A molecular sieves prior to use (and stored in the glovebox); the samples were protected from the atmosphere by an O-ring-sealed Presslok holder (available from Aldrich Chemicals).

NMR spectra were recorded on a JEOL GS 270 MHz NMR spectrometer, using the proton impurities of the deuterated solvent as reference for $^1H$ spectra and the $^{13}C$ resonance of the solvent as a reference for $^{13}C\{^1H\}$ spectra. Chemical shifts were also independently referenced to tetramethysilane (*ca.* 1%) added by volume. All chemical shifts are reported positive to high frequency of the standard.

Mass spectrometric studies were performed on a Kratos MS 30 (University of London Mass Spectrometry Service at the Royal School of Pharmacy) or a VG Autospec-Q (Imperial College Mass Spectrometry Service) operating in electron impact (positive) mode (70 eV) using a direct-insertion probe and operating over the temperature range 50−200 °C. The samples were prepared in micro sure-seal bottles.

Controlled thermal analysis of the complexes was investigated using a Polymer Laboratories STA 1500H simultaneous thermal analyzer, controlled by an Omni Pro 486DX-33 PC. The weights of the samples investigated were between 12 and 22 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 mL/min) nitrogen gas, using heating rates of 5 °C/min. The descriptions that follow in this section detail the percent weight losses observed and the calculated loss of certain ligands that compare well with the observed losses. GC or MS studies would be required to ascertain the exact nature of the effluents.

**Synthesis.** All reactions were performed with dry oxygen-free solvents, stored over 4A molecular sieves. 2,2,6,6-tetramethyl-3,5-heptanedione was obtained from Inorgtech of Mildenhall, Suffolk, U.K. The tetrasolvated metal ethoxides $[M(OEt)_2(EtOH)_4]_\infty$ (M = Ca, Sr, Ba) were prepared according to literature procedures.[24]

**Preparation of $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ (1).** To a suspension of tetraethanol-solvated calcium ethoxide (7.04 g, 22.42 mmol) in hexane (20 mL) was introduced H-tmhd (4.68 mL, 22.42 mmol), producing a clear solution on stirring for 10 min. The solution was reduced to dryness *in vacuo* to yield a white paste and kept at 50 °C for 1 h, to yield a white solid. This solid was redissolved in toluene (15 mL), and the solution was left to stand at −25 °C, yielding colorless crystals. Yield: 5.98 g, 85%.

Anal. Calc for $C_{60}H_{120}Ca_4O_{16}$: C, 57.32; H, 9.55. Found: C, 57.01; H, 8.98. Mp: desolvates at 67 °C, sublimes 170−200 °C at $5 \times 10^{-3}$ Torr. TGA: 90−200 °C, 18.1% loss of 4 EtOH (calc %); 220−400 °C, 62.8% loss of 4 tmhd and 2 EtO (calc %); 590−650 °C, 4% loss of 2 Et (calc %). DSC: 147.3 °C, −14.6 mcal/mg desolvation of EtOH.

**Preparation of $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n(toluene)_{0.66}$ (2).** An experimental workup similar to that described for **1** was performed, starting from tetraethanol-solvated strontium ethoxide dissolved in *n*-hexane (20 mL). Yield: 4.67 g, 79%.

Mp: desolvates at 72 °C. $^1H$ NMR ($C_6D_6$, 270 MHz, 70 °C): $\delta$ 1.17 (18 H, $Me_{tmhd}$), 1.20 (9 H, t, Me), 2.08 (s, toluene), 2.60 (2 H, s br, OH), 3.79 (6 H, q, CH), 5.73 (1 H, d, CH). TGA: 40−180 °C, 20.1% loss of 0.66 EtOH and 0.66 toluene (calc 22.3%); 230−550 °C, 42.8% loss of tmhd (calc 44.8%); 800−950 °C, 10.6% loss of Et (calc 7.2%); residue of 26.2% (calc for SrO 25.5%). DSC: 89.0 °C, −15.77 mcal/mg desolvation of EtOH and toluene; 458 °C, −13.15 mcal/mg; 929.8 °C, −49.18 mcal/mg.

**Preparation of $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n\cdot 0.33(toluene)$ (3).** An experimental workup similar to that described for **1** was performed, starting from tetraethanol-solvated barium ethoxide dissolved in *n*-hexane (20 mL). Yield: 2.24 g, 84%.

Mp: 246−250 °C. TGA: 55−120 °C, 7% loss of 0.25 EtOH and 0.25 toluene (calc 7%); 290−430 °C, 58% loss of 1.5 tmhd (calc

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(13) Rees, W. S., Jr.; Carris, M. W.; Hesse, W. *Inorg. Chem.* **1991**, *30*, 4479.

(14) Rossetto, G.; Benetollo, P. F.; Porchia, M.; Zanella, P. *Polyhedron* **1992**, *11*, 979.

(15) Arunasalam, V. C.; Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A. *Inorg. Chem.*, submitted for publication.

(16) Drake, S. R.; Otway, D. J.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 2883.

(17) (a) Gleizes, A.; Sans-Lenain, S.; Medus, D. *C. R. Acad. Sci., Ser. II* **1991**, *313*, 761. (b) Drozdov, A.; Troyanov, S. *Polyhedron* **1992**, *11*, 2877.

(18) (a) Van der Sluis, P.; Spek, A. L.; Timmer, K.; Meinema, H. A. *Acta Crystallogr.* **1990**, *C46*, 1741. (b) Timmer, K.; Meinema, H. A. *Inorg. Chim. Acta* **1991**, *187*, 99. (c) Gardiner, R.; Brown, D. W.; Kirlin, P. S.; Rheingold, A. L. *Chem. Mater.* **1991**, *3*, 1053.

(19) (a) Norman, J. A. T.; Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1991**, 971. (b) Norman, J. A. T.; Pez, G. P. Volatile crown ligand beta-diketonate alkaline earth metal complexes. Eur. Pat. Applied, 460627, 1990.

(20) Drake, S. R.; Miller, S. A.; Williams, D. J. *Inorg. Chem.* **1993**, *32*, 3227.

(21) (a) Schulz, D. L.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Inorg. Chem.* **1993**, *32*, 249. (b) Schulz, D. L.; Hinds, B. J.; Neumayer, D. A.; Stern, C. L.; Marks, T. J. *Chem. Mater.* **1993**, *5*, 1605. (c) Rees, W. S., Jr.; Caballero, C. R.; Hesse, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 735. (d) Rees, W. S., Jr.; Dippel, K. A.; Carris, M. W.; Caballero, C. R.; Moreno, D. A.; Hesse, W. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 127.

(22) Miele, P.; Foulon, J-D.; Hovnanian, N. *Polyhedron* **1993**, *12*, 209.

(23) Hubert-Pfalzgraf, L. G.; Labrize, F.; Bois, C.; Vaissermann, J. *Polyhedron* **1994**, *13*, 2163.

(24) (a) Arunasalam, V-C.; Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Otway, D. J. *Polyhedron*, submitted for publication. (b) Staeglich, H.; Weiss, E. *Chem. Ber.* **1978**, *111*, 901. (c) Novoselova, A. V.; Turova, N. Y.; Turevskaya, E. P.; Yanovskaya, M. I.; Kozunov, V. A.; Koslova, N. I. *Izv. Akad. Nauk SSSR, Neorg. Mat.* **1979**, *15*, 1055.

58.6%); 500−530 °C, 6% loss of 0.5 Et (calc 3%); residue of 31.2% (calc for BaO 32.6%). DSC: 106 °C, −5.50 mcal/mg desolvation of EtOH and toluene; 226 °C, −2.90 mcal/mg melting point; 542 °C, −12.77 mcal/mg, final loss of Et.

**Preparation of $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ (4).** To a clear solution of **1** (4.25 g, 13.53 mmol) in toluene (20 mL) was added *N,N*-dimethylethanolamine (1.36 mL, 13.53 mmol), resulting in an exothermic reaction. The resulting solution was stirred for 30 min and then the solvent removed *in vacuo*, to give a white solid, which was kept at 80 °C for 1 h under reduced pressure. The resulting solid was redissolved in toluene (15 mL), and the solution was left to stand at −25 °C to crystallize as colorless plates. Yield: 3.01 g, 62%.

Anal. Calc for $C_{74}H_{134}N_2Ca_4O_{14}$: C, 69.70; H, 10.52; N, 2.20. Found: C, 69.25; H, 10.38; N, 1.98. Mp: dec > 280 °C, sublimes in low yield 185−220 °C at $5 \times 10^{-3}$ Torr. TGA: 200−410 °C, 75.8% loss of 6 tmhd (calc 76.4%); 630−690 °C, 10.4% loss of OR + R (calc 11.3%); residue of 14.8% (calc for CaO 15.6%). DSC: 305 °C, −18.33 mcal/mg dec/loss of tmhd; 682 °C, −14.62 mcal/mg dec/loss of OR + R.

**Preparation of $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ (5).** An experimental workup similar to that described for **4** was performed, starting from **1** and isopropoxyethanol. Yield: 2.45 g, 67%.

Anal. Calc for $C_{19}H_{34}CaO_4$: C, 62.30; H, 9.29: Found: C, 61.89; H, 9.02.

**Preparation of $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n{\cdot}C_7H_8$ (6).** An experimental workup similar to that described for **4** was performed, starting from **2** and *N,N*-dimethylethanolamine. Yield: 3.52 g, 60%.

Anal. Calc for $C_{20.5}H_{39}NSrO_4$: C, 54.55; H, 8.85; N, 3.10. Found: C, 54.12; H, 8.18; N, 2.90. Mp: dec > 225 °C. TGA: 50−100 °C, 20% loss of toluene (calc 20.4%); 260−400 °C, 37 loss of tmhd O (calc 37%); 500−560 °C, 10% loss of 0.5 dmae (calc 9.75%); 840−940 °C, 9.5% loss of 0.5 dmae (calc 9.75%); residue of 22.9% (calc for SrO 23.0%). DSC: 74.7 °C, −4.8 mcal/mg desolvation of toluene; 389 °C, −20.93 mcal/mg dec/loss of tmhd; 537 °C, −21.6 mcal/mg; 931 °C, −78.5 mcal/mg.

**Preparation of $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ (7).** An experimental workup similar to that described for **4** was performed, starting from **2** and methoxyethanol. Yield: 2.96 g, 62%.

Anal. Calc for $C_{19.5}H_{36}SrO_5$: C, 53.42; H, 8.22. Found: C, 52.96; H, 8.15. Mp: dec > 170 °C. TGA: 310−560 °C, 59% loss of 1.5 tmhd O (calc 62%); 800−900 °C, 11.6% loss of $H_{0.5}OR$ (calc 17%); residue of 27.3% (calc for SrO 23.8%). DSC: 261 °C, −30.5 mcal/mg melting and phase changes; 339 °C, 43.8 mcal/mg dec/loss of tmhd; 916 °C, −95 mcal/mg.

**Preparation of $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ (8).** An experimental workup similar to that described for **4** was performed, starting from **3** and isopropoxyethanol. Single crystals of **8** were grown from a saturated toluene solution at 0 °C. Yield: 3.45 g, 67%.

Anal. Calc for $C_{86}H_{158}Ba_4O_{20}$: C, 50.05; H, 7.66. Found: C, 49.78; H, 7.45. Mp: 108−111 °C, sublimes to yield $[Ba(tmhd)_{1.5}(OR)_{0.5}]$ 95−110 °C at $5 \times 10^{-3}$ Torr. TGA: 110−220 °C, 12% loss of 2 $HOCH_2CH_2OPr^i$ (calc 10.1%); 230−410 °C, 42% loss of 5 tmhd (calc 44%); 470−570 °C, 9% loss of 1 tmhd (calc 8.8%); 955−1050 °C, 6.5% loss of 2 $CH_2CH_2OPr^i$ (calc 8%); residue of 26.7% (calc for BaO 29.7%). DSC: 120 °C, −11.0 mcal/mg melting point; 170−290 °C, −11.4 mcal/mg; 470−560 °C, −13.05 mcal/mg; 806 °C, −4.04 mcal/mg phase change; 1015−1055 °C, −12.7 mcal/mg.

**Preparation of $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ (9)** An experimental workup similar to that described for **4** was performed starting from **3** and methoxyethanol. Yield: 3.20 g, 59%.

Anal. Calc for $C_{19.5}H_{36}BaO_5$: C, 47.95; H, 7.38. Found: C, 47.57; H, 7.16. Mp: 106−110 °C. TGA: 90−180 °C, 7.5% loss of 2 $HOCH_2CH_2OMe$ (calc 7.8%); 230−420 °C, 64.3% loss of 6 tmhd (calc 56%) and some sublm; 950−1050 °C, 9.8% loss of 2 $CH_2CH_2OMe$ (calc 6%); residue of 23% (calc for BaO 31%). DSC: 124 °C, −16.9 mcal/mg melting point; 210−390 °C, −14.8 mcal/mg; 790−830 °C, −3.8 mcal/mg; 950−1040 °C, −19.68 mcal/mg.

**Table 1.** Crystallographic Data for $[Ca_4(tmhd)_4(C_2H_5O)_4(C_2H_5OH)_4]$ (**1**), $[Ca_4(tmhd)_6(C_4H_{10}NO)_2]$ (**4**), and $[Ba_4(tmhd)_6(C_5H_{11}O_2)_2(C_5H_{12}O_2)_2]$ (**8**)[a]

| | **1** | **4** | **8** |
|---|---|---|---|
| chem formula | $C_{60}H_{120}Ca_4O_{16}$ | $C_{74}H_{134}Ca_4N_2O_{14}$ | $C_{86}H_{158}Ba_4O_{20}$ |
| fw | 1257.92 | 1436.15 | 2061.48 |
| space group | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) | $C2/c$ (No. 15) |
| $a$/Å | 14.781(2) | 14.180(1) | 30.899(7) |
| $b$/Å | 26.959(7) | 12.047(3) | 11.395(2) |
| $c$/Å | 20.443(2) | 25.114(5) | 29.782(5) |
| $\beta$/deg | 110.60(2) | 100.64(1) | 103.08(1) |
| $V$/Å$^3$ | 7625.3 | 4216.6 | 10214 |
| Z | 4 | 2 | 4 |
| $D_c$/g cm$^{-3}$ | 1.096 | 1.131 | 1.341 |
| $\mu$(Mo K$\alpha$)/cm$^{-1}$ | 3.3 | 3.1 | 15.8 |
| $R^b$ | 0.054 | 0.067 | 0.057 |
| $R_w$ | 0.063[c] | 0.157[d] | 0.125[d] |

[a] Parameters in common: X-radiation, Mo K$\alpha$, $\lambda = 0.710\,69$ Å, $T = 150$ K. [b] $R = \Sigma(\Delta F)/\Sigma(F_o)$. [c] $R_w = [\Sigma\{w(\Delta F)^2\}/\Sigma\{w(F_o)^2\}]^{1/2}$, $w = 1$. [d] $R_w = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o{}^2)^2\}]^{1/2}$, $w = 1/\sigma^2(F_o{}^2)$.

**X-ray Crystallography of $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ (1), $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ (4), and $[Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_2(Pr^iOCH_2CH_2OH)_2]$ (8).** The X-ray measurements were made on crystals of approximate dimensions $0.25 \times 0.15 \times 0.10$ mm$^3$ (**1**), $0.30 \times 0.25 \times 0.20$ mm$^3$ (**4**) and $0.20 \times 0.15 \times 0.15$ mm$^3$ (**8**), which were mounted using silicone oil and then transferred to the goniostat. All data were collected at 150 K using Mo K$\alpha$ radiation ($\lambda = 0.7106\,9$ Å, graphite monochromator) on a Delft FAST TV area detector diffractometer equipped with a rotating-anode generator (50 kV, 50 mA), a bufferboard, a DEP image intensifier, and an Oxford Cryostream low-temperature cooling system by following previously described procedures.[25] The data were corrected for Lorentz and polarization effects and also for absorption using the program DIFABS.[26] The crystal data are presented in Table 1.

The structures were solved *via* direct methods (SHELX-S)[27] and difference electron density syntheses and refined by full-matrix least squares on $F$ (compound **1**) (SHELX-80)[28] and $F^2$ (compounds **4** and **8**) (SHELXL-93).[29] The structure of **1** was refined using only those data with $F_o > 4\sigma(F_o)$, while the structures of **4** and **8** were refined using all unique data with intensities above the background. In all three compounds, several *tert*-butyl groups were rotationally disordered about the C−CMe$_3$ axis as suggested by very large or unacceptable anisotropic behavior of the attached methyl carbons. Five such methyl groups were identified as disordered in **1**, three in **4**, and six in **8**. In addition, three carbons belonging to two of the terminally bonded EtOH molecules in **1** and one −CH$_2$− group in **4** were also disordered. Each of the disordered atoms was assigned two positions and refined with partial occupancies. The non-hydrogen atoms were all refined with ansiotropic displacement coefficients, except one in **1** and three in **8**, of the partially occupied carbons which were treated as isotropic. In compound **8**, the C−Me$_3$ distances involving the disordered Me groups showed large variations from the expected values; so in the final refinement these distances were constrained at 1.54(1) Å. In **1**, the hydrogen atoms on the disordered carbons were ignored; others were included in calculated positions (C−H 0.96 Å) and a common $U_{iso}$ was refined for all. In **4**, all hydrogens were included in idealized positions with site occupancies equal to those, and $U_{iso}$'s set at 1.5 times the $U_{eq}$'s, of the parent carbons. In **8**, the hydrogens were similarly treated except those on the alcohol groups, which were ignored. The final unweighted $R$ values were 0.054 (**1**), 0.0422 (**4**), and 0.029 (**8**) for 5456, 3974, and 4488 reflections with $F_o > 4\sigma(F_o)$, respectively. The weighting schemes used in the refinements were $w = 1$ for **1** and $1/\sigma^2(F_o)^2$ for **4** and **8**, which gave satisfactory agreement analyses. It is to be noted that there were considerable difficulties in resolving the disorder problems, because most of the disordered atoms had smeared-out electron density, resulting in poor atomic resolution and high thermal

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(25) Darr, J. A.; Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A. *Inorg. Chem.* **1993**, *32*, 5704.

(26) Walker, N. P. C.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158 (adapted for FAST geometry by A. K. Karaulov, University of Wales Cardiff, 1991).

(27) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(28) Sheldrick, G. M. SHELX-80 Program for Crystal Structure Analysis. University of Gottingen, Germany, 1980.

(29) Sheldrick, G. M. SHELXL-93 Program for Crystal Structure Analysis. *J. Appl. Crystallogr.*, submitted for publication.

**Table 2.** Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Equivalent Temperature Factors (Å$^2$ × $10^3$) for $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ (**1**)$^a$

| atom$^b$ | $x$ | $y$ | $z$ | $U_{eq}$ | atom$^b$ | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ca(1) | 2850.9(9) | 1439.3(5) | 1385.1(6) | 30.0(5) | C(20) | 3069(7) | −1427(4) | −464(6) | 135(2) |
| Ca(2) | 3268.3(9) | 108.7(4) | 1597.8(6) | 29.9(5) | C(21) | 1669(7) | −960(6) | −389(7) | 223(2) |
| Ca(3) | 4813.5(9) | 965.6(5) | 2777.0(7) | 36.9(5) | C(22) | 2822(8) | −538(5) | −818(5) | 149(2) |
| Ca(4) | 2369.1(10) | 785.3(5) | 2709.3(6) | 33.1(4) | C(23) | 6902(6) | 2285(3) | 2847(5) | 75(2) |
| O(1) | 2172(3) | 1656(2) | 245(2) | 37(1) | C(24) | 6386(5) | 1901(3) | 3144(4) | 56(2) |
| O(2) | 1557(3) | 1963(2) | 1350(2) | 38(1) | C(25) | 6668(6) | 1827(3) | 3867(5) | 76(2) |
| O(3) | 4651(3) | −389(2) | 1793(2) | 36(1) | C(26) | 6306(6) | 1470(4) | 4211(4) | 76(2) |
| O(4) | 2935(3) | −345(2) | 605(2) | 44(1) | C(27) | 6663(8) | 1442(5) | 5022(5) | 125(2) |
| O(5) | 5681(3) | 1673(2) | 2691(2) | 49(1) | C(28) | 7005(7) | 2089(4) | 2179(6) | 113(2) |
| O(6) | 5709(4) | 1145(2) | 3903(3) | 66(2) | C(29) | 6272(6) | 2758(3) | 2667(6) | 105(2) |
| O(7) | 1377(3) | 108(2) | 2727(2) | 39(1) | C(30) | 7907(6) | 2418(4) | 3326(6) | 129(2) |
| O(8) | 2332(3) | 780(2) | 3809(2) | 43(1) | C(31) | 7325(13) | 992(6) | 5240(7) | 322(2) |
| O(9) | 4081(3) | 845(1) | 1556(2) | 31(1) | C(32) | 5807(9) | 1359(6) | 5246(5) | 179(2) |
| O(10) | 3401(3) | 1419(1) | 2606(2) | 35(1) | C(33) | 7181(10) | 1882(6) | 5370(6) | 207(2) |
| O(11) | 3745(3) | 327(1) | 2783(2) | 34(1) | C(34) | 111(5) | −380(3) | 2865(4) | 58(2) |
| O(12) | 2069(3) | 712(1) | 1499(2) | 32(1) | C(35) | 925(4) | 5(2) | 3143(3) | 36(2) |
| O(13) | 4133(3) | 2015(2) | 1517(3) | 54(1) | C(36) | 1146(5) | 202(2) | 3808(4) | 44(2) |
| O(14) | 2124(4) | −415(2) | 1863(2) | 51(2) | C(37) | 1845(5) | 566(2) | 4113(3) | 39(2) |
| O(15) | 5879(3) | 305(2) | 2712(3) | 57(1) | C(38) | 2058(6) | 727(3) | 4877(4) | 58(2) |
| O(16) | 1135(3) | 1414(2) | 2358(2) | 47(1) | C(39) | −499(7) | −254(4) | 2152(5) | 126(2) |
| C(1) | 1315(6) | 1972(3) | −898(3) | 50(2) | C(40) | −460(7) | −474(4) | 3361(5) | 117(2) |
| C(2) | 1527(5) | 1956(2) | −99(3) | 35(2) | C(41) | 594(7) | −900(3) | 2872(5) | 91(2) |
| C(3) | 1011(5) | 2272(2) | 187(3) | 41(2) | C(42) | 1986(8) | 1290(3) | 4883(5) | 105(2) |
| C(4) | 1073(5) | 2275(2) | 884(3) | 40(2) | C(43) | 3116(7) | 591(4) | 5280(4) | 107(2) |
| C(5) | 515(6) | 2669(3) | 1140(4) | 67(2) | C(44) | 1443(7) | 497(4) | 5233(4) | 94(2) |
| C(6)$^a$ | 1487(9) | 1439(4) | −1148(5) | 64(2) | C(45) | 4697(5) | 844(3) | 1157(3) | 45(2) |
| C(6′)$^b$ | 1952(15) | 1674(9) | −1110(12) | 46(3)$^c$ | C(46) | 4158(6) | 811(4) | 386(4) | 79(2) |
| C(7)$^a$ | 2207(10) | 2296(5) | −970(6) | 84(2) | C(47) | 3485(7) | 1896(3) | 2937(4) | 70(2) |
| C(7′)$^b$ | 1092(20) | 2509(9) | −1166(10) | 68(2) | C(48) | 3691(9) | 1881(4) | 3659(5) | 142(2) |
| C(8)$^a$ | 388(8) | 2171(6) | −1332(5) | 76(2) | C(49) | 4011(7) | −69(3) | 3275(4) | 69(2) |
| C(8′)$^b$ | 165(15) | 1716(10) | −1192(10) | 57(2) | C(50) | 4464(8) | 61(4) | 3983(4) | 111(2) |
| C(9)$^c$ | −452(9) | 2337(5) | 1174(8) | 73(2) | C(51) | 1102(5) | 660(3) | 1030(3) | 47(2) |
| C(9′)$^d$ | −17(16) | 2538(8) | 1575(10) | 56(2) | C(52) | 1035(5) | 505(3) | 310(3) | 56(2) |
| C(10) | 48(6) | 3087(3) | 593(4) | 70(2) | C(53) | 4297(9) | 2340(5) | 952(9) | 212(2) |
| C(11)$^c$ | 1040(13) | 2824(5) | 1814(7) | 69(2) | C(54) | 3824(10) | 2685(5) | 969(8) | 210(2) |
| C(11′)$^d$ | 1496(14) | 3030(6) | 1728(9) | 71(2) | C(55)$^e$ | 1369(9) | −763(5) | 1306(7) | 54(2) |
| C(12) | 5732(5) | −1060(3) | 1866(4) | 52(2) | C(55′)$^f$ | 2227(12) | −984(6) | 1857(10) | 65(2) |
| C(13) | 4778(5) | −784(2) | 1491(3) | 37(2) | C(56)$^e$ | 1769(14) | −1236(6) | 1380(9) | 94(2) |
| C(14) | 4144(5) | −964(3) | 863(4) | 45(2) | C(56′)$^f$ | 2436(19) | −1152(8) | 2545(18) | 174(2) |
| C(15) | 3290(5) | −731(3) | 443(4) | 47(2) | C(57) | 6872(6) | 258(3) | 3062(6) | 98(2) |
| C(16) | 2696(6) | −929(4) | −312(5) | 86(2) | C(58) | 7456(7) | 647(4) | 3178(8) | 169(2) |
| C(17) | 5883(6) | −1104(3) | 26466(4) | 69(2) | C(59)$^g$ | 640(10) | 1613(5) | 2781(7) | 51(2) |
| C(18) | 5767(7) | −1591(3) | 1576(5) | 87(2) | C(59′)$^g$ | 88(12) | 1273(6) | 2164(9) | 73(2) |
| C(19) | 6543(5) | −754(3) | 1756(4) | 68(2) | C(60) | −245(7) | 1353(4) | 2738(5) | 85(2) |

$^a$ $U_{eq}$'s in this and Tables 3 and 4 are defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. $^b$ Superscripts indicate atoms belonging to the disordered groups and refined with fixed partial occupancies: $a = 0.70$, $b = 0.30$, $c = 0.65$, $d = 0.35$, $e = 0.55$, $f = 0.45$, $g = 0.50$. $^c$ $U_{iso}$.

motion and, in some cases, variable bond lengths. But most of these atoms were terminally located and do not appear to affect the geometrical parameters involving the metal centers. We believe that the structural results presented in this paper are quite satisfactory to determine unambiguously the identity of the complexes and their bonding features. The fractional coordinates of the non-hydrogen atoms (including the site occupancies of the disordered atoms) are given in Tables 2−4 for compounds **1**, **4**, and **8**, respectively. All calculations were done on a 486DX2/66 personal computer. Sources of scattering factors are as in ref 29. The diagrams were drawn with the program SNOOPI.[30]

## Results and Discussion

The crystalline metal ethoxides $[M(OEt)_2(EtOH)_4]_\infty$ (M = Ca, Sr, or Ba) when suspended/dissolved in *n*-hexane react very rapidly with 1 equiv of tetramethylheptane-3,5-dione (H-tmhd) at ambient temperature to give clear colorless solutions; see Scheme 1. Crystallization of the products from toluene solutions at −25 °C gave colorless crystals of the first examples of group 2 metal mixed *β*-diketonate alkoxides $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ (**1**), $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ (**2**), and $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ (**3**). The complex $[Ca(tmhd)_4(OEt)_4(EtOH)_4]$ (**1**) has been fully characterized crystallographically.

Having established the structure of **1**, we studied its reactions and those of the related compounds **2** and **3** with bifunctional alcohols. This has yielded the new compounds $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ (**4**), $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ (**5**), $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$ (**6**), $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ (**7**), $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ (**8**), and $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ (**9**); see Scheme 1. Complexes **4** and **8** were further characterized by single-crystal X-ray analysis.

**Spectroscopic Characterization.** The infrared spectra of complexes **1**−**9** were studied as both hexachlorobutadiene and Nujol mulls between CsI windows. Selected infrared frequencies of complexes **1**−**9** are listed in Table 5. The IR bands are tentatively assigned on the basis of the infrared data of previously characterized alkoxides and *β*-diketonates.[5,31] Noteworthy absorptions were broad bands associated with coordinated ethanol molecules at ca. 3340 cm$^{-1}$ for complexes **1**−**3**, while complexes **7**−**9** exhibited weaker absorbtion frequencies

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(30) Davies, K. SNOOPI Program for Crystal Structure Drawing. University of Oxford, 1983.

(31) Pinchas, S.; Silver, B. L.; Laulicht, I. *J. Chem. Phys.* **1967**, *46*, 1506.

**Table 3.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[Ca_4(tmhd)_6(Me_2NCH_2CH_2O)_2]$ (**4**)

| atom$^a$ | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ca(1) | 6088.2(4) | 4318.0(4) | 199.7(2) | 18.4(2) |
| Ca(2) | 5315.2(4) | 4984.3(4) | −1241.5(2) | 20.9(2) |
| O(1) | 7454(1) | 4383(2) | 825(1) | 27(1) |
| O(2) | 6936(1) | 2844(2) | −37(1) | 26(1) |
| C(1) | 8865(2) | 4028(3) | 1471(1) | 30(1) |
| C(2) | 8161(2) | 3731(2) | 949(1) | 24(1) |
| C(3) | 8342(2) | 2824(2) | 634(1) | 27(1) |
| C(4) | 7752(2) | 2444(2) | 159(1) | 26(1) |
| C(5) | 8100(2) | 1486(2) | −164(1) | 36(1) |
| C(6) | 9404(3) | 5065(3) | 1354(2) | 59(1) |
| C(7) | 8284(3) | 4279(4) | 1911(1) | 58(1) |
| C(8) | 9587(3) | 3121(3) | 1674(1) | 45(1) |
| C(9)$^a$ | 9022(5) | 947(6) | 79(3) | 75(2) |
| C(10)$^a$ | 7296(5) | 631(6) | −287(3) | 65(2) |
| C(11)$^a$ | 8224(7) | 2019(6) | −711(3) | 77(2) |
| C(9′)$^b$ | 7424(9) | 1243(11) | −675(5) | 75(2) |
| C(10′)$^b$ | 9073(8) | 1776(10) | −297(5) | 65(2) |
| C(11′)$^b$ | 8189(12) | 449(10) | 211(5) | 77(2) |
| O(3) | 4671(2) | 5697(2) | −2069(1) | 30(1) |
| O(4) | 6503(2) | 4711(2) | −1722(1) | 31(1) |
| C(12) | 4206(2) | 6151(3) | −3005(1) | 35(1) |
| C(13) | 4941(2) | 5685(2) | −2522(1) | 29(1) |
| C(14) | 5819(2) | 5263(3) | −2606(1) | 34(1) |
| C(15) | 6546(2) | 4790(2) | −2290(2) | 27(1) |
| C(16) | 7451(2) | 4353(3) | −2402(1) | 33(1) |
| C(17) | 3908(3) | 7299(3) | −2852(2) | 62(1) |
| C(18) | 4603(3) | 6253(4) | −3526(1) | 71(1) |
| C(19) | 3332(3) | 5397(3) | −3090(2) | 54(1) |
| C(20) | 8026(3) | 3622(3) | −1961(2) | 57(1) |
| C(21) | 8067(3) | 5341(3) | −2500(2) | 60(1) |
| C(22) | 7206(3) | 3658(3) | −2918(2) | 54(1) |
| O(5) | 4777(1) | 6547(1) | −801(1) | 21(1) |
| O(6) | 6511(1) | 5485(2) | −473(1) | 22(10 |
| C(23) | 4780(2) | 8444(2) | −1085(1) | 30(1) |
| C(24) | 5298(2) | 7352(2) | −897(1) | 22(1) |
| C(25) | 6301(2) | 7292(2) | −823(1) | 27(1) |
| C(26) | 6868(2) | 6411(2) | −582(1) | 22(1) |
| C(27) | 7957(2) | 6541(2) | −410(1) | 27(1) |
| C(28) | 3734(3) | 8201(3) | −1325(2) | 48(1) |
| C(29) | 5251(3) | 9026(3) | −1514(1) | 43(1) |
| C(30) | 4836(3) | 9177(3) | −584(2) | 53(1) |
| C(31) | 8374(3) | 7299(3) | −793(2) | 51(1) |
| C(32) | 8442(3) | 5409(3) | −392(2) | 49(1) |
| C(33) | 8148(3) | 7048(3) | 162(1) | 47(1) |
| O(7) | 4747(1) | 4189(1) | −508(1) | 19(1) |
| N(1) | 4630(2) | 3098(2) | −1519(1) | 43(1) |
| C(43) | 3818(4) | 3175(4) | −1937(2) | 108(2) |
| C(35) | 5323(4) | 2400(4) | −1708(3) | 145(3) |
| C(36)$^c$ | 4687(5) | 2454(4) | −1006(2) | 33(2) |
| C(36′)$^d$ | 3868(6) | 2897(6) | −1141(3) | 30(2) |
| C(37) | 4313(2) | 3131(2) | −590(1) | 31(1) |

[a] Superscripts indicate disordered atoms refined with partial occupancies: $a = 0.620$, $b = 0.380$, $c = 0.590$, $d = 410$.

**Table 4.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[Ba_4(tmhd)_6(C_5H_{11}O_2)_2(C_5H_{12}O_2)_2]$ (**8**)

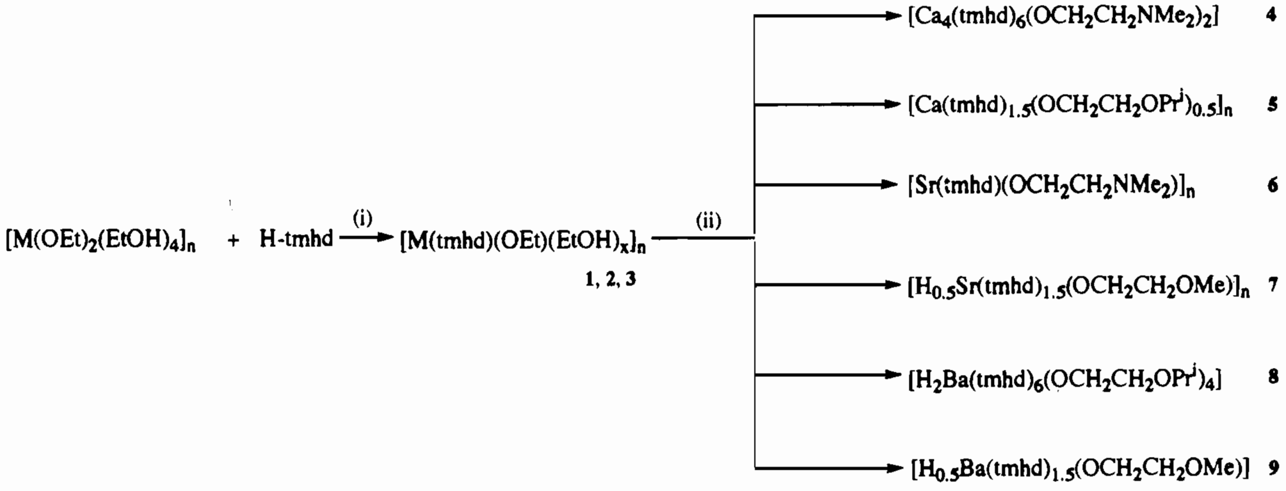
| atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ba(1) | 3923.1(1) | 2359.4(1) | 1575.7(1) | 25.2(1) |
| Ba(2) | 4625.7(1) | 2506.3(1) | 2935.3(1) | 24.6(1) |
| O(1) | 3950(1) | 1211(3) | 2417(1) | 33(1) |
| O(2) | 4676(1) | 929(3) | 1988(1) | 40(1) |
| C(1) | 3485(2) | −482(5) | 2417(2) | 37(1) |
| C(2) | 3865(2) | 182(4) | 2270(2) | 31(1) |
| C(3) | 4095(2) | −400(4) | 1982(2) | 35(1) |
| C(4) | 4499(2) | −65(4) | 1887(2) | 28(1) |
| C(5) | 4743(2) | −949(4) | 1638(2) | 35(1) |
| C(6) | 3125(2) | −757(6) | 1985(2) | 60(2) |
| C(7) | 3654(2) | −1612(6) | 2664(3) | 70(2) |
| C(8) | 3286(2) | 283(6) | 2740(2) | 59(2) |
| C(9)$^a$ | 5243(3) | −921(16) | 1839(6) | 47(4) |
| C(10)$^a$ | 4458(6) | −1121(20) | 1157(4) | 64(5) |
| C(11)$^a$ | 4600(7) | −2236(9) | 1660(9) | 71(6) |
| C(9′)$^b$ | 5191(5) | −423(17) | 1608(9) | 58(6) |
| C(10′)$^b$ | 4682(7) | −557(19) | 1133(4) | 60(5) |
| C(11′)$^b$ | 4835(11) | −2053(16) | 1933(8) | 88(9) |
| O(3) | 3050(1) | 2282(3) | 1441(1) | 31(1) |
| O(4) | 3499(1) | 4105(3) | 1102(1) | 41(1) |
| C(12) | 2261(2) | 2367(5) | 1300(2) | 35(1) |
| C(13) | 2713(2) | 2901(5) | 1265(2) | 30(1) |
| C(14) | 2731(2) | 3969(5) | 1043(2) | 32(1) |
| C(15) | 3119(2) | 4526(5) | 983(2) | 34(1) |
| C(16) | 3089(2) | 5707(5) | 726(2) | 48(2) |
| C(17) | 2287(2) | 2076(6) | 1811(2) | 54(2) |
| C(18) | 2198(2) | 1232(6) | 1028(2) | 52(2) |
| C(19) | 1863(2) | 3177(6) | 1130(2) | 51(2) |
| C(20)$^c$ | 3168(5) | 5463(9) | 249(9) | 125(6) |
| C(21)$^c$ | 2635(3) | 6267(10) | 607(6) | 125(6) |
| C(22)$^c$ | 3442(4) | 6519(8) | 988(4) | 122(6) |
| C(20′)$^d$ | 3507(12) | 5880(48) | 534(19) | 49(15)$^b$ |
| C(21′)$^d$ | 2855(23) | 6629(40) | 965(21) | 56(16)$^b$ |
| C(22′)$^d$ | 3137(25) | 6676(40) | 1095(16) | 55(17)$^b$ |
| O(5) | 4358(1) | 1793(3) | 3689(1) | 47(1) |
| O(6) | 4680(1) | 4080(3) | 3610(1) | 35(1) |
| C(23) | 4066(2) | 1358(6) | 4350(2) | 51(2) |
| C(24) | 4258(2) | 2211(6) | 4035(2) | 43(2) |
| C(25) | 4294(2) | 3411(5) | 4162(2) | 44(2) |
| C(26) | 4488(2) | 4282(5) | 3942(2) | 33(1) |
| C(27) | 4493(2) | 5557(5) | 4096(2) | 41(1) |
| C(28) | 4135(3) | 87(7) | 4209(3) | 89(3) |
| C(29) | 3567(3) | 1550(8) | 4245(3) | 106(3) |
| C(30) | 4276(4) | 1530(9) | 4847(3) | 140(5) |
| C(31) | 4289(2) | 6315(5) | 3688(2) | 49(2) |
| C(32) | 4237(3) | 5776(6) | 4475(2) | 73(2) |
| C(33) | 4976(2) | 5891(6) | 4275(2) | 68(2) |
| O(7) | 4595(1) | 3463(3) | 2092(1) | 26(1) |
| O(8) | 3919(1) | 4204(3) | 2454(2) | 48(1) |
| C(34) | 4481(2) | 4632(5) | 2050(3) | 59(2) |
| C(35) | 4193(3) | 5058(5) | 2326(3) | 70(2) |
| C(36) | 3555(2) | 4641(6) | 2628(2) | 48(2) |
| C(37) | 3181(2) | 5022(8) | 2245(8) | 83(3) |
| C(38) | 3434(2) | 3704(7) | 2935(3) | 92(3) |
| O(9) | 4555(1) | 2876(4) | 1071(1) | 52(1) |
| O(10) | 3843(1) | 1483(3) | 643(1) | 34(1) |
| C(39) | 4529(2) | 2415(6) | 627(2) | 52(2) |
| C(40) | 4051(2) | 2269(6) | 383(2) | 47(2) |
| C(41) | 3439(2) | 976(5) | 373(2) | 36(1) |
| C(42) | 3081(2) | 1881(5) | 222(20 | 45(2) |
| C(43) | 3298(2) | 42(5) | 665(2) | 54(2) |

[a] Superscripts indicate atoms in the disordered *tert*-butyl groups with partial occupancies: $a = 0.510$, $b = 0.490$, $c = 0.875$, $d = 0.125$.
[b] $U_{iso}$.

associated with the OH at a slightly lower frequency. The asymmetric and symmetric $\upsilon$(C−O) stretches were observed in the region 1108−1018 cm$^{-1}$. The $\upsilon$(C$\overset{\dots}{=}$O) and $\upsilon$(C$\overset{\dots}{=}$C) absorption frequencies corresponding to the β-diketonate ligand, tmhd$^-$, were observed in the region 1595−1504 cm$^{-1}$ and are tentatively assigned.

Multinuclear NMR spectroscopy ($^1$H and $^{13}$C{$^1$H}) studies for complexes **1**−**9** were recorded; the $^1$H NMR data are detailed in Table 6, and the $^{13}$C{$^1$H} NMR signals are summarized in Table 7. Compounds **1** and **3** reveal only one tmhd and one alkoxide environment, in support of our solid state studies. Similarly, complexes **4**, **5**, **8**, and **9** show only one, each broad time-averaged alkoxide and tmhd signal, suggesting that these molecules are fluxional in solution at room temperature on the NMR time scale. Compound **2**, however, shows at least three β-diketonate environments at room temperature, whereas a high-temperature study (20−70 °C; see Figure 1) shows a steady progression toward one time-averaged tmhd and alkoxide environment each. The $^{13}$C{$^1$H} NMR spectra of the strontium compounds **6** and **7** also reveal three and two distinct tmhd

**Scheme 1.** Reaction conditions for the synthesis of complexes **1**–**9**.



**Conditions** : (i) n-hexane, R. T., 10 min. and M = Ca, x = 1, n = 4, **1**; M = Sr, x = 0.66, **2**; or M = Ba, $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$, **3**

(ii) Toluene and One equiv. of the respective alcohol at R. T.

**Table 5.** Selected IR Data for Complexes **1**–**9**, $cm^{-1}$

| complex | no. | $\upsilon$(O–H)[a] | $\upsilon$(C–H)[a] | $\upsilon$(C=O)[b] | $\upsilon$(C=O)[b] | $\delta$(C–H)[a] | $\upsilon$(C–O)[b] |
|---|---|---|---|---|---|---|---|
| $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ | **1** | 3300 | 2957, 2929, 2903, 2867 | 1593, 1580 | 1536, 1505 | 1452, 1418, 1390, 1359 | 1102, 1053 |
| $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ | **2** | 3385 | 2962, 2924, 2870 | 1593, 1579 | 1536, 1504 | 1452, 1416, 1388, 1359 | 1108, 1082, 1054 |
| $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ | **3** | 3341 | 2963, 2903, 2867 | 1591, 1575 | 1536, 1504 | 1451, 1417, 1389, 1360 | 1093, 1020 |
| $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ | **4** |  | 2951, 2901, 2865, 2833 | 1592, 1578, 1565 | 1537, 1548, 1506 | 1487, 1454, 1414, 1358 | 1102, 1084, 1044, 1020 |
| $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ | **5** |  | 2950, 2927, 2904, 2869 | 1592, 1579 | 1537, 1506 | 1493, 1462, 1418, 1379 | 1097, 1050 |
| $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$ | **6** |  | 2955, 2861, 2825 | 1591, 1578 | 1534, 1504 | 1455, 1418, 1388, 1359 | 1095, 1073, 1044, 1031 |
| $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **7** | 3158 | 2961, 2863, 2828 | 1595, 1579 | 1536, 1504 | 1449, 1419, 1389, 1359 | 1098, 1076, 1068, 1018 |
| $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ | **8** | 3165 | 2967, 2868, 2810 | 1588, 1574 | 1532, 1503 | 1451, 1417, 1387, 1355 | 1097, 1057, 1024 |
| $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **9** | 3157 | 2960, 2900, 2866 | 1588, 1576 | 1536, 1504 | 1451, 1418, 1388, 1358 | 1068, 1057, 1023, 1019 |

[a] Hexachlorobutadiene mull. [b] Nujol mull.

**Table 6.** Selected $^1H$ NMR Signals for Complexes **1**–**9**, ppm[a]

| | | tmhd | | RO | | | | |
|---|---|---|---|---|---|---|---|---|
| complex | no. | *CH* | *CH*$_3$ | *CH* | *CH*$_2$ | *CH*$_3$ | *OH* | solvent |
| $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ | **1** | 5.88 (1 H) | 1.27 (18 H) |  | 3.90 (4 H) | 1.33 (6 H) | 5.36 (1 H) | $C_6D_6$ |
| $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ | **2** | 5.69 (1H)<br>1.20, 1.11 | 1.42, 1.27 (18 H) |  | 3.88 (3.3 H) | 1.26 (5 H) | 3.76 (0.66 H) | $C_6D_6$ |
| $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ | **3** | 5.79 (1.5 H) | 1.21 (27 H) |  | 3.85 (1.66 H) | 1.35 (2.5 H) | 3.52 (0.33 H) | $C_6D_6$ |
| $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ | **4** | 5.82 (1.5 H) | 1.26 (27 H) |  | 4.06 (1 H)<br>2.44 (1 H) | 2.21 (3 H) |  | $C_7D_8$ |
| $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ | **5** | 5.86 (1.5 H) | 1.22 (27 H) | 4.01 (0.5 H) | 3.58 (1 H)<br>4.49 (1 H) | 1.09 (3 H) |  | $C_7D_8$ |
| $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$ | **6** | 5.93 (1 H)<br>5.77 | 1.38, 1.16 (18 H)<br>1.08 |  | 3.87 (4 H)<br>3.34 | 2.18 (6 H)<br>2.45 |  | $C_6D_6$ |
| $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **7** | 5.95 (1.5 H)<br>5.72 | 1.37, 1.17 (27 H)<br>1.08 |  | 4.25 (2 H)<br>4.01 (2 H) | 3.34 (3 H) | not obsd | $C_6D_6$ |
| $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ | **8** | 5.79 (1.5 H) | 1.25 (27 H) | 4.02 (1 H) | 3.46 (4 H) | 1.09 (6 H) | not obsd | $C_6D_6$ |
| −70 °C |  | 5.87, 5.86, 5.82, 5.79 | 1.44, 1.43, 1.33 | *b* | *b* | 1.22, 1.16, 1.01, 0.92 | *b* | $C_7D_8$ |
| $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **9** | 5.77 (1.5 H) | 1.22 (27 H) |  | 3.87 (4 H)<br>3.34 | 3.19 (3 H) | 7.45 (0.5 H) | $C_6D_6$ |

[a] The numbers in the parentheses represent the integral values for that environment. All $^1H$ NMR spectra were run at 270 MHz and at room temperature unless stated otherwise. [b] A large number of peaks were observed in the range 3–4.5 ppm, but exact assignment was not possible (see Figure 2).

environments, respectively, at room temperature, indicative of a range of tmhd coordinating modes in the molecules.

Low-temperature $^1H$ and $^{13}C\{^1H\}$ NMR studies in $C_7D_8$ were carried out on complex **8** in an attempt to obtain some further structural information in solution. An $^1H$ study showed that as the temperature was lowered toward −70 °C, a number of environments could be observed for each of the original resonances (see Figure 2). At −70 °C, at least four tmhd environments were observed, but the alkoxyalkoxide/alcohol resonances had become very broad and complex. Similarly, $^{13}C\{^1H\}$ NMR at −70 °C exhibited five distinct $\beta$-diketonate and three alkoxyalkoxide/alcohol environments. From these results it may be noted that at room temperature we are observing a highly fluxional system, whereas at low temperature

**Table 7.** $^{13}C\{^1H\}$ NMR Signals for Complexes **1**–**9**, ppm[a]

| | | tmhd | | | | RO | | | |
|---|---|---|---|---|---|---|---|---|---|
| complex | no. | *C*O | *C*H | *C*(CH$_3$)$_3$ | *C*H$_3$ | *C*H | *C*H$_2$ | *C*H$_3$ | solvent |
| $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ | **1** | 200.2 | 90.2 | 41.2 | 29.0 | | 58.6 | 19.5 | $C_6D_6$ |
| $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ | **2** | 199.4 | 90.0 | 40.7 | 28.5 | | 57.9 | 20.0 | $C_6D_6$ |
| $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ | **3** | 199.7 | 90.0 | 41.0 | 28.6 | | 57.4 | 19.5 | $C_6D_6$ |
| $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ | **4** | 198.9 | 89.0 | 40.7 | 28.6 | | 63.6, 58.9 | 44.5 | $C_7D_8$ |
| $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ | **5** | 200.1 | 88.9 | 40.7 | 28.6 | 69.9 | 72.6, 61.8 | 20.6 | $C_7D_8$ |
| $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$ | **6** | 200.5, 198.1, 197.0 | 90.1, 89.5, 87.8 | 41.2, 40.8, 40.7 | 28.9, 28.7, 28.5 | | 64.9, 60.4 | 45.2, 43.2 | $C_6D_6$ |
| $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **7** | 200.8, 197.9 | 90.1, 87.7 | 41.1, 40.3 | 29.0, 28.4 | | 78.6, 61.4 | 58.0 | $C_6D_6$ |
| $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ | **8** | 198.5 | 89.0 | 40.9 | 28.7 | 70.7 | 72.5, 61.3 | 21.4 | $C_6D_6$ |
| −70 °C | | 202.2, 200.9, 197.3, 196.0 | 90.6, 89.0, 87.9 | 41.8, 41.6, 41.4, 40.9 | 29.5, 28.8 | n/a | 72.5, 72.0, 61.4, 60.8 | 22.7 | $C_7D_8$ |
| $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **9** | 198.2 | 88.8 | 40.8 | 28.7 | | 74.9, 60.8 | 58.1 | $C_6D_6$ |

[a] All $^{13}C\{^1H\}$ NMR spectra were run at 67.94 MHz and at room temperature unless otherwise stated.

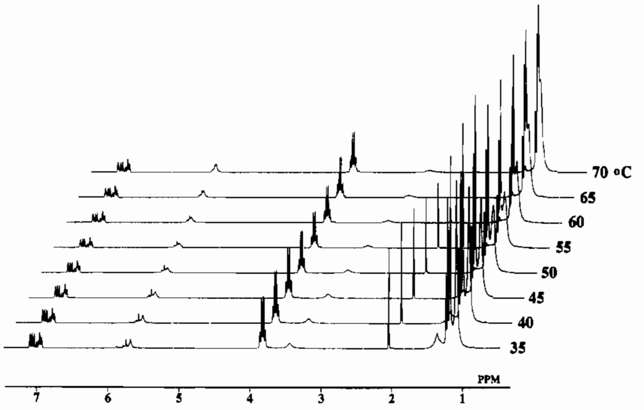


**Figure 1.** VT $^1H$ NMR study of $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ (**2**) in $C_6D_6$.

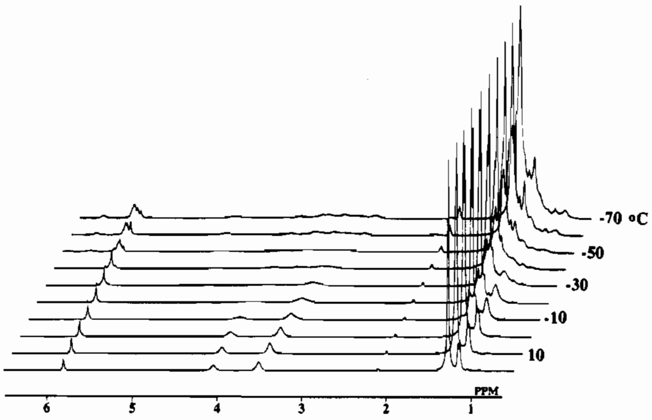


**Figure 2.** VT $^1H$ NMR study of $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ (**8**) in $C_7D_8$.

this fluxionality is eliminated; these data are in support of a tetrameric composition for **8** in solution, similar to that isolated in the solid state.

Electron impact mass spectrometry studies were performed for complexes **1**–**9**, and the major ions observed are shown in Table 8. Complexes **1**, **4**–**7**, and **9** exhibited ions of tetrameric composition and subsequently a distinct pattern of decomposition to their monomeric fragments $[M(tmhd)(OR)]^+$ was observed. Similar fragmentation pathways were also observed for complexes **2**, **3**, and **8**, but from a trimeric configuration in the gas phase. Other researchers have also observed in their mass spectra high-mass molecular ions.[32]

The thermogravimetric analysis plots for complexes **1**–**3** show initial loss of coordinated ethanol molecules, followed by the loss of tmhd$^-$ and ethyl groups to yield the corresponding metal oxide. Complexes **1** and **2** do not exhibit true melting point behavior, while compound **3** shows a sharp endothermic peak (226.4 °C, −2.90 mcal/mg) in the DSC plot indicative of the melting process.

Similarly, the TGA studies of complexes **4**–**9** show decomposition to metal oxide powders (by calculation only), with poor sublimation properties. The DSC-derived melting points of the compounds are recorded in the Experimental Section, along with the heats of decomposition.

**X-ray Structures of 1, 4, and 8.** In an effort to obtain more detailed structural information on these complexes, single-crystal X-ray structures were determined for compounds **1**, **4**, **and 8**. Selected interatomic distances and angles for these compounds are presented in Tables 9–11, respectively.

The structure of $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ **1** is shown in Figure 3. It consists of a distorted array of four calcium and four ethoxy oxygen atoms. The Ca–Ca distances span the range 3.507(6)–3.640(6) Å, average of 3.552 Å. This type of metal–oxygen cubane structural motif has been observed quite extensively for other metal alkoxides, e.g. $[M(OBu^t)]_4$ (M = K, Rb),[33] $[CpMgOEt]_4$,[34] and more recently $[Ba_4(OBu^t)_8(Bu^tOH)_{16}]$,[35] although we note that this is the first observation for an alkoxide of calcium. Interestingly, **1** may be viewed as a structural precursor of the recently reported $[Ca_6(O)_2(OEt)_8(EtOH)_{14}]$,[6] which has a bis(cubane) structure.

All four calcium atoms of **1** have very similar six-coordinate distorted octahedral geometry, comprising a chelating tmhd ligand, a terminal ethanol, and bonding interactions with three $\mu_3$-ethoxide groups. Similar distorted octahedral geometry has been previously observed around calcium atoms in the related trimeric complex $[Ca_3(tmhd)_6]$.[15]

The Ca–O bond distances fall into three distinct groups. First, in the cubane building block with the vertices occupied by the oxygen atoms of the four $\mu_3$-capping ethoxide groups, the Ca–O distances span the range 2.328(6) [O(12)–Ca(1)] to 2.364(6) Å [O(12)–Ca(4)] with an average Ca–O$_{(OEt)}$ distance of 2.347 Å. The cube in **1** is distorted in such a manner that all the O–Ca–O angles are acute [78.0(2)–82.6(2)°] and the Ca–O–Ca angles obtuse [96.1(2)–101.8(2)°].

The second set of Ca–O bond distances which involve the four neutral ethanol molecules bonded terminally to the calcium atoms range from 2.390(7) to 2.411(7) Å (an average Ca–O$_{(EtOH)}$ distance of 2.404 Å). These distances are about 0.05 Å

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(32) Purdy, A. P.; Berry, A. D.; Holm, R. T.; Fatemi, M.; Gaskill, D. K. *Inorg. Chem.* **1989**, *28*, 2799.

(33) Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 337.

(34) Lehmkuhl, H.; Mehler, K.; Benn, R.; Rufinska, A.; Krüger, C. *Chem. Ber.* **1986**, *119*, 1054.

(35) Borup, B.; Samuels, J. A.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 994.

**Table 8.** Electron Impact Mass Spectrometry Data for Complexes **1**−**9**, $m/z^+$ (amu)

| complex | no. | $[M(tmhd)(OR)]^+$ | $[M_2(tmhd)_x(OR)_{3-x}]^+$ | $[M_3(tmhd)_x(OR)_{5-x}]^+$ | $[M_4(tmhd)_x(OR)_{7-x}]^+$ |
|---|---|---|---|---|---|
| $[Ca_4(tmhd)_4(OEt)_4(EtOH)_4]$ | **1** | 268 | 491 (2) | 759 (3) | |
| $[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$ | **2** | | 587 (2) | 1041 (4) | |
| $[Ba(tmhd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ | **3** | | 829 (3) | 1331 (5) | |
| $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ | **4** | | 439 (1), 534 (2) | 750 (2), 845 (3) | 1061 (3), 1156 (4) |
| $[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$ | **5** | 311 | 535 (2) | 846 (3) | |
| $[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$ | **6** | 359 | 630 (2) | 794 (1), 893 (2), 989 (3), 1084 (4) | 1253 (3), 1348 (4 |
| $[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **7** | 346, 448 | 509 (1), 615 (2), 725 (3) | 959 (3), 1067 (4) | 1413 (5), 1521 (6 |
| $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ | **8** | | 743 (2) | 1249 (4) | |
| $[H_{0.5}Ba(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$ | **9** | | | 1008 (2), 1112 (3), 1221 (4) | 1508 (4), 1617 (5), 1724 (6) |

[a] Number in parentheses denotes value of $x$. All listed peaks correspond to molecular fragments.

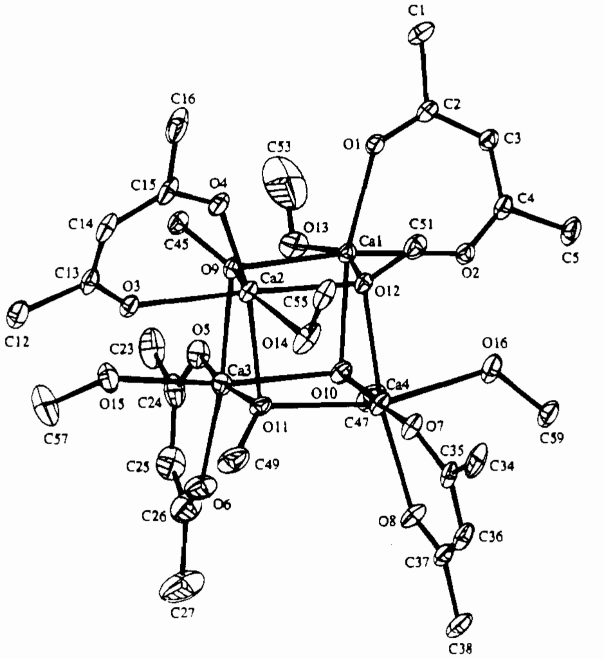

**Figure 3.** Molecular structure of $[Ca_4(tmhd)_4(\mu_3\text{-}OEt)_4(EtOH)_4]$ (**1**) showing the atom-numbering scheme. The $CH_3$ fragments of the terminal EtOH molecules and methyls of the *tert*-butyl groups on the β-diketonates are omitted for clarity.

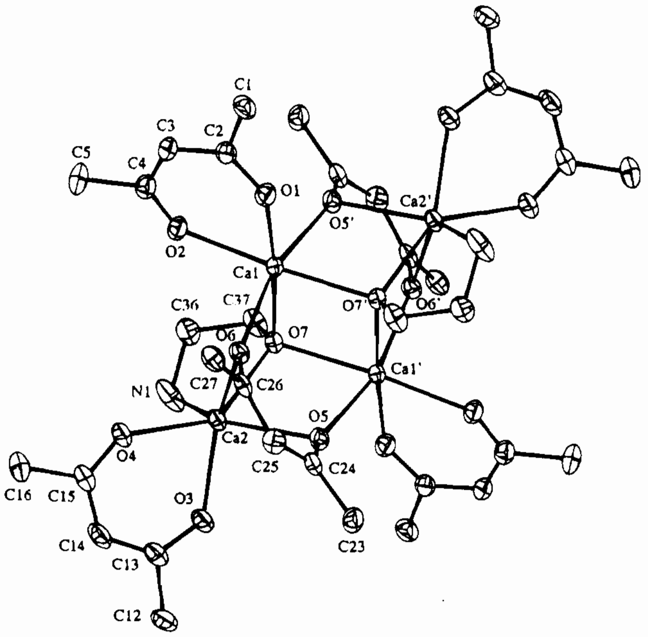

**Figure 4.** Molecular structure of $[Ca_4(tmhd)_6(OCH_2CH_2NMe_2)_2]$ (**4**) showing the atom-numbering scheme. The *tert*-butyl methyl groups on the β-diketonates are omitted for clarity.

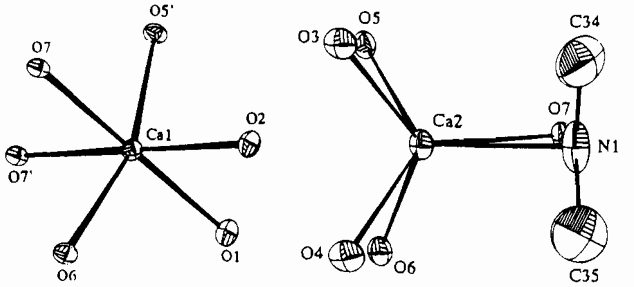

**Figure 5.** Illustration of the coordination geometry around the two unique Ca atoms in **4**.

longer than the $Ca-O_{(EtO)}$ distances. The $Ca-O_{(OEt/EtOH)}$ bond lengths are comparable with those in the recently reported aggregate $[Ca_6(O)_2(OEt)_8(EtOH)_{14}]$.[6] Similar differences in the metal−oxygen lengths involving $\mu_3$-capping alkoxide groups and either bridging or terminally bound alcohol ligands have also been observed in the giant aggregate $[Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2]$.[36]

The third set of Ca−O bond distances are for the β-diketonate (tmhd) ligands which are bonded in an asymmetric chelating manner. The Ca−O bond distances in this group lie in the range 2.266(6)− 2.359(6) Å, with an average bond length of 2.310(7) Å. This distance is markedly shorter than the corresponding average values in the recently reported trimeric complex $[Ca_3(tmhd)_6]$, 2.35(5) Å,[15] and in the complexes $[Ca_4(dppd)_8(EtOH)_2]$, 2.37 Å,[37] $[Ca(pd)_2(H_2O)_2]\cdot H_2O$, 2.33 Å,[38] and $[Ca_2(hfpd)_4(H_2O)_4]$, 2.44 Å.[12] The chelate bonds are all asymmetric, as shown by the difference of 0.05−0.09 Å in a given pair of Ca−O bonds involving each tmhd ligand.

The structure of compound **4** is shown in Figure 4. It is composed of two $\{Ca_2(tmhd)_3(Me_2NCH_2CH_2O)\}$ units related by a center of symmetry and bridged by the two (dimethylamino)ethoxy and two tmhd ligands. The overall structure is based on a $Ca_4O_4$ ladder-like building block consisting of steps defined by Ca(2)−O(5)−Ca(1′)−O(7) and Ca(1)−O(7′)−Ca(2′)−O(5′) and the riser defined by Ca(1)−O(7′)−Ca(1′)−O(7). An alternative description of the ladder with the same riser would have steps Ca(2)−O(6)−Ca(1′)−O(7) and Ca(1′)−O(7)−Ca(2′)−O(6′).

The structure is remarkable and has several very interesting features. Thus the two unique metal centers in the tetramer are both six-coordinate, but surprisingly their coordination geometries are different, as seen from Figure 5. Ca(1) has a distorted octahedral geometry, with the *cis* and *trans* angles varying from 76.96 to 106.62° and from 162.46 to 174.84°, respectively. The coordination sphere of this atom is made up

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(36) Goel, S. C.; Matchett, M. A.; Chiang, M. Y.; Buhro, W. E. *J. Am. Chem. Soc.* **1991**, *113*, 1844.

(37) Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Acta Cryst.* **1973**, *B29*, 1295.

(38) Sahbari, J. J.; Olmstead, M. M. *Acta Crystallogr.* **1983**, *C39*, 208.

**Table 9.** Selected Interatomic Distances (Å) and Angles (deg) for [Ca$_4$(thmd)$_4$(OEt)$_4$(EtOH)$_4$] (**1**)

| | | | |
|---|---|---|---|
| Ca(2)···Ca(1) | 3.640(6) | Ca(3)···Ca(1) | 3.512(6) |
| Ca(4)···Ca(1) | 3.507(6) | Ca(3)···Ca(2) | 3.534(6) |
| Ca(4)···Ca(2) | 3.519(6) | Ca(4)···Ca(3) | 3.600(6) |
| Ca(1)−O(1) | 2.266(6) | Ca(1)−O(2) | 2.357(7) |
| Ca(1)−O(9) | 2.356(6) | Ca(1)−O(10) | 2.338(6) |
| Ca(1)−O(12) | 2.328(6) | Ca(1)−O(13) | 2.390(7) |
| Ca(2)−O(3) | 2.359(6) | Ca(2)−O(4) | 2.271(7) |
| Ca(2)−O(9) | 2.336(6) | Ca(2)−O(11) | 2.348(6) |
| Ca(2)−O(12) | 2.362(6) | Ca(2)−O(14) | 2.407(7) |
| Ca(3)−O(5) | 2.338(7) | Ca(3)−O(6) | 2.267(7) |
| Ca(3)−O(9) | 2.367(6) | Ca(3)−O(10) | 2.337(6) |
| Ca(3)−O(11) | 2.341(6) | Ca(3)−O(15) | 2.411(7) |
| Ca(4)−O(7) | 2.350(7) | Ca(4)−O(8) | 2.268(7) |
| Ca(4)−O(10) | 2.348(6) | Ca(4)−O(11) | 2.338(7) |
| Ca(4)−O(12) | 2.364(6) | Ca(4)−O(16) | 2.407(7) |

| | | | |
|---|---|---|---|
| O(2)−Ca(1)−O(1) | 75.7(3) | O(9)−Ca(1)−O(1) | 111.6(3) |
| O(9)−Ca(1)−O(2) | 170.8(2) | O(10)−Ca(1)−O(1) | 165.0(2) |
| O(10)−Ca(1)−O(2) | 91.1(3) | O(10)−Ca(1)−O(9) | 82.2(2) |
| O(12)−Ca(1)−O(1) | 105.3(2) | O(12)−Ca(1)−O(2) | 94.6(3) |
| O(12)−Ca(1)−O(9) | 78.3(2) | O(12)−Ca(1)−O(10) | 82.6(2) |
| O(13)−Ca(1)−O(1) | 89.7(3) | O(13)−Ca(1)−O(2) | 102.5(3) |
| O(13)−Ca(1)−O(9) | 83.4(3) | O(13)−Ca(1)−O(10) | 86.1(3) |
| O(13)−Ca(1)−O(12) | 159.6(1) | O(4)−Ca(2)−O(3) | 75.3(2) |
| O(9)−Ca(2)−O(3) | 93.6(3) | O(13)−Ca(2)−O(4) | 112.2(3) |
| O(11)−Ca(2)−O(3) | 92.3(2) | O(11)−Ca(2)−O(4) | 161.7(2) |
| O(11)−Ca(2)−O(9) | 81.6(2) | O(12)−Ca(2)−O(3) | 170.4(1) |
| O(12)−Ca(2)−O(4) | 112.0(2) | O(12)−Ca(2)−O(9) | 78.0(2) |
| O(12)−Ca(2)−O(11) | 81.9(2) | O(14)−Ca(2)−O(3) | 105.3(3) |
| O(14)−Ca(2)−O(4) | 86.4(3) | O(14)−Ca(2)−O(9) | 156.5(2) |
| O(14)−Ca(2)−O(11) | 83.9(3) | O(14)−Ca(2)−O(12) | 81.8(3) |
| O(10)−Ca(3)−O(9) | 82.0(2) | O(11)−Ca(3)−O(9) | 81.1(2) |
| O(11)−Ca(3)−O(10) | 79.4(2) | O(5)−Ca(3)−O(9) | 95.3(3) |
| O(5)−Ca(3)−O(10) | 92.7(3) | O(5)−Ca(3)−O(11) | 171.7(2) |
| O(6)−Ca(3)−O(9) | 170.6(2) | O(6)−Ca(3)−O(10) | 102.2(3) |
| O(6)−Ca(3)−O(11) | 107.8(3) | O(6)−Ca(3)−O(5) | 76.3(3) |
| O(15)−Ca(3)−O(9) | 84.6(3) | O(15)−Ca(3)−O(10) | 160.8(1) |
| O(15)−Ca(3)−O(11) | 84.9(3) | O(15)−Ca31)−O(5) | 102.3(3) |
| O(15)−Ca(3)−O(6) | 93.1(3) | O(11)−Ca(4)−O(10) | 79.2(3) |
| O(12)−Ca(4)−O(10) | 81.7(2) | O(12)−Ca(4)−O(11) | 82.1(2) |
| O(7)−Ca(4)−O(10) | 174.3(2) | O(7)−Ca(4)−O(11) | 97.0(3) |
| O(7)−Ca(4)−O(12) | 93.6(2) | O(8)−Ca(4)−O(10) | 109.6(3) |
| O(8)−Ca(4)−O(11) | 104.9(3) | O(8)−Ca(4)−O(12) | 167.5(2) |
| O(8)−Ca(4)−O(7) | 75.4(3) | O(16)−Ca(4)−O(10) | 84.8(3) |
| O(16)−Ca(4)−O(11) | 160.4(2) | O(16)−Ca(4)−O(12) | 84.4(3) |
| O(16)−Ca(4)−O(7) | 98.1(3) | O(16)−Ca(4)−O(8) | 91.1(3) |
| Ca(2)−O(9)−Ca(1) | 101.7(3) | Ca(3)−O(9)−Ca(1) | 96.1(3) |
| Ca(3)−O(9)−Ca(2) | 97.4(3) | Ca(3)−O(10)−Ca(1) | 97.4(3) |
| Ca(4)−O(10)−Ca(1) | 96.9(2) | Ca(4)−O(10)−Ca(3) | 100.4(2) |
| Ca(3)−O(11)−Ca(1) | 97.8(3) | Ca(4)−O(11)−Ca(2) | 97.3(2) |
| Ca(4)−O(11)−Ca(3) | 100.6(3) | Ca(2)−O12)−Ca(1) | 101.8(3) |
| Ca(4)−O(12)−Ca(1) | 96.7(2) | Ca(4)−O(12)−Ca(2) | 96.3(2) |
| C(2)−O(1)−Ca(1) | 135.6(4) | C(4)−O(2)−Ca(1) | 130.5(5) |
| C(13)−O(3)−Ca(2) | 131.2(3) | C(15)−O(4)−Ca(2) | 134.4(4) |
| C(24)−O(5)−Ca(3) | 131.7(5) | C(26)−O(6)−Ca(3) | 136.1(6) |
| C(35)−O(7)−Ca(4) | 130.7(4) | C(37)−O(8)−Ca(4) | 135.8(4) |
| C(45)−O(9)−Ca(1) | 122.1(4) | C(45)−O(9)−Ca(2) | 117.5(5) |
| C(45)−O(9)−Ca(3) | 117.3(4) | C(47)−O(10)−Ca(1) | 114.9(5) |
| C(47)−O(10)−Ca(3) | 118.2(5) | C(14)−O(10)−Ca(4) | 124.0(6) |
| C(49)−O(11)−Ca(2) | 116.7(5) | C(49)−O(11)−Ca(3) | 122.4(5) |
| C(49)−O(11)−Ca(4) | 117.4(6) | C(51)−O(12)−Ca(1) | 115.6(5) |
| C(51)−O(12)−Ca(2) | 122.5(5) | C(51)−O(12)−Ca(4) | 119.2(5) |
| C(53)−O(13)−Ca(1) | 127.9(6) | C(55)−O(14)−Ca(2) | 123.8(7) |
| C(55′)−O(14)−Ca(2) | 120.1(9) | C(57)−O(15)−Ca(3) | 129.0(6) |
| C(59)−O(16)−Ca(4) | 125.6(7) | C(59′)−O(16)−Ca(4) | 120.1(8) |

**Table 10.** Selected Interatomic Distances (Å) and Angles (deg) for [Ca$_4$(tmhd)$_6$(Me$_2$NCH$_2$CH$_2$O)$_2$] (**4**)[a]

| | | | |
|---|---|---|---|
| Ca(1)···Ca(1′) | 3.477(1) | Ca(1)···Ca(2′) | 3.665(1) |
| Ca(1)···Ca(2) | 3.672(1) | Ca(1)−O(1) | 2.259(2) |
| Ca(1)−O(2) | 2.283(2) | Ca(1)−O(5′) | 2.358(2) |
| Ca(1)−O(6) | 2.359(2) | Ca(1)−O(7) | 2.357(2) |
| Ca(1)−O(7′) | 2.361(2) | Ca(2)−O(3) | 2.279(2) |
| Ca(2)−O(4) | 2.270(2) | Ca(2)−O(5) | 2.379(2) |
| Ca(2)−O(6) | 2.399(2) | Ca(2)−O(7) | 2.346(2) |
| Ca(2)−N(1) | 2.518(3) | | |

| | | | |
|---|---|---|---|
| O(1)−Ca(1)−O(2) | 77.45(7) | O(1)−Ca(1)−O(7) | 174.84(7) |
| O(2)−Ca(1)−O(7) | 98.22(7) | O(1)−Ca(1)−O(5′) | 92.90(7) |
| O(2)−Ca(1)−O(5′) | 100.62(7) | O(7)−Ca(1)−O(5′) | 90.65(7) |
| O(1)−Ca(1)−O(6) | 100.30(7) | O(2)−Ca(1)−O(6) | 93.53(7) |
| O(7)−Ca(1)−O(6) | 77.01(6) | O(5′)−Ca(1)−O(6) | 162.46(7) |
| O(1)−Ca(1)−O(7′) | 99.38(7) | O(2)−Ca(1)−O(7′) | 175.99(6) |
| O(7)−Ca(1)−O(7′) | 85.07(6) | O(5′)−Ca(1)−O(7′) | 76.96(6) |
| O(6)−Ca(1)−O(7′) | 89.45(7) | O(4)−Ca(2)−O(3) | 77.38(8) |
| O(4)−Ca(2)−O(7) | 138.95(7) | O(3)−Ca(2)−O(7) | 137.03(7) |
| O(4)−Ca(2)−O(5) | 134.02(7) | O(3)−Ca(2)−O(5) | 90.97(7) |
| O(7)−Ca(2)−O(5) | 76.84(6) | O(4)−Ca(2)−O(6) | 88.89(7) |
| O(3)−Ca(2)−O(6) | 138.09(7) | O(7)−Ca(2)−O(6) | 76.43(6) |
| O(5)−Ca(2)−O(6) | 70.54(6) | O(4)−Ca(2)−N(1)) | 90.45(9) |
| O(3)−Ca(2)−N(1) | 91.02(8) | O(7)−Ca(2)−N(1) | 71.24(7) |
| O(5)−Ca(2)−N(1) | 134.62(9) | O(6)−Ca(2)−N(1) | 128.97(8) |
| C(2)−O(1)−Ca(1) | 133.4(2) | C(4)−O(2)−Ca(1) | 133.1(2) |
| C(13)−O(3)−Ca(2) | 132.7(2) | C(15)−O(4)−Ca(2) | 133.6(2) |
| C(24)−O(5)−Ca(1′) | 148.2(2) | C(24)−O(5)−Ca(2) | 105.6(2) |
| Ca(1′)−O(5)−Ca(2) | 101.39(7) | C(26)−O(6)−Ca(1) | 146.9(2) |
| C(26)−O(6)−Ca(2) | 107.3(2) | Ca(1)−O(6)−Ca(2) | 101.01(7) |
| C(37)−O(7)−Ca(2) | 117.3(2) | C(37)−O(7)−Ca(1) | 115.9(2) |
| Ca(2)−O(7)−Ca(1) | 102.65(7) | C(37)−O(7)−Ca(1′) | 120.2(2) |
| Ca(2)−O(7)−Ca(1′) | 102.27(7) | Ca(1)−O(7)−Ca(1′) | 94.93(6) |
| C(36)−N(1)−Ca(2) | 105.8(2) | | |

[a] The primed atoms are generated from the unprimed ones by the symmetry operation 1 − x, 1 − y, −z.

of a terminally chelating tmhd ligand [O(1) and O(2)] and interactions with two $\mu_2-\mu_2$ tmhd ligands [O(5′) and O(6)] and two $\mu_3$-OCH$_2$CH$_2$NMe$_2$ ligands [O(7) and O(7′)]. In contrast, Ca(2) has a distorted trigonal prismatic geometry, with bonds to a terminally chelating tmhd ligand and interactions with two $\mu_2-\mu_2$ tmhd ligands [O(5) and O(6′)] and a chelating $\mu_3$-OCH$_2$CH$_2$NMe$_2$ ligand [N(1) and O(7)]. The two trigonal faces of the prism are defined by the atoms O(3), O(4), N(1) and O(5), O(6), O(7), from which the distances of the metal atom are 1.440 and 1.690 Å, respectively. The dihedral angle between the two triangles is 10.1°. Two sides of the triangle containing the nitrogen atom are significantly longer than others (3.403, 3.426 *vs* 2.759, 2.936 Å), which appears to be caused by the interligand interactions between the *N*-methyl groups and the diketone oxygens [C(34)···O(3) = 3.308 and C(35)···O(4) = 3.252 Å]. The distances along the intersecting edges of the three rectangular faces are also different [O(3)···O(5) = 3.222; O(4)···O(6) = 3.270; N(1)···O(7) = 2.837 Å] and seem to be determined by the interligand interactions between the two tmhd ligands bonded to Ca(2), one of which also forms bridges with two other Ca atoms and consequently suffers from considerable strain, and the bite angles associated with the particular ligands. The dihedral angles involving the planes Ca(2)N(1)O(7) (A), Ca(2)O(3)O(5) (B), and Ca(2)O(4)O(6) (C) are 123.6 (A and B), 119.8 (A and C), and 116.4° (B and C), which deviate from an ideal situation of 120.0° and are indicative of the distortions in the trigonal prism.

The Ca−O bond distances again fall into several defined groups. The Ca−O distances involving the $\mu_2-\mu_2$ tmhd ligands span the range 2.356(2)−2.397(2) Å, an average of 2.373 Å. The second group of Ca−O bond distances involve the tmhd ligands bound in a pure chelating manner and lie in the range 2.254(2)−2.282(2) Å, an average of 2.270 Å. These distances are significantly shorter than those in the bridging tmhd ligands and also those in **1**. The most probable reasons for the shortening is that these ligands lie on the edge of the ladder-like structure and appear to have less steric hindrance from neighboring ligands.

The Ca−O distances involving the $\mu_3$-oxygen lie in the range 2.347(2)−2.362(2) Å, an average of 2.354 Å. These distances are slightly smaller than the Ca−O distances involving the $\mu_2$-

**Table 11.** Selected Interatomic Distances (Å) and Angles (deg) for $[Ba_4(tmhd)_6(C_5H_{11}O_2)_2(C_5H_{12}O_2)_2]$ (**8**)[a]

| | | | |
|---|---|---|---|
| Ba(1)···Ba(2) | 4.142(1) | Ba(1)···Ba(2′)* | 4.393(1) |
| Ba(2)···Ba(2′) | 3.845(1) | Ba(1)−O(1) | 2.812(3) |
| Ba(1)−O(2) | 2.879(4) | Ba(1)−O(3) | 2.638(3) |
| Ba(1)−O(4) | 2.612(4) | Ba(1)−O(7) | 2.610(3) |
| Ba(1)−O(8) | 3.358(4) | Ba(1)−O(9) | 2.784(4) |
| Ba(1)−O(10) | 2.910(3) | Ba(2)−O(1) | 2.731(3) |
| Ba(2)−O(2′) | 2.776(3) | Ba(2)−O(2) | 3.378(3) |
| Ba(2)−O(5) | 2.688(3) | Ba(2)−O(6) | 2.670(3) |
| Ba(2)−O(7′) | 2.660(3) | Ba(2)−O(7) | 2.721(3) |
| Ba(2)−O(8) | 3.024(4) | Ba(2)−O(9′) | 3.457(3) |

| | | | |
|---|---|---|---|
| O(7)−Ba(1)−O(4) | 100.7(1) | O(7)−Ba(1)−O(3) | 139.1(1) |
| O(4)−Ba(1)−O(3) | 64.7(1) | O(7)−Ba(1)−O(9) | 69.7(1) |
| O(4)−Ba(1)−O(9) | 82.8(1) | O(3)−Ba(1)−O(9) | 138.1(1) |
| O(7)−Ba(1)−O(41 | 80.8(1) | O(4)−Ba(1)−O(1) | 138.2(1) |
| O(3)−Ba(1)−O(1) | 86.7(1) | O(9)−Ba(1)−O(1) | 134.2(1) |
| O(7)−Ba(1)−O(2) | 64.1(1) | O(4)−Ba(1)−O(2) | 156.8(1) |
| O(3)−Ba(1)−O(2) | 138.3(1) | O(9)−Ba(1)−O(2) | 75.6(1) |
| O(1)−Ba(1)−O(2) | 59.9(1) | O(7)−Ba(1)−O(10) | 127.7(1) |
| O(4)−Ba(1)−O(10) | 79.8(1) | O(3)−Ba(1)−O(10) | 88.9(1) |
| O(9)−Ba(1)−O(10) | 58.4(1) | O(1)−Ba(1)−O(10) | 132.1(1) |
| O(2)−Ba(1)−O(10) | 95.7(1) | O(1)−Ba(1)−O(8) | 66.5(1) |
| O(3)−Ba(1)−O(8) | 87.4(1) | O(4)−Ba(1)−O(8) | 81.6(1) |
| O(7)−Ba(1)−O(8) | 51.9(1) | O(1)−Ba(2)−O(2) | 54.2(1) |
| O(2′)−Ba(2)−O(2) | 156.5(1) | O(7)−Ba(2)−O(2) | 56.0(1) |
| O(1)−Ba(2)−O(7) | 80.4(1) | O(8)−Ba(2)−O(2) | 96.3(1) |
| O(6)−Ba2)−O(2) | 168.2(1) | O(5)−Ba(2)−O(2) | 128.1(1) |
| O(5)−Ba(2)−O(9′) | 68.0(1) | O(6)−Ba(2)−O(9′) | 50.6(1) |
| O(2′)−Ba(2)−O(9′) | 66.7(1) | O(7′)−Ba(2)−O(9′) | 58.9(1) |
| O(7′)−Ba(2)−O(5) | 126.9(1) | O(6)−Ba(2)−O(5) | 63.5(1) |
| O(7′)−Ba(2)−O(7) | 69.5(1) | O(6)−Ba(2)−O(7) | 114.1(1) |
| O(5)−Ba(2)−O(7) | 160.0(1) | O(7′)−Ba(2)−O(1) | 141.8(1) |
| O(6)−Ba(2)−O(1) | 134.2(1) | O(5)−Ba(2)−O(1) | 88.2(1) |
| O(7)−Ba(2)−O(1) | 80.4(1) | O(7′)−Ba(2)−O(2′) | 64.9(1) |
| O(6)−Ba(2)−O(2′) | 117.2(1) | O(5)−Ba(2)−O(2′) | 96.6(1) |
| O(7)−Ba(2)−O(2′) | 101.5(1) | O(1)−Ba(2)−O(2′) | 100.2(1) |
| O(7′)−Ba(2)−O(8) | 106.5(1) | O(6)−Ba(2)−O(8) | 80.9(1) |
| O(5)−Ba(2)−O(8) | 105.3(1) | O(7)−Ba(2)−O(8) | 55.6(1) |
| O(1)−Ba(2)−O(8) | 72.6(1) | O(2′)−Ba(2)−O(8) | 156.5(1) |
| O(7′)−Ba(2)−O(6) | 81.0(1) | Ba(1)−O(1)−Ba(2) | 96.7(1) |
| Ba(1)−O(2)−Ba(2) | 82.5(1) | Ba(2′)−O(2)−Ba(1) | 101.9(1) |
| Ba(2′)−O(2)−Ba(2) | 76.6(1) | Ba(1)−O(7)−Ba(2′) | 112.9(1) |
| Ba(1)−O(7)−Ba(2) | 101.9(1) | Ba(2′)−O(7)−Ba(2) | 91.2(1) |
| Ba(1)−O(8)−Ba(2) | 80.8(1) | Ba(1)−O(9)−Ba(2′) | 88.8(1) |
| C(2)−O(1)−Ba(2) | 140.6(3) | C(2)−O(1)−Ba(1) | 99.3(3) |
| C(4)−O(2)−Ba(1) | 98.1(3) | C(4)−O(2)−Ba(2) | 125.1(1) |
| C(4)−O(2)−Ba(2′) | 152.4(3) | C(13)−O(3)−Ba(1) | 139.4(3) |
| C(15)−O(4)−Ba(1) | 140.7(3) | C(24)−O(5)−Ba(2) | 139.6(4) |
| C(26)−O(6)−Ba(2) | 137.6(3) | C(34)−O(7)−Ba(1) | 105.0(4) |
| C(34)−O(7)−Ba(2′) | 127.6(3) | C(34)−O(7)−Ba(2) | 115.2(3) |
| C(35)−O(8)−Ba(1) | 96.5(1) | C(36)−O(8)−Ba(1) | 129.9(1) |
| C(35)−O(8)−Ba(2) | 99.1(4) | C(36)−O(8)−Ba(2) | 126.4(3) |
| C(39)−O(9)−Ba(1) | 121.9(3) | C(39)−O(9)−Ba(2′) | 129.4(1) |
| C(39)−O(9)−Ba(1) | 121.9(3) | C(40)−O(10)−Ba(1) | 110.5(3) |
| C(41)−O(10)−Ba(1) | 123.0(3) | | |

[a] The primed atoms are generated from the unprimed ones by the symmetry operation $1 - x, y, 0.5 - z$.

oxygen (tmhd) but comparable with the $Ca-O_{(EtO)}$ distances found in **1**. The chelating and bridging tmhd ligands are all bonded to the calcium metals in a nearly symmetrical manner. Similarly, the $\mu_3$-oxygen atom of the $OCH_2CH_2NMe_2$ ligand is also nearly symmetrically bonded to the three metal atoms. The Ca−N distance is 2.519(3) Å, which is somewhat longer than would be expected on the basis of atomic radii sum (2.49 Å) and probably results from the steric requirements of the methyl groups on the nitrogen atom.

It may be noted here that, in the case of a six-coordinate metal, an octahedral geometry is more frequent than a trigonal prism and also it is very unusual to observe both types of geometry in the same complex. It appears that, in the present compound, a trigonal prismatic environment is favored around Ca(2) due to the fact that all three multidentate ligands (two tmhd and one $\mu_3$-$OCH_2CH_2NMe_2$) form chelate bonds to it. The situation is quite interesting since trigonal prismatic in preference to octahedral geometry has been reported almost exclusively for the tris(dithiolato) complexes of transition metals,[39−47] for a few tris(*o*-phenylenediamine) complexes of rhenium,[48] for $[Y(tmhd)_3]$ in both the gas and solid states,[49] and for the tris[(methylamino)pyridine] complex of indium.[50] Studies[41,51−55] carried out on these complexes on the basis of various geometrical and electronic factors have not been conclusive as to exactly what factors are responsible for the stability of prismatic geometry or deviations from it. The present compound seems to be not the first example of only a trigonal prismatic geometry involving an alkaline earth metal but also a rare case where this and the more common octahedral coordinations are observed together in the same species. Another unusual feature observed in the present compound is that each of the two chelating diketonate moieties occupy two corners of the *same* triangular face, which is in sharp contrast to the other trigonal prismatic complexes noted above,[39−50] where the three chelating ligands are always positioned along the vertical edges of the prism.

The structure of $[Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_2(HOCH_2CH_2OPr^i)_2]$ (**8**) is shown in Figure 6. It consists of two centrosymmetrically related $\{Ba_2(tmhd)_3(OCH_2CH_2OPr^i)(HOCH_2CH_2OPr^i)\}$ dimers bridged by two $\mu_3-\mu_2$ $OCH_2CH_2OPr^i$ and two $\mu_3-\mu_2$ tmhd ligands. It has several features in common with compound **4**, particularly in that the overall structure is again built up from a $Ba_4O_4$ ladder-like unit consisting of two steps defined by Ba(1)−O(1)−Ba(2)−O(7) and Ba(2′)−O(7′)−Ba(1′)−O(1′) and the riser defined by Ba(2′)−O(7)−Ba(2)−O(7′). The oxygen atoms involved in the ladder formation belong to the deprotonated $\mu_3-\mu_2$ alkoxy and $\mu_3-\mu_2$ tmhd ligands. The Ba(2)···Ba(2′), Ba(1)···Ba(2), and Ba(1)···Ba(2′) separations are 3.845(1), 4.142(1), and 4.393(1) Å, respectively. These distances are comparable with those in the recently characterized tmhd dimer $[Ba_2(tmhd)_4(NH_3)_4]$,[13] 3.83 Å, and tetramer $[Ba_4(tmhd)_8]$,[16] 4.10−4.21 Å, and also with those in barium siloxides,[25] 3.77−3.81 Å, and alkoxides,[8] all of which contain strongly bonded bridging ligands pulling the metal centers closer together. A larger Ba···Ba separation [5.130(2) Å] was observed in the loose dimer $[Ba(tmhd)_2(diglyme)]_2$, in

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(39) King, R. B. *Inorg. Chem.* **1963**, *2*, 641.
(40) Davidson, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *J. Am. Chem. Soc.* **1964**, *86*, 2799.
(41) Stiefel, E. I.; Eisenberg, R.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 2956.
(42) Davidson, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1965**, *4*, 55.
(43) Brown, G. F.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1970**, 729.
(44) Eisenberg, R.; Ibers, J. A. *J. Am. Chem. Soc.* **1965**, *87*, 3776.
(45) Hoskins, B. F.; Kelly, J. *J. Chem. Soc., Chem. Commun.* **1968**, 511.
(46) Gardner, J. K.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1978**, *17*, 897.
(47) Bennett, M. J.; Cowie, M.; Martin, J. L.; Takats, J. *J. Am. Chem. Soc.* **1973**, *95*, 7504.
(48) Danopoulas, A. A.; Wong, A. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain-Bates, B. *J. Chem. Soc., Dalton Trans.* **1990**, 315.
(49) (a) Shibata, S.; Iijima, K.; Inuzuka, T. *J. Mol. Struct*, **1986**, *144*, 181. (b) Gleizes, A.; Sans-Lenain, S.; Medus, D.; Hovnanian, N.; Miele, P.; Foulon, J-D. *Inorg. Chim. Acta* **1993**, *209*, 47.
(50) Hussain-Bates, B. Ph.D. Thesis, University of London, 1992; p 203.
(51) Stiefel, E. I.; Brown, G. F. *Inorg. Chem.* **1972**, *11*, 434.
(52) Hoffamn, R.; Howell, J. W.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.
(53) Baldas, J.; Boas, J. F.; Bonnyman, J.; Pilbrow, J. R.; Williams, A. *J. Am. Chem. Soc.* **1985**, *107*, 1886.
(54) Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1976**, *15*, (a) 1584; (b) 1595.
(55) Chiu, K. W.; Wong, W. K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 37.
(56) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A. *Inorg. Chem.* **1993**, *32*, 4653.

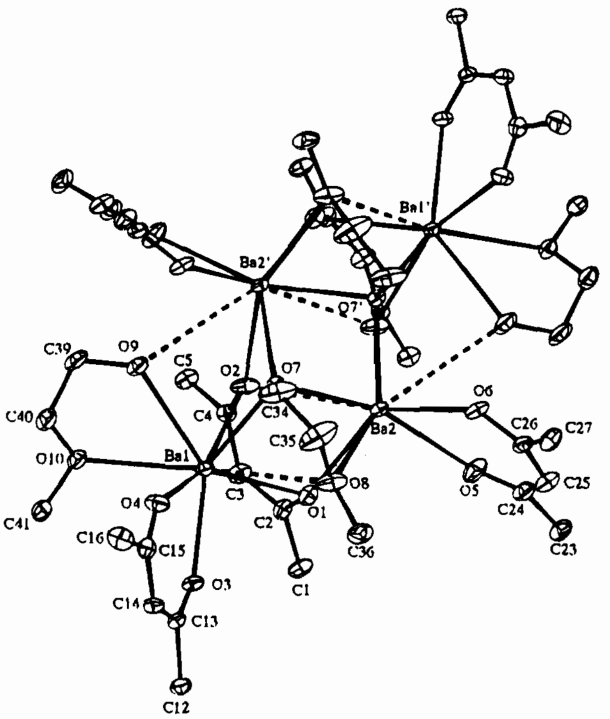

**Figure 6.** Molecular structure of $[H_2Ba_4(tmhd)_6(OCH_2CH_2OPr^i)_4]$ (**8**) showing the atom-numbering scheme. The *tert*-butyl methyl groups on the β-diketonates are omitted for clarity.

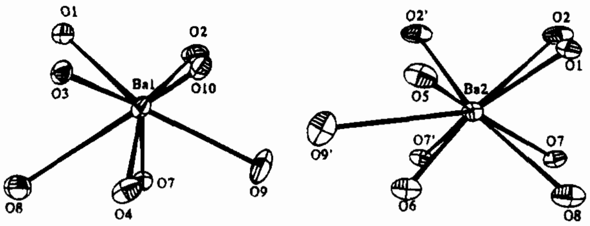

**Figure 7.** Illustration of the coordination geometry around the two unique Ba atoms in **8**.

which the $Ba-O_{(bridge)}$ bonds are fairly long, 3.173(6) Å, and involve only the weakly bound diglyme ligands.[56]

The coordination environments around the two unique Ba atoms in the structure are different and are more clearly illustrated in Figure 7. Ba(1) is eight-coordinate and has bonding interactions with one terminally chelating tmhd ligand [O(3) and O(4)], one $\mu_3-\mu_2$ tmhd ligand [O(1) and O(2)], one chelating $HOCH_2CH_2OPr^i$ ligand [O(9) and O(10)], and the deprotonated $\mu_3-\mu_2$ $OCH_2CH_2OPr^i$ ligand [O(7) and O(8)]. The geometry around this atom is best described as distorted bicapped trigonal prismatic with the O(1), O(2), O(7) and O(3), O(4), O(10) atoms defining the trigonal faces and the O(8) and O(9) atoms capping two rectangular faces. In contrast, Ba(2) is nine-coordinate and has a distorted monocapped square prismatic geometry with O(9′) as the capping atom. Ba(2) has bonding interactions with one terminally chelating tmhd ligand [O(5) and O(6)], two $\mu_3-\mu_2$ tmhd ligands [O(1), O(2), and O(2′)], two deprotonated $\mu_3-\mu_2$ $OCH_2CH_2OPr^i$ ligands [O(7), O(8, and O(7′)], and the $HOCH_2CH_2OPr^i$ ligand [O(9′)] chelated to Ba(1′).

The Ba−O distances involving the two unique metals in the aggregate show large variations, 2.612(4)−3.457(4) Å, which is not surprising since the tmhd, isopropoxyethoxy, and isopropoxyethanol ligands are all involved in different modes of linkages with the metals and the overall ladder-like structure is highly crowded with considerable interligand interactions. It is to be mentioned here that barium shows variable coordination numbers ranging from 6 to 10 and that the Ba−O distances also vary depending on the coordination number of the metal and the nature of the bonding ligands. It has been reported that the Ba−O distances lie in a relatively narrow range in mononuclear species such as $[Ba(hfpd)_2(tetraglyme)]$,[57] 2.68−2.89 Å, $[Ba(hfpd)_2(18\text{-crown-}6)]$,[18] 2.70−2.80 Å, $(enH_2)_{1.5}[Ba(hfpd)_5](C_2H_5OH)$,[10] 2.73−2.86 Å, $[Ba(tmhd)_2(CH_3OH)_2(H_2O)_2]$,[58] 2.72−2.78 Å, and $[Ba\{(OC_2H_4)N(C_2H_4OH)_2\}_2]_2(EtOH)_2$,[18] 2.73−2.78 Å, and also in several polynuclear complexes such as $[Ba_2(tmhd)_4(NH_3)_4]$,[13] 2.59−2.88 Å, $[Ba_2(hfpd)_4(Et_2O)]_n$,[59] 2.68−2.82 Å, and $[Ba_4(OBu^t)_8(HOBu^t)_8]$,[35] 2.67−2.80 Å. However, these values show larger variations in other polynuclear complexes such as $[Ba_4(tmhd)_8]$,[16] 2.58−3.14 Å, $[Ba_2(tmhd)_4(diglyme)_2]$,[56] 2.57−3.17 Å, $[Ba_5(tmhd)_9(H_2O)_3(OH)]$,[10] 2.57−3.16 Å, $[Ba_2(tmhd)_4(bipy)_2]$,[60] 2.76−3.01 Å, and $[Ba_7(tmhd)_2(piv)_{12}(py)_4(H_2O)_4](py)_2$,[60] 2.63−3.08 Å. In the present compound, most of the Ba−O distances lie in the range 2.610(3)−3.024(4) Å and are comparable with those mentioned above, but three distances [Ba(2)−O(2) 3.378(4), Ba(1)−O(8) 3.358(4), and Ba(2)−O(9′) 3.457(4) Å] are considerably longer. Nevertheless, we consider these distances also to indicate definite, *albeit weak*, bonding interactions. This we suggest that since the atom O(9′), which has the longest distance from Ba(2), is only 2.71 and 3.09 Å, respectively, from O(6) and O(7′) and that as a result of its [O(9′)] occupying the capping position, the central Ba(2) atom is pulled more toward the face O(5)O(6)O(2′)O(7′) (1.290 Å) than toward the opposite face O(1)O(2)O(7)O(8) (2.078 Å) and also the dihedral angle between Ba(2)O(5)O(6) and Ba(2)O(2′)O(7′) becomes larger than that between Ba(2)O(1)O(8) and Ba(2)O(2)O(7) (68.8 *vs* 63.9°).

The metal−oxygen distances within compound **8** can also be divided into several distinct groups. First, the Ba−O distances involving the two terminally chelating tmhd ligands are 2.612(4) and 2.638(3) Å for Ba(1) and 2.670(3) and 2.688(3) Å for Ba(2) (average 2.652 Å), indicating that these ligands are nearly symmetrically bonded to the metals. It is also noted that these bonds to Ba(2) are *ca.* 0.054 Å longer than the corresponding bonds to Ba(1), which may be explained by the higher coordination number of Ba(2) and also by the greater steric crowding around it, as shown by the two very close contacts from the capping atom O(9′) to O(5) and O(6) (discussed above).

The second set of Ba−O distances correspond to those associated with the $\mu_3-\mu_2$ tmhd ligands [O(1) and O(2)]. Four of these bridge bonds span the range 2.731(3)−2.879(4) Å while the fifth is very weak at 3.378(4) Å. These values are as expected generally longer than those involving the purely chelating tmhd ligands.

The Ba−O distances associated with the $\mu_3-\mu_2$-isopropoxyethoxide ligands fall into two sets; those involving the alkoxide oxygen O(7) [2.610(4), 2.660(4), and 2.721(4) Å, average 2.664 Å] and those to the alkoxy ether oxygen O(8) [3.024(4) and 3.358(4) Å, average 3.191 Å]. The Ba−O bonds to the ether oxygen O(8) are quite long and indicate only weak interactions.

Last, the Ba−O distances to the alcohol ligand [Ba(1)−O(9) 2.784(4) and Ba(1)−O(10) 2.910(3) Å] are again different and reflect the fact that the bond to the ether oxygen is longer than that to the alcohol oxygen, the latter also having an additional, very long and weak interaction with Ba(2). It is noted that

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(57) Hubert-Pfalzgraf, L. G.; Poncelet, O.; Toupet, L.; Daran, J. C. *Polyhedron* **1991**, *10*, 2045.

(58) Gleizes, A.; Heughbaert, M.; Sans-Lenain, S. *C. R. Acad. Sci., Ser. II* **1992**, *315*, 299.

(59) Drozdov, A.; Troyanov, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1619.

(60) Drozdov, A.; Troyanov, S. *Polyhedron* **1993**, *12*, 2973.

although the alcoholic oxygen was not experimentally located, we believe that O(9) is the atom which carries the proton. This assumption is consistent with the fact that the O(9)−C(39) bond [1.407(7) Å] on the alcohol ligand is longer than the O(7)−C(34) bond [1.376(6) Å] on the alkoxy ligand. If the alcoholic group on O(9) were also deprotonated, then that would lead to an overall anionic charge of −2 on the metal cluster, and with the absence of any counterion in the crystal, this is highly unlikely. Moreover, an O−H stretching vibration mode was observed at 3165 $cm^{-1}$ in the IR spectrum, confirming the presence of an alcohol ligand in the aggregate.

Both complexes **4** and **8** are based on a similar ladder-like structural motif, with the alkoxy oxygens in each case $\mu_3$-bonded to three different metal centers in the ladder frame. The notable difference is the presence in **8** of two coordinating alcohol ligands which are chelated to Ba(1) and at the same time form long bridge bonds to Ba(2). Obviously, the barium atoms in **8** with larger atomic sizes than the calcium atoms in **4** prefer higher coordination numbers and can accommodate more donor atoms around them. Furthermore, upon the introduction of a bifunctional alcohol, the more compact cubane structure for **1** has been opened up to form the ladder-like structures **4** and **8**.

Complexes **1**, **4**, and **8** can be compared with the recently reported copper(II) compounds $[Cu_4(hfpd)_4(OMe)_4(thf)_4]$ (**10**), $[Cu_4(hfpd)_4(OCH_2CH_2OMe)_4]$ (**11**), and $[Cu_4(tmhd)_4(OCH_2CH_2OMe)_4]$ (**12**).[61] Complex **10** has a strong structural similarity to **1**, both structures being based on the same cube motif. Furthermore, the metal atoms are in octahedral environments, being supported by interactions with three $\mu_3$-alkoxide groups, a chelating tmhd, and a solvent molecule. Complex **11** retains the $Cu_4O_4$ cube motif, but with the ether oxygen of the methoxyethoxide completing the octahedral coordination around the copper atoms. Thus, the methoxyethoxide group is behaving as a $\mu_3$-chelating type ligand observed as in our complexes **4** and **8**. The interaction of the sterically bulky $\beta$-diketonate ligand tmhd and of methoxyethoxide with copper yields a more open ladder-like structure than present in **4** and **8**. Whereas, in **12** the steric bulk alone might be responsible for the ladder-like structure, the presence of both the bifunctional alcohol and the bulky tmhd appear to play a crucial role for compounds **4** and **8**. This is further borne out by the ladder-like structure found in $[Cu_4(OMe)_4(tmhd)_4]$[62] and the distorted cubane for $[Ba_4(OBu^t)_8(Bu^tOH)_{16}]$.[35]

## Conclusions

An important point to note is the total absence of any oxo or hydroxo ligands in the final products **1**−**9**. This effectively implies that our starting materials $[M(OEt)_2(EtOH)_4]_\infty$ and synthetic strategy are highly reproducible, and therefore important as a starting point to develop the chemistry of the alkoxides, $\beta$-diketonates, and other oxygen-based ligands of the heavier group 2 metals. From the above results it would appear that the compounds **1**−**9** have poor physical properties for CVD but may find suitable application as sol−gel precursors.

The basis of the sol−gel process for metal−organic compounds is the susceptibility of alkoxides to hydrolysis. However, the hydrolysis reactions of most alkoxides result in precipitates or often lead to inconsistent hydrolysis behavior. This can be overcome by introducing bifunctional oxygen-donor ligands (such as alkoxy alcohols, amino alcohols, $\beta$-diketone, or carboxylic acids) which better control the hydrolysis to yield gelatinous precipitates.[63] Our preliminary studies for compounds **1**−**9** are in support of this, with gelation observed on the addition of stoichiometric quantities of water.

Studies of these complexes are currently in progress to elucidate their controlled hydrolysis behavior and subsequent evaporation pathways to yield metal oxide ceramics. The synthetic strategy developed for these metal complexes may be adopted to other metal alkoxides, in particular those with more highly functionalized ligands.

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**Supporting Information Available:** Tables of full crystallographic data together with data collection and refinement details, anisotropic displacement parameters of the non-hydrogens atoms, hydrogen atom parameters, and complete bond lengths and angles for compounds **1**, **4**, **and 8** (20 pages). Ordering information is given on any current masthead page.

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(61) Bidell, W.; Shklover, V.; Berke, H. *Inorg. Chem.* **1992**, *31*, 5561.

(62) Watson, W. H.; Holley, W. W. *Croat. Chem. Acta* **1984**, *57*, 467.

(63) Lee, G. R; Crayston, J. A. *Adv. Mater.* **1993**, *5*, 434.