

Monomeric Group IIA Metal  $\beta$ -Diketonates Stabilized by Multidendate Glymes

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The reaction of the oligomeric alkaline earth metal  $\beta$ -diketonate complexes,  $[M(\beta\text{-diket})_2]_n$  with a glyme ligand, yields the monomeric materials  $[M(\beta\text{-diketonate})_2(L\text{-L})]$ . The complexes  $[\text{Ca}(\text{thd})_2(\text{triglyme})]$  (1),  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]$  (2), and  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (3), have been characterized by IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass spectrometry, and single-crystal X-ray studies. For  $[\text{Ca}(\text{thd})_2(\text{triglyme})]$  (1) is triclinic,  $a = 10.378(3)$  Å,  $b = 11.601(4)$  Å,  $c = 15.483(3)$  Å,  $\alpha = 84.03(3)^\circ$ ,  $\beta = 71.75(2)^\circ$ ,  $\gamma = 82.61(3)^\circ$ , and  $Z = 2$ ; a monomeric eight-coordinate calcium complex is observed. The complex  $[\text{Cu}(\text{hfa})_2(\text{tetraglyme})]$  (2) is triclinic, and is also eight coordinate, binding to only four of the five available oxygen atoms of the glyme ligand, leaving a dangling uncoordinated arm:  $a = 9.453(2)$  Å,  $b = 12.600(2)$  Å,  $c = 13.215(4)$  Å,  $\alpha = 70.30(2)^\circ$ ,  $\beta = 83.09(2)^\circ$ ,  $\gamma = 76.49(2)^\circ$ , and  $Z = 2$ . The complex  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (3) is monoclinic,  $a = 10.688(2)$  Å,  $b = 23.614(6)$  Å,  $c = 15.650(3)$  Å,  $\beta = 109.11^\circ$ , and  $Z = 4$ . The structure is similar to that of 1 in that it is also eight coordinate, binding to the two  $\beta$ -diketonate ligands and the four oxygen atoms of the glyme ligand. The coordination geometry is markedly different, being bicapped trigonal antiprismatic compared with the square antiprismatic geometry observed for compounds 1 and 2.

## Introduction

In the last 5 years metal alkoxides have found extensive applications as polymerization catalysts<sup>1</sup> and as molecular precursors for metal oxide superconductors and other speciality electroceramic materials, e.g.  $\text{BaTiO}_3$ ,  $\text{K}_{0.4}\text{Ba}_{0.6}\text{BiO}_3$ , and  $\text{TaO}_2$ .<sup>2</sup> Such materials find application in both sol-gel and MOCVD processes, since they are highly soluble in organic solvents, and moreover rapidly form bimetallic species by simple mixing of the component parts. These materials give the possibility of accurate and selective control of metal stoichiometry at the molecular level, and allow the possibility of formation of a single source precursor of exceptionally high purity, e.g.  $\text{MM}'(\text{OR})_n$ .

The use of these materials as precursors for mixed metal oxides has several inherent advantages over traditional ceramic routes to these materials. First, multimetallic alkoxides may be prepared directly in organic solution, thus avoiding the problem of unreacted ionic impurities. These materials may be readily converted to metal oxide films by the use of chemical vapor deposition (CVD); if the films obtained are amorphous they may be converted to crystalline materials via calcining processes. The purity and ratio of the metal oxides are wholly dependent on the stoichiometry of the molecular alkoxide complexes. Therefore, carefully controlled CVD is extremely important as a preparative route to uniform monodispersed metal oxide films with epitaxial morphologies.

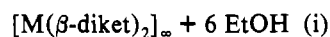
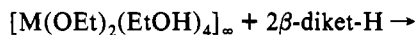
Previous researchers have extensively used either (tetramethylheptane-2,4-dionato)alkaline earth metal salts, which yielded via a barium hydroxide aqueous route the pentameric aggregate  $\text{Ba}_5(\text{OH})(\text{thd})_9(\text{H}_2\text{O})_3$ ,<sup>3</sup> and from carefully controlled non-aqueous routes via the Lewis base adducts with either ammonia or diethyl ether,  $[\text{Ba}_2(\text{thd})_4(\text{L})_2]$ .<sup>4</sup> With the corresponding hexafluoroacetylacetonate ligand, Bradley *et al.* recently isolated the hydrated calcium and barium complexes, e.g.  $[\text{Ca}(\text{hfa})_2(\text{H}_2\text{O})_2]_n$ ,<sup>5</sup> while other researchers have recently obtained the monomeric species  $[\text{Ba}(\text{hfa})_2(18\text{-crown-6})]$ ,<sup>6</sup> and  $[\text{Ba}(\text{hfa})_2$

(tetraglyme)].<sup>7</sup> However, their behavior at high temperature is poor, and sample decomposition is often the norm.

In the course of our research directed toward volatile single source CVD precursors we have used the metal ethoxides  $[\text{M}(\text{OEt})_2(\text{HOEt})_4]_n$   $\{\text{M} = \text{Ca}, \text{Sr} \text{ or } \text{Ba}\}$  as soluble sources of these metals.<sup>8</sup> We and others have observed a facile reaction with these metal ethoxides and a range of  $\beta$ -diketonates in hexane at room temperature, analogous to the previous work of Bradley *et al.*<sup>5,10</sup>

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M = Ca, Sr, or Ba;  $\beta$ -diket =

acac, Ph<sub>2</sub>acac, tfa, hfa, and thd

A notable feature of these metals is their strong Lewis acidity, which ensures that in the absence of Lewis base solvents they generally form polymeric insoluble materials. But, on the addition of Lewis base solvents to Group IIA organometallics, the polymeric ensembles are cleaved to yield simpler molecular species.<sup>11</sup> A wide variety of molecular geometries are available, provided that judicious choice of hydrocarbyl ligands (or other organic substrates) and or Lewis bases are used to achieve coordinative saturation of the large M<sup>2+</sup> cations, to reduce potential polymerization processes. For such a strategy a precedent is available, with the prior use of macrocyclic ligands, e.g. crown ethers and cryptands.<sup>9</sup>

We consider that the formally "unsaturated" group IIA metal  $\beta$ -diketonate complexes may show reactivity similar to the previously studied pentamethylcyclopentadienyl complexes with ethers, phosphines, halides, nitriles, etc.<sup>11</sup>

We report in this paper a general synthetic route to monomeric complexes of the type  $[M(\beta\text{-diket})_2(L-L)]$ , by the use of multidendate chelating glyme ligands and the molecular structures of  $[\text{Ca}(\text{thd})_2(\text{triglyme})]$  (1),  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]$  (2), and  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (3).

### Experimental Section

**General.** The manipulations of all reactants and products were carried out under a nitrogen atmosphere (Schlenk line), under an argon atmosphere (glovebox), or *in vacuo*, with rigorous exclusion of moisture and air. The solvent *n*-hexane was predried and then distilled prior to use and stored over 4A molecular sieves under an atmosphere of nitrogen in a glass storage vessel fitted with a Youngs high vacuum PTFE stopcock.

**Physical Techniques.** Infrared spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer as either nujol or hexachlorobutadiene mulls, in the region 4000–400 cm<sup>-1</sup>. The NMR spectra were recorded on a Jeol GS 270 at 270 MHz in dry and oxygen-free benzene-*d*<sub>6</sub> or dimethyl-*d*<sub>6</sub> sulfoxide as appropriate, using the protio impurities of the deuterated solvents as a reference for <sup>1</sup>H NMR and the <sup>13</sup>C NMR resonances of the solvent as a reference for <sup>13</sup>C NMR. Elemental analyses were performed by Imperial College and Butterworth Laboratories, and all compounds were handled in an inert atmosphere. Mass spectroscopic data were obtained on a Kratos MS30 by the Royal School of Pharmacy Mass Spectrometry Service, University of London. The melting points recorded are uncorrected values.

**Synthesis.** All reactions were performed using standard Schlenk techniques with dry oxygen-free solvents, stored over 4A molecular sieves. 2,2,6,6-tetramethyl-3,5-heptanedione, 1,1,1,6,6,6-hexafluoro-3,5-pentanedione, were obtained from Inorgtech of Mildenhall, Suffolk, U.K. The metal ethoxides,  $[M(OEt)_2(EtOH)_4]_{\infty}$  and  $\beta$ -diketonates  $[M(\beta\text{-diket})_2]_{\infty}$  were prepared according to the literature procedures.<sup>9,9</sup>

**Synthesis of  $[\text{Ca}(\text{thd})_2(\text{triglyme})]$  (1).**  $[\text{Ca}(OEt)_2(EtOH)_4]_{\infty}$  (2.78 g, 8.87 mmol) was weighed into a Schlenk tube and *n*-hexane (30 mL) added. To the resulting clear solution was added thd-H (3.18 cm<sup>3</sup>, 17.74 mmol) and the reaction was left to stir for 5 min, and then triglyme (1.6 cm<sup>3</sup>, 8.87 mmol) was added and the reaction mixture left for a further 10 min. The solvent and liberated ethanol were then removed under vacuum to yield a white solid, which was redissolved in *n*-hexane (15 cm<sup>3</sup>) and left to crystallize at 0 °C. Yield: 4.2 g, 81 %. IR (hexachlorobutadiene;  $\nu$ , cm<sup>-1</sup>): 2948 (vs), 1590 (vs), 1534 (vs), 1505 (s), 1429 (vs), 1386 (s), 1356 (s), 1261 (s), 1224 (m), 1098 (vs), 1024 (s), 731 (w), 594 (w). MS (electron impact, positive ion amu): 813  $[\text{Ca}_2(\text{thd})_4]^+$ , 3%; 727  $[\text{Ca}(\text{thd})_2(\text{Bu}^+\text{COCHCOCMeH})(\text{triglyme})]^+$ , 12.5%; 629  $[\text{Ca}(\text{thd})_2(\text{triglyme})\text{EtOH}]^+$ , 85%; 422  $[\text{Ca}(\text{thd})_2(\text{H}_2\text{O})]^+$ , 18%; 349  $[\text{Ca}(\text{thd})(\text{Bu}^+\text{COCHCO})]^+$ , 56%; 321  $[\text{Ca}(\text{thd})(\text{Bu}^+\text{COCH})]^+$ , 17%; 223  $[\text{Ca}(\text{thd})]^+$ , 100%.

**Synthesis of  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]$  (2).**  $[\text{Ca}(OEt)_2(EtOH)_4]_{\infty}$  (2.78 g, 8.87 mmol) was weighed into a Schlenk tube and *n*-hexane (20 mL)

Table I. Crystallographic Data for Complexes 1–3

	1	2	3
formula	C <sub>30</sub> H <sub>56</sub> CaO <sub>8</sub>	C <sub>20</sub> H <sub>24</sub> CaO <sub>9</sub> F <sub>12</sub>	C <sub>30</sub> H <sub>56</sub> BaO <sub>8</sub>
mol wt	584.8	676.5	682.1
color and habit	clear blocks	clear blocks	clear blocks
cryst size/mm	0.32 × 0.37 × 0.50	0.21 × 0.33 × 0.33	0.12 × 0.23 × 0.43
cryst syst	triclinic	triclinic	monoclinic
a/Å	10.378(3)	9.453(2)	10.668(2)
b/Å	11.601(4)	12.600(3)	23.614(6)
c/Å	15.483(3)	13.215(4)	15.650(3)
α/deg	84.03(3)	70.30(2)	
β/deg	71.75(2)	83.09(2)	109.11(2)
γ/deg	82.61(3)	76.49(2)	
V/Å <sup>3</sup>	1751.7(10)	1439.2(7)	3725.0(14)
space group	P-1	P-1	P2 <sub>1</sub> /c
Z	2	2	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.109	1.561	1.216
λ/Å	1.54178 (Cu)	1.54178 (Cu)	0.71073 (Mo)
μ/cm <sup>-1</sup>	18.8	30.3	11.1
F(000)	640	688	1424
transm factors:	0.5004; 0.6066		
max; min			
no. of unique data	4716	3857	6561
no. of obsd data	4146	3616	3926
with F > 4σ(F)			
scan type	ω	ω	ω
2θ range/deg	0–116	0–116	4–50
final Δρ/(e Å <sup>-3</sup> )	0.49	0.61	1.12
final Δ/σ	0.112	0.045	0.000
R = Σw(F <sub>o</sub> - F <sub>c</sub> ) <sup>2</sup>	5.41	7.07	5.02
R <sub>w</sub>	5.96 <sup>a</sup>	8.43 <sup>a</sup>	4.71 <sup>a</sup>
temp/K	291	291	293

<sup>a</sup> The form of the weighting function is  $w^{-1} = \sigma^2(F) + 0.0005F^2$ .

added. To the resulting clear solution was added hfa-H (2.51 cm<sup>3</sup>, 17.76 mmol) and the reaction left to stir for 5 min, and then tetraglyme (1.96 cm<sup>3</sup>, 8.87 mmol) was added and the reaction mixture worked up as for 1. Yield: 3.4 g, 64.2%. IR (hexachlorobutadiene;  $\nu$ , cm<sup>-1</sup>): 2949 (s), 1978 (w), 1590 (s), 1534 (s), 1505 (s), 1425 (s), 1356 (s), 1224 (m), 1100 (s), 1023 (m), 748 (m), 731 (m), 594 (w). MS (electron impact, positive ion amu): 716  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]^+$ , 26%; 646  $[\text{Ca}(\text{hfa})(\text{CF}_3\text{-COCHCO})(\text{tetraglyme})]^+$ , 8%; 509  $[\text{Ca}(\text{hfa})(\text{tetraglyme})]^+$ , 3%; 247  $[\text{Ca}(\text{hfa})]^+$ , 15%.

**Synthesis of  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (3).**  $[\text{Ba}(OEt)_2(EtOH)_4]_{\infty}$  (3.28 g, 7.98 mmol) was weighed into a Schlenk tube and *n*-hexane (20 mL) added. To the resulting clear solution was added thd-H (3.35 cm<sup>3</sup>, 15.96 mmol) and the reaction left to stir for 5 min, and then triglyme (1.0 cm<sup>3</sup>, 7.98 mmol) was added and the reaction mixture worked up as for 1. Yield: 4.43 g, 81.6%. IR (hexachlorobutadiene;  $\nu$ , cm<sup>-1</sup>): 2949 (s), 1425 (s), 1356 (s), 1223 (m), 1100 (s), 1022 (m), 748 (m), 731 (m), 592 (w). MS (electron impact, positive ion amu): 824  $[\text{Ba}_2(\text{thd})_3]^+$ , 38%; 727  $[\text{Ba}(\text{thd})_2(\text{triglyme})(\text{EtOH})]^+$ , 17%; 680  $[\text{Ba}(\text{thd})_2(\text{triglyme})]^+$ , 5%; 321  $[\text{Ba}(\text{thd})]^+$ , 100%.

**Single-Crystal X-ray Analysis.** Single crystals of complexes 1–3 were obtained directly from saturated *n*-hexane solutions. All of the crystals were subsequently mounted onto glass fibers with epoxy resin and were coated with epoxy to reduce any possible crystal decomposition during data collection. The accurate unit cell parameters for each compound were obtained by means of least-squares analysis of between 18 and 25 centered reflections. Data for compounds 1 and 2 were collected on a Siemens P3/PC diffractometer using graphite monochromated Cu K $\alpha$  radiation. Data for 3 were measured on a Siemens P4/PC diffractometer with graphite monochromated Mo K $\alpha$  radiation. A summary of the crystallographic data and data collection and refinement parameters is given in Table I. The intensity data were collected according to the options specified in Table I. Two standard reflections were monitored every 50 and showed no significant variation over the data collection. The structures of 1 and 2 were solved by direct methods and that of 3 was solved by the heavy-atom method and refined with the full-matrix least-squares technique, using anisotropic thermal parameters for non-hydrogen atoms.<sup>20</sup>

In complex 1, one of the *tert*-butyl groups [that attached to C(18)] displays rotational disorder, and two discrete orientations with occupancies of 0.75 and 0.25 were refined. The minor occupancy atoms were refined isotropically.

Table II. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Complex 1									
Ca	705(1)	4930(1)	2407(1)	45(1)	O(16)	-1208(2)	3942(2)	3212(2)	63(1)
C(1)	-737(4)	6427(4)	4322(3)	99(2)	C(17)	-2908(3)	2638(3)	3819(2)	60(1)
O(2)	495(2)	5788(2)	3847(2)	70(1)	C(171)	-3195(4)	1678(4)	4579(3)	113(2)
C(3)	1646(4)	6199(4)	3977(3)	92(2)	C(172)	-3846(4)	3713(4)	4156(4)	107(2)
C(4)	2856(4)	5364(4)	3578(3)	84(2)	C(173)	-3224(4)	2298(5)	2998(3)	115(2)
O(5)	2970(2)	5326(2)	2646(2)	64(1)	C(18)	-2826(3)	7899(3)	2383(2)	63(1)
C(6)	4110(3)	4572(3)	2188(3)	74(2)	C(181)	-3111(7)	8454(9)	3239(5)	140(4)
C(7)	4101(3)	4534(3)	1243(3)	75(2)	C(182)	-3785(5)	6982(5)	2473(7)	136(5)
O(8)	2908(2)	4054(2)	1261(2)	64(1)	C(183)	-3110(5)	8803(6)	1642(4)	100(3)
C(9)	2813(4)	3980(4)	377(3)	95(2)	C(184)	-3354(25)	7892(25)	1735(17)	134(8)
C(10)	1556(5)	3445(4)	484(3)	99(2)	C(185)	-2928(27)	7892(25)	1735(17)	134(8)
O(11)	436(2)	4162(2)	1035(2)	73(1)	C(185)	-2928(27)	9190(21)	2531(21)	143(9)
C(12)	-842(4)	3872(4)	1043(3)	102(2)	C(186)	-3650(22)	7239(20)	3300(15)	111(6)
C(13)	2074(3)	1152(2)	3381(2)	56(1)	C(19)	-1339(3)	7317(3)	2109(2)	49(1)
C(131)	3192(3)	1148(3)	2460(3)	74(2)	O(19)	-1169(2)	6273(2)	2352(2)	61(1)
C(132)	2683(4)	1349(3)	4127(3)	81(2)	C(20)	-284(3)	7991(3)	1615(2)	62(1)
C(133)	1510(4)	-22(3)	3585(3)	73(2)	C(21)	1073(3)	7570(2)	1285(2)	48(1)
C(14)	1013(3)	2196(2)	3328(2)	47(1)	O(21)	1537(2)	6528(2)	1376(1)	59(1)
O(14)	1479(2)	3167(2)	3085(1)	54(1)	C(22)	2149(3)	8404(3)	753(2)	56(1)
C(15)	-370(3)	2035(3)	3556(2)	59(1)	C(221)	3303(4)	8237(3)	1186(3)	83(2)
C(16)	-1406(3)	2923(2)	3505(2)	50(1)	C(222)	2700(4)	8055(4)	-222(3)	94(2)
C(223)	1610(4)	9686(3)	754(3)	75(2)					
Complex 2									
Ca	3640(1)	7653(1)	2551(1)	44(1)	C(19)	4646(4)	5134(3)	2004(3)	48(1)
C(1)	2375(7)	6648(6)	5175(4)	105(1)	O(19)	4981(3)	5982(2)	2113(2)	60(1)
O(2)	3593(4)	7010(3)	4508(2)	79(1)	C(20)	5893(4)	4383(3)	1532(3)	66(1)
C(3)	4915(6)	6683(5)	5053(4)	87(1)	F(201)	6726(6)	3647(5)	2290(3)	144(1)
C(4)	5976(5)	7331(4)	4379(3)	72(1)	F(202)	5465(4)	3790(3)	1020(3)	85(1)
O(5)	6072(3)	7212(2)	3328(2)	61(1)	F(203)	6750(5)	4983(3)	835(3)	89(1)
C(6)	7076(4)	7851(4)	2612(4)	66(1)	F(204)	7086(9)	4411(11)	1922(10)	161(1)
C(7)	7012(4)	7747(4)	1528(4)	65(1)	F(205)	6089(12)	3275(4)	2024(10)	148(1)
O(8)	5566(3)	8295(2)	1164(2)	53(1)	F(206)	6253(11)	4929(10)	538(5)	132(1)
C(9)	5366(5)	8235(4)	131(3)	61(1)	C(21)	3930(3)	11025(3)	3214(3)	62(1)
C(10)	3852(5)	8789(4)	-140(3)	67(1)	F(211)	4069(7)	11841(4)	2306(3)	127(1)
O(11)	2908(3)	8242(3)	693(2)	59(1)	F(212)	5241(4)	10562(4)	3554(7)	166(1)
C(12)	1418(4)	8463(4)	414(4)	70(1)	F(213)	3261(4)	11588(3)	3859(3)	85(1)
C(13)	1255(5)	7609(4)	-117(4)	70(1)	F(214)	4306(12)	10630(10)	4210(4)	148(1)
O(14)	-190(3)	7841(4)	-368(3)	93(1)	F(215)	3141(11)	12039(6)	3147(11)	166(1)
C(15)	-455(6)	7031(6)	-798(6)	116(1)	F(216)	5212(7)	11029(10)	2737(9)	146(1)
C(16)	785(4)	4914(3)	2991(3)	73(1)	C(22)	3148(4)	10176(3)	3055(3)	47(1)
F(161)	899(6)	3882(4)	2992(7)	125(1)	O(22)	3959(3)	9445(2)	2682(2)	58(1)
F(162)	257(9)	4918(8)	3932(5)	174(1)	C(23)	1675(4)	10317(3)	3287(3)	58(1)
F(163)	-214(5)	5509(6)	2325(5)	143(1)	C(24)	856(4)	9624(3)	3105(3)	53(1)
F(164)	438(10)	4606(11)	2239(8)	218(1)	O(24)	1284(3)	8778(2)	2794(2)	61(1)
F(165)	959(8)	4013(7)	3830(7)	130(1)	C(25)	-786(5)	9909(5)	3323(4)	79(1)
F(166)	-371(6)	5548(6)	3251(9)	131(1)	F(251)	-1271(3)	10823(4)	3603(5)	169(1)
C(17)	2170(4)	5398(3)	2693(3)	50(1)	F(252)	-1253(4)	9047(4)	4063(3)	114(1)
O(17)	2062(3)	6320(2)	2870(2)	60(1)	F(253)	-1493(3)	10062(3)	2440(3)	107(1)
C(18)	3338(4)	4795(3)	2257(3)	54(1)					
Complex 3									
Ba	2353(1)	2176(1)	4290(1)	52(1)	C(16)	3184(7)	997(3)	5872(5)	57(3)
C(1)	5152(12)	1364(5)	4123(10)	151(8)	O(16)	3020(5)	1512(2)	5709(3)	69(2)
O(2)	4187(7)	1681(3)	3526(5)	112(4)	C(17)	4044(8)	835(4)	6835(5)	78(4)
C(3)	4428(13)	1982(7)	2883(9)	151(8)	C(171)	4275(11)	201(4)	6993(7)	135(6)
C(4)	3318(10)	2177(5)	2183(7)	102(5)	C(172)	5368(9)	1128(5)	7009(7)	121(6)
O(5)	2405(6)	2442(3)	2549(3)	80(3)	C(173)	3386(10)	1066(5)	7491(6)	111(5)
C(6)	1241(10)	2638(4)	1856(6)	97(5)	C(18)	6394(8)	3361(4)	5574(6)	78(4)
C(7)	415(8)	2943(4)	2318(6)	89(4)	C(181)	6728(10)	3546(7)	4795(9)	204(10)
O(8)	13(5)	2549(2)	2863(3)	74(2)	C(182)	7129(10)	2824(5)	5916(11)	195(9)
C(9)	-914(9)	2766(4)	3259(6)	83(4)	C(183)	6860(10)	3787(6)	6312(9)	181(8)
C(10)	-1356(9)	2295(4)	3714(7)	94(5)	C(19)	4898(7)	3252(3)	5289(5)	55(3)
O(11)	-282(5)	2088(2)	4432(4)	74(2)	O(19)	4536(5)	2761(2)	5001(4)	81(3)
C(12)	-619(9)	1590(4)	4805(6)	94(5)	C(20)	4031(7)	3681(3)	5317(5)	59(3)
C(13)	1286(10)	140(3)	3712(6)	79(4)	C(21)	2664(7)	3667(3)	5031(5)	54(3)
C(131)	-176(13)	205(7)	3352(11)	223(11)	O(21)	1992(4)	3232(2)	4719(4)	67(2)
C(132)	1810(11)	163(4)	2922(7)	133(7)	C(22)	1866(8)	4198(3)	5090(6)	71(4)
C(133)	1606(19)	-425(4)	4155(8)	242(13)	C(221)	734(11)	4023(4)	5452(9)	150(8)
C(14)	1867(8)	652(3)	4327(5)	64(4)	C(222)	1258(14)	4414(5)	4170(7)	178(8)
O(14)	1573(6)	1122(2)	3960(3)	77(2)	C(223)	2646(10)	4647(4)	5729(8)	134(6)
C(15)	2627(8)	568(3)	5231(5)	70(4)					

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

In complex 2, there is rotational disorder in three of the CF<sub>3</sub> groups: those attached to C(16), C(20), and C(21). The occupancies for the orientations of the CF<sub>3</sub> group on C(16) are 0.6 and 0.4 and for C(20)

are 0.7 and 0.3, and for C(21), 0.7 and 0.3 occupancies were refined. The minor occupancy fluorine atoms on C(20) and C(21) were refined isotropically.

Table III. Bond Lengths (Å) and Angles (deg)

Complex 1							
Ca-O(2)	2.471(3)	Ca-O(5)	2.594(3)	C(14)-C(15)	1.399(4)	C(15)-C(16)	1.405(4)
Ca-O(8)	2.578(2)	Ca-O(11)	2.492(3)	C(16)-O(16)	1.240(3)	C(16)-C(17)	1.549(4)
Ca-O(14)	2.365(2)	Ca-O(16)	2.355(2)	C(17)-C(171)	1.519(6)	C(17)-C(172)	1.510(5)
Ca-O(19)	2.348(2)	Ca-O(21)	2.379(2)	C(17)-C(173)	1.509(7)	C(18)-C(181)	1.464(9)
C(1)-O(2)	1.416(4)	O(2)-C(3)	1.419(6)	C(18)-C(182)	1.515(7)	C(18)-C(183)	1.545(7)
C(3)-C(4)	1.491(5)	C(4)-O(5)	1.416(5)	C(18)-C(184)	1.288(31)	C(18)-C(185)	1.524(26)
O(5)-C(6)	1.416(4)	C(6)-C(7)	1.472(6)	C(18)-C(186)	1.586(20)	C(18)-C(19)	1.549(4)
C(7)-O(8)	1.412(4)	O(8)-C(9)	1.415(5)	C(19)-O(19)	1.237(3)	C(19)-C(20)	1.402(4)
C(9)-C(10)	1.472(7)	C(10)-O(11)	1.431(5)	C(20)-C(21)	1.381(4)	C(21)-O(21)	1.253(3)
O(11)-C(12)	1.406(6)	C(13)-C(131)	1.531(4)	C(21)-C(22)	1.549(4)	C(22)-C(221)	1.528(6)
C(13)-C(132)	1.529(6)	C(13)-C(133)	1.516(4)	C(22)-C(222)	1.515(5)	C(22)-C(223)	1.520(4)
C(13)-C(14)	1.542(4)	C(14)-O(14)	1.258(3)				
Complex 2							
Ca-O(2)	2.434(3)	Ca-O(5)	2.497(3)	C(16)-C(17)	1.526(6)	C(17)-O(17)	1.239(5)
Ca-O(8)	2.493(3)	Ca-O(11)	2.449(3)	C(17)-C(18)	1.370(5)	C(18)-C(19)	1.369(6)
Ca-O(17)	2.401(3)	Ca-O(19)	2.402(3)	C(19)-O(19)	1.240(6)	C(19)-C(20)	1.540(5)
Ca-O(22)	2.410(3)	Ca-O(24)	2.395(3)	C(20)-F(201)	1.306(5)	C(20)-F(202)	1.315(7)
C(1)-O(2)	1.428(7)	O(2)-C(3)	1.423(7)	C(20)-F(203)	1.309(5)	C(20)-F(204)	1.308(12)
C(3)-C(4)	1.465(7)	C(4)-O(5)	1.436(6)	C(20)-F(205)	1.304(6)	C(20)-F(206)	1.306(7)
O(5)-C(6)	1.439(5)	C(6)-C(7)	1.490(8)	C(21)-F(211)	1.307(5)	C(21)-F(212)	1.302(5)
C(7)-O(8)	1.438(5)	O(8)-C(9)	1.429(6)	C(21)-F(213)	1.303(6)	C(21)-F(214)	1.301(7)
C(9)-C(10)	1.467(6)	C(10)-O(11)	1.423(5)	C(21)-F(215)	1.300(8)	C(21)-F(216)	1.298(8)
O(11)-C(12)	1.439(5)	C(12)-C(13)	1.513(9)	C(21)-C(22)	1.515(6)	C(22)-O(22)	1.251(5)
C(13)-O(14)	1.386(6)	O(14)-C(15)	1.404(10)	C(22)-C(23)	1.373(5)	C(23)-C(24)	1.385(7)
C(16)-F(161)	1.278(7)	C(16)-F(162)	1.284(8)	C(24)-O(24)	1.234(6)	C(24)-C(25)	1.525(6)
C(16)-F(163)	1.285(7)	C(16)-F(164)	1.283(14)	C(25)-F(251)	1.293(8)	C(25)-F(252)	1.318(6)
C(16)-F(165)	1.285(8)	C(16)-F(166)	1.280(8)	C(25)-F(253)	1.348(7)		
Complex 3							
Ba-O(2)	2.856(9)	Ba-O(5)	2.814(6)	C(13)-C(14)	1.543(11)	C(14)-O(14)	1.242(9)
Ba-O(8)	2.889(5)	Ba-O(11)	2.900(6)	C(14)-C(15)	1.395(10)	C(15)-C(16)	1.412(10)
Ba-O(14)	2.624(5)	Ba-O(16)	2.621(5)	C(16)-O(16)	1.243(9)	C(16)-C(17)	1.534(10)
Ba-O(19)	2.622(5)	Ba-O(21)	2.643(5)	C(17)-C(171)	1.525(14)	C(17)-C(172)	1.515(13)
C(1)-O(2)	1.364(13)	O(2)-C(3)	1.325(18)	C(17)-C(173)	1.522(15)	C(18)-C(181)	1.444(18)
C(3)-C(4)	1.402(15)	C(4)-O(5)	1.426(14)	C(18)-C(182)	1.495(15)	C(18)-C(183)	1.490(16)
O(5)-C(6)	1.432(10)	C(6)-C(7)	1.495(15)	C(18)-C(19)	1.532(11)	C(19)-O(19)	1.256(9)
C(7)-O(8)	1.421(12)	O(8)-C(9)	1.422(12)	C(19)-C(20)	1.383(11)	C(20)-C(21)	1.378(10)
C(9)-C(10)	1.478(14)	C(10)-O(11)	1.404(10)	C(21)-O(21)	1.257(8)	C(21)-C(22)	1.534(11)
O(11)-C(12)	1.410(11)	C(13)-C(131)	1.483(16)	C(22)-C(221)	1.548(17)	C(22)-C(222)	1.465(13)
C(13)-C(132)	1.515(16)	C(13)-C(133)	1.490(13)	C(22)-C(223)	1.507(12)		
Bond Angles							
Complex 1							
O(2)-Ca-O(5)	64.0(1)	O(2)-Ca-O(8)	127.1(1)	C(132)-C(13)-C(133)	108.9(3)	C(131)-C(13)-C(14)	107.3(2)
O(5)-Ca-O(8)	64.2(1)	O(2)-Ca-O(11)	169.0(1)	C(132)-C(13)-C(14)	107.7(3)	C(133)-C(13)-C(14)	114.6(3)
O(5)-Ca-O(11)	126.7(1)	O(8)-Ca-O(11)	63.8(1)	C(13)-C(14)-O(14)	115.6(2)	C(13)-C(14)-C(15)	120.3(2)
O(2)-Ca-O(14)	85.9(1)	O(5)-Ca-O(14)	74.8(1)	O(14)-C(14)-C(15)	124.0(3)	Ca-O(14)-C(14)	133.7(2)
O(8)-Ca-O(14)	71.7(1)	O(11)-Ca-O(14)	99.0(1)	C(14)-C(15)-C(16)	124.5(3)	C(15)-C(16)-O(16)	124.5(3)
O(2)-Ca-O(16)	87.6(1)	O(5)-Ca-O(16)	137.3(1)	C(15)-C(16)-C(17)	119.3(3)	O(16)-C(16)-C(17)	116.2(2)
O(8)-Ca-O(16)	126.2(1)	O(11)-Ca-O(16)	84.7(1)	Ca-O(16)-C(16)	135.7(2)	C(16)-C(17)-C(171)	113.1(3)
O(14)-Ca-O(16)	71.9(1)	O(2)-Ca-O(19)	85.1(1)	C(16)-C(17)-C(172)	109.8(3)	C(171)-C(17)-C(172)	108.0(3)
O(5)-Ca-O(19)	128.2(1)	O(8)-Ca-O(19)	137.0(1)	C(16)-C(17)-C(173)	107.7(3)	C(171)-C(17)-C(173)	110.4(4)
O(11)-Ca-O(19)	85.4(1)	O(14)-Ca-O(19)	146.7(1)	C(172)-C(17)-C(173)	107.7(4)	C(181)-C(18)-C(182)	111.5(5)
O(16)-Ca-O(19)	75.7(1)	O(2)-Ca-O(21)	98.5(1)	C(181)-C(18)-C(183)	109.9(5)	C(182)-C(18)-C(183)	104.6(5)
O(5)-Ca-O(21)	72.8(1)	O(8)-Ca-O(21)	75.3(1)	C(184)-C(18)-C(185)	103.3(18)	C(184)-C(18)-C(186)	112.8(15)
O(11)-Ca-O(21)	83.9(1)	O(14)-Ca-O(21)	141.2(1)	C(185)-C(18)-C(186)	109.1(13)	C(181)-C(18)-C(19)	109.1(4)
O(16)-Ca-O(21)	146.4(1)	O(19)-Ca-O(21)	72.0(1)	C(182)-C(18)-C(19)	109.0(3)	C(183)-C(18)-C(19)	112.7(3)
Ca-O(2)-C(1)	120.5(3)	Ca-O(2)-C(3)	120.0(2)	C(184)-C(18)-C(19)	110.9(10)	C(185)-C(18)-C(19)	113.0(10)
C(1)-O(2)-C(3)	111.7(3)	O(2)-C(3)-C(4)	107.6(4)	C(186)-C(18)-C(19)	107.8(8)	C(18)-C(19)-O(19)	116.6(2)
C(3)-C(4)-O(5)	107.0(3)	Ca-O(5)-C(4)	112.4(2)	C(18)-C(19)-C(20)	118.9(2)	O(19)-C(19)-C(20)	124.4(3)
Ca-O(5)-C(6)	113.6(2)	C(4)-O(5)-C(6)	112.1(3)	Ca-O(19)-C(19)	135.9(2)	C(19)-C(20)-C(21)	124.9(3)
O(5)-C(6)-C(7)	108.3(3)	C(6)-C(7)-O(8)	108.4(3)	C(20)-C(21)-O(21)	124.9(3)	C(20)-C(21)-C(22)	120.2(2)
Ca-O(8)-C(7)	114.5(2)	Ca-O(8)-C(9)	114.5(2)	O(21)-C(21)-C(22)	115.0(2)	Ca-O(21)-C(21)	133.3(2)
C(7)-O(8)-C(9)	112.5(3)	O(8)-C(9)-C(10)	107.3(3)	C(21)-C(22)-C(221)	107.9(3)	C(21)-C(22)-C(222)	107.6(3)
C(9)-C(10)-O(11)	107.8(4)	Ca-O(11)-C(10)	118.3(3)	C(221)-C(22)-C(222)	109.4(3)	C(21)-C(22)-C(223)	114.4(2)
Ca-O(11)-C(12)	120.2(2)	C(10)-O(11)-C(12)	113.2(3)	C(221)-C(22)-C(223)	108.2(3)	C(222)-C(22)-C(223)	109.2(3)
C(131)-C(13)-C(132)	109.4(3)	C(131)-C(13)-C(133)	108.8(3)				
Complex 2							
O(2)-Ca-O(5)	65.5(1)	O(2)-Ca-O(8)	131.8(1)	F(162)-C(16)-C(17)	112.1(6)	F(163)-C(16)-C(17)	111.3(4)
O(5)-Ca-O(8)	67.4(1)	O(2)-Ca-O(11)	162.4(1)	F(164)-C(16)-C(17)	112.0(5)	F(165)-C(16)-C(17)	110.7(5)
O(5)-Ca-O(11)	131.9(1)	O(8)-Ca-O(11)	65.7(1)	F(166)-C(16)-C(17)	118.1(5)	C(16)-C(17)-O(17)	113.7(3)
O(2)-Ca-O(17)	82.4(1)	O(5)-Ca-O(17)	125.7(1)	C(16)-C(17)-C(18)	117.7(4)	O(17)-C(17)-C(18)	128.6(4)
O(8)-Ca-O(17)	135.5(1)	O(11)-Ca-O(17)	83.5(1)	Ca-O(17)-C(17)	134.3(3)	C(17)-C(18)-C(19)	122.1(4)
O(2)-Ca-O(19)	103.3(1)	O(5)-Ca-O(19)	74.8(1)	C(18)-C(19)-O(19)	128.1(4)	C(18)-C(19)-C(20)	117.8(4)
O(8)-Ca-O(19)	73.1(1)	O(11)-Ca-O(19)	82.1(1)	O(19)-C(19)-C(20)	114.0(3)	Ca-O(19)-C(19)	134.4(2)
O(17)-Ca-O(19)	71.5(1)	O(2)-Ca-O(22)	84.8(1)	C(19)-C(20)-F(201)	110.7(3)	C(19)-C(20)-F(202)	114.6(3)
O(5)-Ca-O(22)	74.4(1)	O(8)-Ca-O(22)	73.6(1)	F(201)-C(20)-F(202)	107.2(4)	C(19)-C(20)-F(203)	113.0(3)
O(11)-Ca-O(22)	101.7(1)	O(17)-Ca-O(22)	147.2(1)	F(201)-C(20)-F(203)	105.9(4)	F(202)-C(20)-F(203)	104.9(4)

Table III (Continued)

Bond Angles			
Complex 2			
O(19)–Ca–O(22)	141.1(1)	O(2)–Ca–O(24)	83.7(1)
O(5)–Ca–O(24)	135.8(1)	O(8)–Ca–O(24)	126.4(1)
O(11)–Ca–O(24)	82.9(1)	O(17)–Ca–O(24)	76.9(1)
O(19)–Ca–O(24)	146.2(1)	O(22)–Ca–O(24)	71.8(1)
Ca–O(2)–C(1)	123.6(3)	Ca–O(2)–C(3)	120.1(3)
C(1)–O(2)–C(3)	114.4(4)	O(2)–C(3)–C(4)	109.4(4)
C(3)–C(4)–O(5)	108.7(5)	Ca–O(5)–C(4)	112.8(2)
Ca–O(5)–C(6)	112.6(2)	C(4)–O(5)–C(6)	111.8(4)
O(5)–C(6)–C(7)	107.6(4)	C(6)–C(7)–O(8)	107.4(3)
Ca–O(8)–C(7)	112.5(2)	Ca–O(8)–C(9)	113.9(2)
C(7)–O(8)–C(9)	112.5(3)	O(8)–C(9)–C(10)	107.6(4)
C(9)–C(10)–O(11)	108.9(3)	Ca–O(11)–C(10)	117.8(3)
Ca–O(11)–C(12)	123.1(2)	C(10)–O(11)–C(12)	115.1(3)
O(11)–C(12)–C(13)	109.2(4)	C(12)–C(13)–O(14)	107.6(4)
C(13)–O(14)–C(15)	111.2(4)	F(161)–C(16)–F(162)	105.4(6)
F(161)–C(16)–F(163)	104.0(6)	F(162)–C(16)–F(163)	107.0(5)
F(164)–C(16)–F(165)	106.6(7)	F(164)–C(16)–F(166)	105.9(7)
F(165)–C(16)–F(166)	102.6(6)	F(161)–C(16)–C(17)	116.4(4)
Complex 3			
O(2)–Ba–O(5)	56.8(2)	O(2)–Ba–O(8)	109.8(2)
O(5)–Ba–O(8)	58.0(2)	O(2)–Ba–O(11)	144.7(2)
O(5)–Ba–O(11)	114.7(2)	O(8)–Ba–O(11)	57.8(2)
O(2)–Ba–O(14)	75.2(2)	O(5)–Ba–O(14)	97.3(2)
O(8)–Ba–O(14)	89.9(2)	O(11)–Ba–O(14)	72.1(2)
O(2)–Ba–O(16)	94.4(2)	O(5)–Ba–O(16)	150.2(2)
O(8)–Ba–O(16)	139.8(2)	O(11)–Ba–O(16)	83.8(2)
O(14)–Ba–O(16)	65.1(1)	O(2)–Ba–O(19)	76.0(2)
O(5)–Ba–O(19)	89.8(2)	O(8)–Ba–O(19)	126.2(2)
O(11)–Ba–O(19)	139.0(2)	O(14)–Ba–O(19)	139.8(2)
O(16)–Ba–O(19)	89.9(2)	O(2)–Ba–O(21)	132.1(2)
O(5)–Ba–O(21)	95.0(2)	O(8)–Ba–O(21)	75.4(1)
O(11)–Ba–O(21)	79.8(2)	O(14)–Ba–O(21)	151.9(2)
O(16)–Ba–O(21)	111.8(2)	O(19)–Ba–O(21)	65.1(2)
Ba–O(2)–C(1)	113.9(8)	Ba–O(2)–C(3)	115.3(8)
C(1)–O(2)–C(3)	121.6(1)	O(2)–C(3)–C(4)	116.5(12)
C(3)–C(4)–O(5)	110.1(10)	Ba–O(5)–C(4)	121.6(5)
Ba–O(5)–C(6)	121.2(6)	C(4)–O(5)–C(6)	112.0(7)
O(5)–C(6)–C(7)	107.0(7)	C(6)–C(7)–O(8)	108.4(7)
Ba–O(8)–C(7)	108.0(4)	Ba–O(8)–C(9)	108.7(4)
C(7)–O(8)–C(9)	114.5(7)	O(8)–C(9)–C(10)	108.4(7)
C(9)–C(10)–O(11)	110.1(7)	Ba–O(11)–C(10)	118.0(6)
Ba–O(11)–C(12)	118.5(5)	C(10)–O(11)–C(12)	111.8(6)
C(131)–C(13)–C(132)	108.0(9)	C(131)–C(13)–C(133)	108.8(12)
C(132)–C(13)–C(133)	108.8(10)	C(133)–C(13)–C(14)	108.3(9)
C(132)–C(13)–C(14)	107.5(8)	C(133)–C(13)–C(15)	115.2(7)
C(13)–C(14)–O(14)	114.9(6)	C(13)–C(14)–C(15)	120.2(7)
O(14)–C(14)–C(15)	124.8(7)	Ba–O(14)–C(14)	137.8(4)
C(14)–C(15)–C(16)	126.0(7)	C(15)–C(16)–O(16)	123.9(6)
C(15)–C(16)–C(17)	119.8(7)	O(16)–C(16)–C(17)	116.3(6)
Ba–O(16)–C(16)	137.8(5)	C(16)–C(17)–C(171)	114.6(7)
C(16)–C(17)–C(172)	106.6(7)	C(171)–C(17)–C(172)	109.0(8)
C(16)–C(17)–C(173)	108.4(7)	C(171)–C(17)–C(173)	109.1(9)
C(172)–C(17)–C(173)	108.9(8)	C(181)–C(18)–C(182)	108.3(11)
C(181)–C(18)–C(183)	109.8(10)	C(182)–C(18)–C(183)	107.1(8)
C(181)–C(18)–C(19)	109.0(7)	C(182)–C(18)–C(19)	109.6(8)
C(183)–C(18)–C(19)	113.0(8)	C(18)–C(19)–O(19)	115.3(7)
C(18)–C(19)–C(20)	120.8(7)	O(19)–C(19)–C(20)	123.9(6)
Ba–O(19)–C(19)	139.8(5)	C(19)–C(20)–C(21)	128.3(6)
C(20)–C(21)–O(21)	123.7(7)	C(20)–C(21)–C(22)	120.7(6)
O(21)–C(21)–C(22)	115.7(6)	Ba–O(21)–C(21)	139.3(5)
C(21)–C(22)–C(221)	108.6(7)	C(21)–C(22)–C(222)	107.5(8)
C(221)–C(22)–C(222)	107.8(9)	C(21)–C(22)–C(223)	114.7(7)
C(221)–C(22)–C(223)	105.8(9)	C(222)–C(22)–C(223)	112.2(8)

For complex 3 all *tert*-butyl groups display a degree of rotational disorder. However, this disorder could not be resolved into alternative partial occupancy orientations.

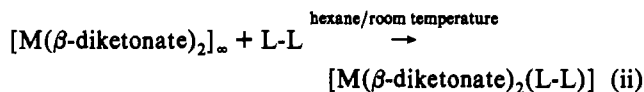
The fractional coordinates for 1–3 are given in Table II and selected bond lengths and angles in Table III.

## Results and Discussion

**Synthesis.** The reaction of the preformed metal ethoxides<sup>8</sup>  $[M(OEt)_2(EtOH)_4]_n$  of the heavier alkaline earth metals, Ca and Ba with tetramethylheptane-2,4-dione in hexane have been previously shown by us to yield the homoleptic base free complexes,  $[M(thd)_2]_n$  as shown in eq i.<sup>9</sup> These materials are known to be highly sensitive to both moisture, heat and the presence of external Lewis bases; given these shortcomings we have sought to eliminate these handling problems. Our approach relies on the prior knowledge that the group IIA cations are not only hard acids but also require high coordination numbers before coordinative saturation is reached.<sup>11</sup> We have investigated the reaction of the homoleptic  $\beta$ -diketonates with chelating O-donor Lewis base ligands, relying on the chelate effect to achieve our objective and realizing that these alkaline earth metal  $\beta$ -diketonate aggregates will be readily cleaved by strong multidendate Lewis bases such as glymes.

The *in situ* reaction of the preformed alkaline earth metal  $\beta$ -diketonates with O-donor glyme ligands (defined as L-L) has been found to yield *monomeric* air stable products in 10 min at ambient temperature as shown in eq ii.

A wide variety of complexes may be made by this route, and we have picked out several examples to illustrate this strategy.



First, the reaction of  $[Ca(thd)_2]_n$  with triglyme over a period of 10 min. in hexane at room temperature produces the monomeric triglyme adduct  $[Ca(thd)_2(\text{triglyme})]$  (1); a similar reaction (using a fluorinated  $\beta$ -diketonate) with the complex  $[Ca(hfa)_2]_n$  and tetraglyme yields the species  $[Ca(hfa)_2(\text{tetraglyme})]$  (2), while the related complex  $[Ba(thd)_2(\text{triglyme})]$  (3) is prepared by a similar route to 1. All of the complexes are obtained as colorless crystals in excellent yield on crystallization from *n*-hexane as air/moisture stable materials.

This synthetic strategy may be compared with other routes to alkaline earth metal  $\beta$ -diketonates. Purdy *et al.* have used the bulk metal as the starting source of the alkaline earth metal  $\beta$ -diketonates with the ligand suspended in THF and the reaction mixture refluxed for a period of several days, resulting in poor to low yields of products being obtained.<sup>12</sup> Other researchers have used the metal hydroxide route, e.g.  $Ba(OH)_2 \cdot 8H_2O$  and *thd*-H to yield the hydrated cluster  $Ba_5(OH)(thd)_9(H_2O)_3$ ,<sup>3</sup> and also separately with *hfa*-H the oligomeric complex  $[Ba(hfa)_2(H_2O)]_n$  is obtained.<sup>5</sup> Since both of these barium complexes contain coordinated water, they consequently have poor mass transport properties and volatility. Finally, a recent report has used  $BaCO_3$  as the barium source and its reaction with the acidic ligand *hfa*-H in EtOH to yield hydrated metal

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

$\beta$ -diketonates stabilized by crown ethers.<sup>13</sup> Commercial sources of these materials have also been shown to be hydrated materials, e.g.  $[\text{Ca}(\text{hfa})_2(\text{H}_2\text{O})_2]_2$  and  $[\text{Ba}(\text{hfa})_2(\text{H}_2\text{O})]_\infty$ .<sup>5</sup> When more rigorous synthetic techniques are used, the Lewis base solvated complexes  $[\text{Ba}_2(\text{thd})_4(\text{L})_2]$   $\{\text{L} = \text{NH}_3$  or  $\text{THF}\}$  are obtained.<sup>4</sup>

Our alternative strategy uses crystalline hydrocarbon soluble metal ethoxides, which may be readily prepared from the bulk metal (using a careful prewash sequence to ensure all metal oxide and metal hydroxide contamination on the metal surface is thoroughly removed) and used as soluble sources of the metals.<sup>9</sup> Such materials are of fundamental importance in expanding the area of group IIA alkoxide/ $\beta$ -diketonate chemistry. These materials have an important advantage over previous routes in that they yield *reproducible oxo- and water-free products* provided that anaerobic techniques are used. These materials are of considerable importance since reaction stoichiometry may now be precisely controlled. This is not generally possible with commercial metal hydrides, since they are notoriously unreliable and the reactivity varies greatly from batch to batch.

If 2 equiv of a glyme ligand is used in the preparations of 1–3, then generally an oily product results. This possibly implies that the complexes are highly soluble in an excess of the Lewis base, presumably forming more highly ligated complexes.

**Spectroscopic Data.** The formulation of these complexes as monomeric species is entirely consistent with the data acquired from IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass spectrometry, and microanalysis.

**IR Spectroscopic Data.** The IR spectra of complexes 1–3 (hexachlorobutadiene) show characteristic bands for the  $\beta$ -diketonates, with strong absorption bands in the region 1570–1635  $[\text{C}^--\text{O}$ , note in parent thd-H ligand 1605  $\text{cm}^{-1}$  and 1500–1540  $\text{C}=\text{C}$ ]. Precise assignment of the different  $\text{C}^--\text{C}$  and  $\text{C}^--\text{O}$  modes is at present not possible since it appears that some of the bands may be coupled.

The bands assigned as  $\nu(\text{C}-\text{O}-\text{C})$  in these complexes for the glyme ligands occur at slightly lower frequencies than the same peaks for the free ligands (either triglyme or tetraglyme), 1350–1360, 1270, and 1220  $\text{cm}^{-1}$  and also at 1110  $\text{cm}^{-1}$ . The shifts from the free parent ligand are ca. 20  $\text{cm}^{-1}$ , indicative of coordinated glyme ligands with relatively weak M–O interactions.<sup>14</sup>

**NMR Spectroscopic Data.** The  $^1\text{H}$  NMR spectra of the complexes in benzene- $d_6$  are recorded in Table IV and exhibit characteristic signals for one type of  $\beta$ -diketonate and glyme ligand environment at room temperature. The integration ratio of  $\beta$ -diketonate to glyme was found to be 2:1. A small shift downfield of the methylene signals in the glyme ligands is observed on coordination to the alkaline earth metal cations Ca and Ba.

The  $^{13}\text{C}$  NMR spectra (see Table IV) have been assigned by direct comparison with both free ligands and the parent homoleptic complexes,  $[\text{M}(\beta\text{-diketonate})_2]_\infty$ . The signals for the methyl and quaternary carbon have been shifted to lower field, whereas those for the CH and CO are shifted to higher field with respect to the parent ligand thd-H. This effect has been observed previously and was ascribed to the formation of an electron rich 1,3-diketonato chelating ring system. The electron density accumulates on the carbon atoms of the ring system (*i.e.* CH and CO), and this therefore results in electron withdrawal from the Bu<sup>t</sup> groups and a resulting deshielding occurs.

For the complex  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]$  (2) similar features are observed in the  $^{13}\text{C}$  NMR, with additional features due to the presence of a  $\text{CF}_3$  group. The glyme ligands also show small changes in chemical shift on coordination, and these may be correlated with the formation of the chelating ring systems.

**Mass Spectrometry.** Mass spectroscopic data (positive ion mode) for complex 1 shows not only the expected monomeric

**Table IV.** Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectroscopic Data for Complexes 1–3

compound	$^1\text{H}^a$	$^{13}\text{C}^b$
<i>Triglyme</i> $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2)_2$		
1	1.33 (s, 36H)	28.83 (s, Me), 40.56 (s, $\text{CMe}_3$ )
	3.16 (s, 6H, a)	58.66 (s, OMe, a)
	3.10 (m, 4H, b)	69.04 (s, $\text{OCH}_2$ , b)
	3.28 (m, 4H, c)	69.45 (s, $\text{OCH}_2$ , c)
	3.47 (s, 4H, d)	71.04 (s, $\text{OCH}_2$ , d)
	5.80 (s, 2H)	87.30 (s, CH), 197.31 (s, CO)
3	1.32 (s, 36H)	28.83 (s, Me), 40.65 (s, $\text{CMe}_3$ )
	3.14 (s, 6H a)	58.22 (s, OMe, a)
	3.11 (m, 4H b)	69.20 (s, $\text{OCH}_2$ , b)
	3.17 (m, 4H c)	69.31 (s, $\text{OCH}_2$ , c)
	3.19 (s, 4H d)	70.56 (s, $\text{OCH}_2$ , d)
	5.80 (s, 2H)	87.21 (s, CH), 196.78 (s, CO)
<i>Tetraglyme</i> $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{O}$		
2	3.05 (s, 6H, a)	58.79 (s, OMe, a)
	2.95 (s, 4H, b)	68.64 (s, $\text{OCH}_2$ , b)
	3.12 (m, 4H, c)	69.91 (s, $\text{OCH}_2$ , c)
	3.14 (s, 4H, d)	70.31 (s, $\text{OCH}_2$ , d)
	3.18 (s, 4H, e)	71.28 (s, $\text{OCH}_2$ , e)
	6.29 (s, 2H)	88.18 (s, CH)
		118.80 (q, $\text{CF}_3$ , $^1J = 296$ Hz)
		176.32 (q, CO, $^2J = 32$ Hz)

<sup>a</sup> All  $^1\text{H}$  NMR spectra were run in  $\text{C}_6\text{D}_6$  at 270 MHz. <sup>b</sup> All  $^{13}\text{C}$  NMR spectra were run at 67.94 MHz in  $\text{C}_6\text{D}_6$ .

species e.g.  $[\text{Ca}(\text{thd})_2(\text{triglyme})]$  (1) with  $m/z$  629 but also *more intense peaks* due to  $[\text{Ca}_2(\text{thd})_4]$  at  $m/z$  813. Cleavage of both the thd and glyme ligands is observed, with a peak at  $m/z$  59 corresponding to a glyme fragment  $[\text{CH}_3\text{CH}_2\text{OCH}_3]^+$ . For complex 1 other intense peaks are observed at  $m/z$  349 for  $[\text{Ca}(\text{thd})(\text{Bu}^t\text{COCHCO})]^+$  and at  $m/z$  321 for  $[\text{Ca}(\text{thd})(\text{Bu}^t\text{COCH})]$ . The related barium complex (3) shows a weak molecular ion at  $m/z$  680 for  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  and in a similar fashion to that of 1 shows more intense peaks due to oligomeric complexes, e.g.  $[\text{Ba}_2(\text{thd})_3]$  and  $[\text{Ba}(\text{thd})]$ , with  $m/z$  824 and 321, respectively.<sup>7</sup>

The calcium complex (2) shows dissimilar behaviour to both 1 and 3 with a very strong molecular ion being observed at  $m/z$  716 corresponding to  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]$  and subsequent cleavage of the hfa ligand to yield  $[\text{Ca}(\text{hfa})(\text{CF}_3\text{COCHCO})-(\text{tetraglyme})]$  with a mass of 646 amu and lower mass species including  $[\text{Ca}(\text{hfa})(\text{tetraglyme})]^+$  at 509 amu and  $[\text{Ca}(\text{hfa})]^+$  at 247 amu.

This data implies that in the vapor state the thd complexes 1 and 3 dissociate to form the oligomeric donor–Lewis base free complexes,  $[\text{M}(\text{thd})_2]_\infty$ . Such behavior is important because as O-donor adducts we can now deliver these materials at a lower temperature than has previously been observed. The corresponding calcium hexafluoroacetylacetonate complex (2) is comparatively stable in the vapor phase and exists as a monomeric Lewis base adducted species.

**Physical Properties.** All of the complexes (1–3) (see Table V) have extensive solubility in both aliphatic and aromatic solvents and show appreciable solubility in coordinating solvents such as ethers (*i.e.* diethyl ether and THF). This pronounced solubility is undoubtedly due to the presence of both glyme and  $\beta$ -diketonate ligands chelating to the metal center. These materials are all air/moisture stable, and hence water coordination to these materials is thus less likely to occur. The glyme stabilized complexes all have relatively low melting points (see Table V) in the range 71–85 °C at atmospheric pressure. This is a significant reduction in melting point when compared to their parent materials, (e.g.  $[\text{Ca}(\text{thd})_2]_\infty$ , 179–181 °C;  $[\text{Ca}(\text{hfa})_2]_\infty$ , 132–135 °C; and  $[\text{Ba}(\text{thd})_2]_\infty$ , 194–197 °C). Sublimation studies are in accord with these results and also our mass spectroscopic

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(14) Iwamoto, R. *Spectrochimica Acta* 1971, 27A, 2385.

Table V. Selected Microanalytical, Solubility, and Melting Point Data for Complexes 1–3

compound	microanal. (%) <sup>a</sup>		solubility <sup>b</sup>				mp/ <sup>c</sup> °C	air/moisture stability	volatility <sup>d</sup> /°C
	C	H	ethers	aromatics	alkanes	others			
[Ca(thd) <sub>2</sub> (triglyme)] (1)	61.8 (61.6)	9.7 (9.6)	soluble	soluble	soluble	soluble in DMSO	71–74	stable	decomp to [Ca(thd) <sub>2</sub> ] <sub>n</sub>
[Ca(hfa) <sub>2</sub> (tetraglyme)] (2)	35.6 (35.5)	3.7 (3.6)	soluble	soluble	soluble (hot)	soluble in DMSO	82–85	v stable	130–150
[Ba(thd) <sub>2</sub> (triglyme)] (3)	53.1 (53.0)	8.0 (7.9)	v soluble	v soluble	soluble	v soluble in DMSO	77–79	v stable	decomp to [Ba(thd) <sub>2</sub> ]

<sup>a</sup> The calculated values are in parentheses. <sup>b</sup> Typical solvents are diethylether, THF, benzene, toluene, *n*-hexane, or *n*-heptane. <sup>c</sup> Uncorrected values; tubes sealed under argon. <sup>d</sup> All sublimations at 10<sup>-3</sup> Torr.

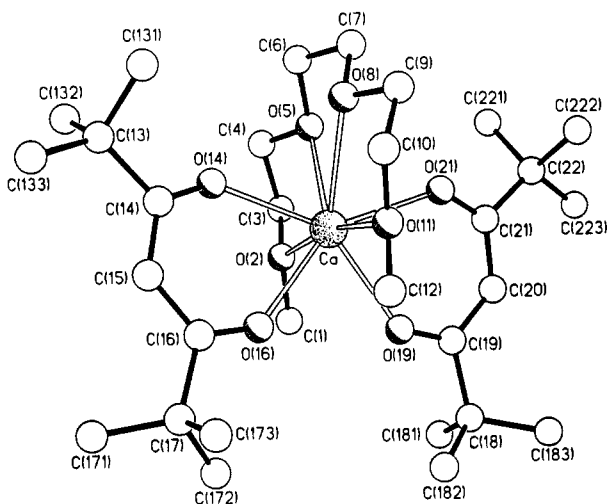


Figure 1. Molecular structure of [Ca(thd)<sub>2</sub>(triglyme)] (1) showing the atom numbering scheme. H-atoms and minor occupancy 'Bu carbon atoms have been omitted for clarity.

data; thus, complexes 1 and 3 decompose (100 °C and 10<sup>-3</sup> Torr) to yield the unadducted thd complexes, while the calcium hfa complex (2) is stable and sublimates at 130–150 °C and 10<sup>-3</sup> Torr. This difference in stability between thd and hfa complexes may possibly be ascribed to both steric and electronic effects due to the R-groups (i.e. Bu<sup>+</sup> vs Me vs F<sub>3</sub>C); thus, in the gas phase, the binding of triglyme to the metal center is considerably weakened, when a thd ligand chelates. This is an important observation since we may thus use the adducted thd complexes of calcium and barium as low temperature "anhydrous" sources of the parent thd complexes.

As the nature of the complexes 1–3 could not be fully elucidated by spectroscopic investigation, X-ray single-crystal structural studies were undertaken to unambiguously identify their structural conformations, i.e. to determine whether the all the potential ligand O-donor sites are bound to the metal centres.

**Single-Crystal X-ray Structures.** [Ca(thd)<sub>2</sub>(triglyme)] (1). The single crystal X-ray structure of complex 1 is illustrated in Figure 1. The solid-state stoichiometry is in accord with the experimental data (Tables IV and V and Experimental Section). The calcium atom is eight coordinate with all of the oxygens of both the thd ligands and the triglyme ligand binding to the metal atom.

In this compound the triglyme is observed to be lying in an meridional plane, with the thd  $\beta$ -diketonate ligands lying respectively above and below the plane in an approximately orthogonal relationship. Given the slight twists in all of the ligands, the overall geometry may formally be described as a distorted propeller. The coordination polyhedron may be considered as a distorted square antiprismatic with O–O distances in the range 2.34–2.68 Å.

Other researchers have previously studied the nature of the interaction of polydentate ether ligands with a wide range of metal halide complexes. Notable contributions include the seminal work of Iwamoto with mercuric chloride,<sup>15</sup> and cadmium chloride.<sup>16</sup> An intriguing feature of the structure of

[HgCl<sub>2</sub>(hexaglyme)] is reported which reveals that the hexaglyme coordinates to two HgCl<sub>2</sub> molecules. Notable contributions have also come from Meerssche *et al.* on glyme stabilized halides and pseudo-halides of the alkaline earths, e.g. Ba(SCN)<sub>2</sub>(tetraglyme).<sup>17</sup>

The Ca–O distances are found to lie in two definite groups. The first for the thd ligands, are in the range from 2.348(2) [O(19)] to 2.379(2) Å [O(21)], while the second are those due to the triglyme oxygens, and are observed in the range from 2.471(3) [O(2)] to 2.594(3) Å [O(5)]. A related calcium complex [Ca<sub>4</sub>(dpp)<sub>8</sub>(EtOH)<sub>2</sub>] is tetrameric with an average Ca–O distance of 2.37 Å. In this complex the calcium coordination numbers are only 6 or 7, due to the congestion of the ligands around the four bridged calcium centers.<sup>18</sup> Further interesting comparisons may be made with the monomeric [Ca(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-H<sub>2</sub>O, in which an octahedral environment is observed for the metal center with an average Ca–O distance of 2.33 Å.<sup>19</sup> A more recent study by Bradley *et al.* has reported the dimeric species [Ca(hfa)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> in which the calcium atoms are both 8-coordinate.<sup>5</sup> The dimeric arrangement arises from Ca<sup>2+</sup>-F-C bridging via CF<sub>3</sub> groups and a further chelating hfa ligand which also bridges the two calciums through one of the oxygens. The average Ca–O distance in this complex was observed to be 2.44 Å, the longer distance primarily being due to the Ca–O bridging hfa ligand between the two metal centres.

It is noteworthy that the two outer glyme oxygens [O(2) and O(11)] bind significantly closer [2.471(3) and 2.492(3) Å] to the calcium than the two central atoms of the polyether chain O(5) and O(8) [2.578(2) and 2.594(3) Å]. This is probably due to the different steric constraints imposed by the two equatorial thd ligands.

[Ca(hfa)<sub>2</sub>(tetraglyme)] (2). The single-crystal X-ray structure of complex 2 is shown in Figure 2. The crystal structure of this complex provides an interesting contrast to that of complex (1). The gross structure is very similar to that of 1 with the calcium atom binding to two bidentate hfa ligands and to four oxygen atoms of the tetraglyme. Despite the apparent space around the calcium center observed in 1, the fifth glyme oxygen atom O(14) is not coordinated to the calcium. Thus the calcium atom prefers to adopt an eight rather than a possible nine coordination mode. The coordination polyhedron of 2 is very similar to that exhibited by 1, being again best described as distorted square antiprismatic.

In this molecule as for 1 the Ca–O bond distances fall into two clearly defined groups, those to the tetraglyme, which lie in the range from 2.434(3) [O(2)] to 2.497(3) Å [O(5)], and those to the  $\beta$ -diketonate ligands, which are between 2.395(3) [O(24)] and 2.410(3) Å [O(22)]. There are no observed short Ca<sup>2+</sup>-F contacts in 2 as has been recently observed in [Ca(hfa)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>.<sup>5</sup>

As in complex 1, both O(2) and O(11) are found to bind closer to the calcium [2.493(3) and 2.497(3) Å, respectively] than O(2)

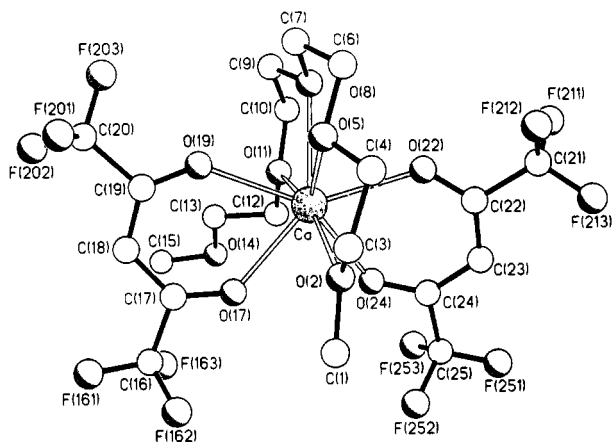
(15) Iwamoto, R. see for example: *Bull. Chem. Soc. Jpn.* 1973, 46, 1114, 1118, 1123, and 1127 and references therein.

(16) Iwamoto, R.; Wakano, H. *J. Am. Chem. Soc.* 1976, 98, 3764.

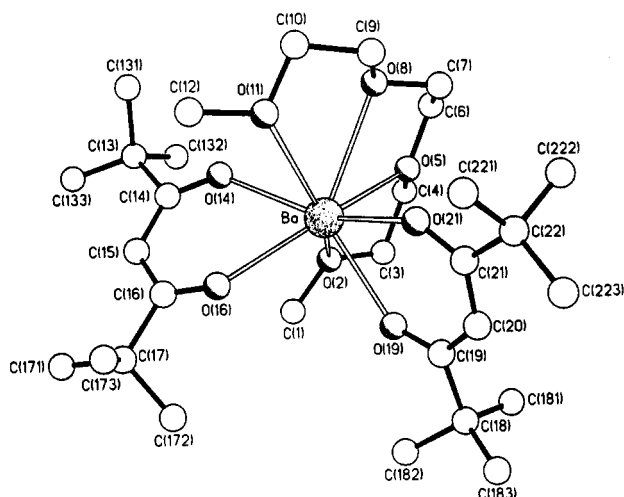
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(19) Sahbari, J. J.; Olmstead, M. M. *Acta Crystallogr.* 1983, C39, 208.



**Figure 2.** Molecular structure of  $[\text{Ca}(\text{hfa})_2(\text{tetraglyme})]$  (**2**) showing the atom numbering scheme. H-atoms and minor occupancy  $\text{CF}_3$  fluorine atoms have been omitted for clarity.



**Figure 3.** Molecular structure of  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (**3**) showing the atom numbering scheme. H-atoms have been omitted for clarity.

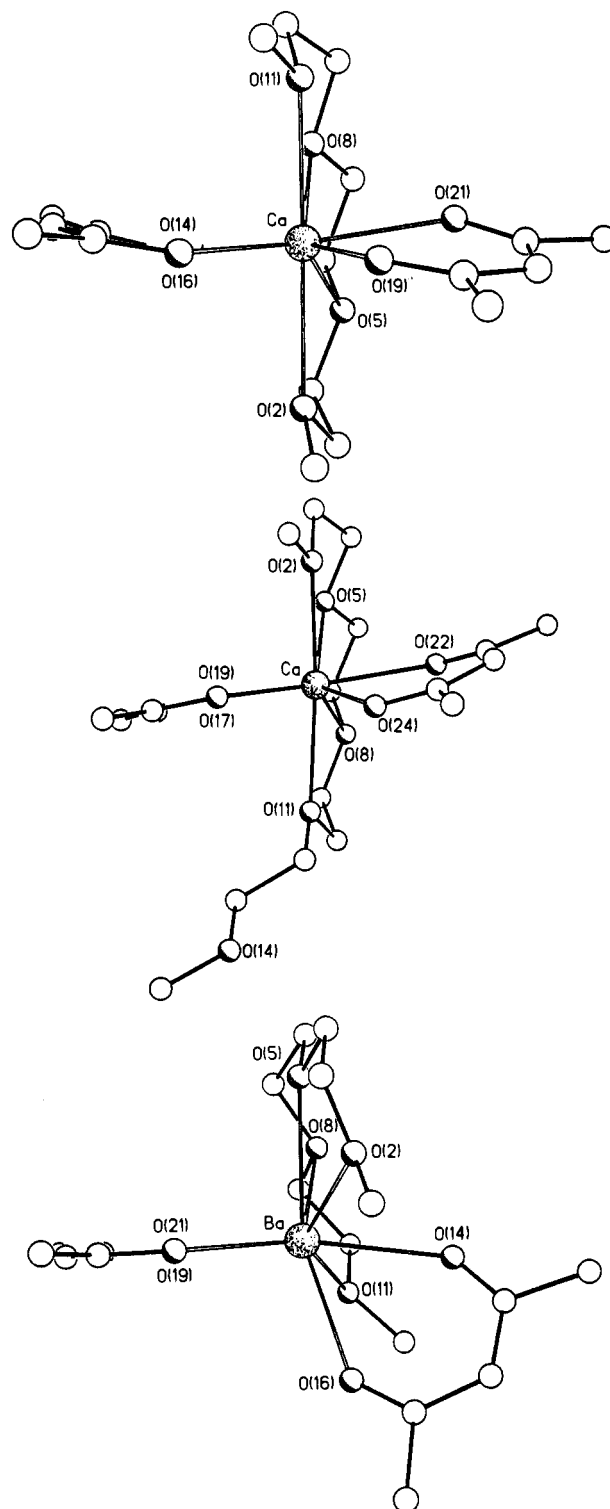
and O(8) [2.434(3) and 2.449(3) Å, respectively]; this effect is attributed to steric factors.

The most noticeable feature of **2** is the uncoordinated portion of the glyme chain C(12)–C(15) which is essentially planar, though this portion of the ligand chain is rotated through ca.  $86^\circ$  about O(11)–C(12) relative to C(10)–O(11). Furthermore, the conventional gauche and anti sequence about the C–C and C–O bonds present in the remainder of the tetraglyme is also destroyed, with the geometry about C(12)–C(13) being anti.

A study of the space-filling model of **2** indicates that the coordination of an additional glyme oxygen center is sterically prohibited, the van der Waals circumference not being large enough to accommodate an additional meridional coordination site without changing significantly the coordination geometry about the calcium center.

$[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (**3**). The single crystal X-ray structure of  $[\text{Ba}(\text{thd})_2(\text{triglyme})]$  (**3**) is shown in Figure 3. As in the related calcium complex (**1**), the barium ion is eight coordinate, binding to both the  $\beta$ -diketonate thd ligands and to all four oxygens of the triglyme ligand. The glyme is observed to be chelating in one plane, and the two thd  $\beta$ -diketonate ligands are oriented above and below this plane. The structure may be described as a distorted propellane type geometry.

The coordination polyhedron can be best described as bicapped trigonal prismatic, with O(2) and O(8) as the capping atoms. The Ba–O bond distances fall into two discrete groups. Those to the  $\beta$ -diketonate are in the range between 2.621(5) [O(10)] and 2.643(5) Å [O(21)], while those to the glyme oxygens are in the range between 2.814(6) [O(5)] and 2.900(6) Å [O(11)].



**Figure 4.** Top to bottom: Perspective views of the complexes (a) **1**, (b) **2**, and (c) **3**, showing the different twists of the  $\beta$ -diketonate ligands relative to the plane of the glyme ligands. The  $\text{Bu}^t$  and  $\text{CF}_3$  groups have been omitted for clarity.

These distances are broadly similar to those for the  $\beta$ -diketonate distances in the recently characterized complexes  $[\text{Ba}(\text{hfa})_2(\text{tetraglyme})]$ ,<sup>7</sup>  $[\text{Ba}(\text{hfa})_2(18\text{-crown-6})]$ ,<sup>6</sup> and dimeric  $[\text{Ba}(\text{thd})_2(\text{Et}_2\text{O})_2]$ .<sup>5</sup>

The polyether ligand again adopts a fairly conventional geometry with gauche and anti relationships around the C–C and C–O bonds, respectively. The pattern of two short and two long M–O<sub>(glyme)</sub> bonds observed in compounds **1** and **2** is noticeably absent in **3**.

A final comparison may be made of all three structures, in terms of dihedral angles between the planes of the  $\beta$ -diketonate



ligands and their dispositions with respect to the glymes. In complex **1** the dihedral angle between the planes formed by O(14)–Ca–O(16) and O(19)–Ca–O(21) is ca. 11°. Figure 4a illustrates this deviation from planarity of the two thd ligands, and the appreciable degree of “puckering” of the rings.

In the related calcium complex (**2**) (Figure 4b) the dihedral angle is ca. 14° between the plane formed by O(17)–Ca–O(19) and O(22)–Ca–O(24). This slightly larger dihedral angle and deviation from coplanarity of the two hfa ligands may be due to the greater saturation of the metal centre. The puckering associated with the thd ligands in **1** is noticeably reduced in complex **2** and is most pronounced in that associated with O(17)–Ca–O(19). There is a marked change on going from calcium to barium as might be expected; this can be described in several different ways. Although the coordination number of eight remains constant throughout the series (complexes **1**–**3**), the coordination polyhedron does change and for barium is bicapped trigonal prismatic (cf. square antiprismatic for complexes **1** and **2**).

The principal change in coordination geometry is due to the steeply inclined relationship of the two thd ligands. These are inclined by ca. 70° (cf. 11–14° for **1** and **2**). The mean plane of the glyme ligand is still essentially orthogonal to one of the thd ligands (see Figure 4c), although of necessity the ends of the glyme chain are markedly displaced relative to the plane of one of the  $\beta$ -diketonate groups. In complexes **1** and **2** the terminal methyl groups of the triglyme components are approximately equidistant above and below one of the  $\beta$ -diketonate ligand planes. In **3** they are almost coincident with one of the ligand planes. The major changes in coordination geometry on going from calcium to barium may be attributed to the different ionic radii (Ca, 1.03 Å; Ba, 1.36 Å). Thus in **3** there is larger hemisphere of space around which the ligands may orient themselves, which results in the thd ligands deviating significantly from coplanarity.

### Conclusions

The X-ray structural characterization of a range of alkaline earth metal  $\beta$ -diketonates stabilized by glyme donor ligands has demonstrated that tailored synthetic strategies can and do work for the heavier metals of group IIA. It is our belief that this strategy has wide scope in developing the chemistry of the metallic organic complexes of this group, which have until recently focused principally on the cyclopentadienyls and pentamethylcyclopentadienyls.

There are several features that are important: (i) this strategy of using a metal  $\beta$ -diketonate prepared from crystalline metal alkoxides is the first example for group IIA complexes and yields *anhydrous* complexes; (ii) the coordinative saturation of the hard acid metal centers by the multidentate Lewis base chelates and  $\beta$ -diketonates leads to *air and moisture stable* precursors of known stoichiometry and is thus highly flexible since L-L may be varied with the use of either O or N functionalized chelates; (iii) the designed synthesis of volatile discrete molecular alkaline earth metal organics is now possible without having to use large sterically hindered ligands, e.g.  $\text{Ph}_3\text{CO}^-$ ,  $\text{OC}_6\text{H}_2\text{Bu}^t_3$ . Indeed, our strategy toward a tailored approach for CVD precursors, need not be limited to pure  $\beta$ -diketonates, any ligand of formula (ARBH), where A is generally a pendant potential chelating site, R is the hydrocarbon chain linker, and B is the predominate site of metalation, e.g. chelating alcohols containing a pendant ether or amine functionality, diolates (i.e. pinacol), alkoxy-substituted  $\beta$ -diketonates (e.g.  $\text{RO}\{\text{CH}_2\}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CR}_3$ , mixed alkoxy  $\beta$ -diketonates, or even acetates, may be prepared, as shown in eq iii.



The use of a range of such ligands will reduce the conventional problems of oligomerization and subsequent low volatility. We consider an important requirement when designing alkaline earth molecular precursors to be that sufficient coordinative saturation be incorporated into both ligand and Lewis base chelate, such that a low molecular mass volatile monomer will result. This approach of using a tailored synthetic rational for group IIA molecular precursors is currently being used for control of thin films by CVD, due to their high stability.

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**Supplementary Material Available:** Tables of crystallographic data, anisotropic thermal parameters, and hydrogen atom parameters, and ORTEP drawings (21 pages). Ordering information is given on any current masthead page.

(20) SHELXTL version 4.2, Siemens X-ray Analytical Instruments 1991.