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Synthesis and Single-Crystal X-ray Structure of the Diglyme-Bridged Barium Complex $[Ba(thd)_2(diglyme)]_2$

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Introduction

The use of metal alkoxides or β-diketonates as organometallic chemical vapor deposition (OMCVD) precursors for metal oxides via low-temperature deposition routes is an area of considerable current interest. Their potential application in the field of electroceramics, e.g. in the preparation of $BaMg_{0.33}Ta_{0.66}O_3$ and $BaTiO_3$ is of immense importance.[1] Until recently, suitable advances in the development of organometallic group IIA precursors were severely limited. This scenario has generally arisen due to the poor solubility of such materials, which are normally polymeric, involatile, and insoluble in most common organic solvents. This has been shown to be the case for the simple binary alkoxides of the group IIA metals, e.g. $[Sr(OMe)_2]_\infty$, which is polymeric and lacks any simple molecular subunits.[2]

Commercial interests have focused on the fluorinated acetylacetonate complexes, e.g. $[Ba(hfa)_2]_n$, due to their high volatility and good mass-transport properties.[3] These materials are unsuitable for epitaxial electroceramic metal oxide films due to their contamination by fluoride ions. In order to improve the mass transport and volatility of these and related materials, previous researchers have added a range of Lewis base additives, including ammonia, amines, or glymes, to the carrier gas flows.[4] Such ligands no doubt reduce the amount of oligomerization of the materials in the gas phase. Indeed, both cyclic and open polyethers have previously been shown to significantly improve the volatility of $[Ba(hfa)_2]_n$, which is not itself volatile below 200 °C (10^{-5} Torr),[5] while $[Ba(hfa)_2(tetraglyme)]$[6] and $[Ba(hfa)_2(18\text{-crown-}6)]$[7] sublime at 120 and 150–180 °C at 10^{-3} Torr, respectively. More recently, functionalized β-diketones based on alkoxyalkyl-substituted β-diketones were reported for barium.[8]

We have previously studied a wide range of group IIA molecular precursors for CVD thin-film applications, notably alkoxides,[9] aryloxides,[10] fluorenyls,[11] and siloxides.[12] Of these materials, the methoxyethoxide complex of barium[9] $[H_4Ba_6(O)(OCH_2CH_2OMe)_{14}]$ and the dimeric siloxide complex $[Ba_2(OSiBu^t{}_3)_4(thf)]$ were found to be the most volatile.[12] Drawbacks in their application as CVD precursors arise from their high sensitivity to both moisture and oxygen and more importantly from their relatively high cost.

Other researchers have extensively used either tetramethylheptane-2,4-dionato or hexafluoropentane-2,4-dionato salts of alkaline earth metals, but such materials have been found to be highly dependent not only on their synthesis but also on their "later history". Suitable examples include $[Ba(thd)_2]_\infty$ prepared by an aqueous route which was found to actually be $[Ba_5(OH)(thd)_9{\cdot}nH_2O]$,[13] while the more volatile hexafluoropentane 2,4-dionato salts available commercially have also been shown to be hydrated species, e.g. $[Ba(hfa)_2(H_2O)]_\infty$.[15] Quantification of the role of the water molecule in such precursors is still lacking, but it is unlikely to remain as a noninnocent spectator ligand. Indeed, given previous research on barium alkoxides and aryloxides, it may possibly favor the formation of hydroxo- or oxo-based aggregates.[9] More recently, other researchers prepared $Ba_2(thd)_4(Et_2O)_2$ from a barium/2-propanol concentrate with thd/Et_2O[16] and with $[Ba(thd)_2]_4$ and ammonia in hexane.[17]

As part of our research studies directed toward single-source volatile molecular barium CVD precursors, we have used the barium β-diketonate $[Ba_4(thd)_8]$.[18] We considered that the formally "unsaturated" group IIA metal β-diketonates may be sufficiently acidic and would react similarly to the highly studied alkaline earth metal pentamethylcyclopentadienides.[19] The molecular architecture of such complexes may possibly be suitably modified by adding a "multipronged" Lewis base, such as glymes or amines, thereby effectively plugging possible vacant coordination sites, e.g. $[Ba(hfa)_2(tetraglyme)]$.[6]

Herein we report the reaction of $[Ba_4(thd)_8]$ with diglyme $[Me\{OCH_2CH_2\}_2OCH_3]$ in hexane at ambient temperature, which yields a material of empirical formula $[Ba_2(thd)_4{\cdot}(diglyme)_2]$.

Experimental Section

General Procedures. The manipulations of all reactants and products were carried out under a nitrogen atmosphere (Schlenk line), under an argon atmosphere (Miller-Howe recirculating glovebox), or *in vacuo*,

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Table I. Crystallographic Data for $[Ba_2(C_{11}H_{19}O_2)_4(C_6H_{14}O_3)_2]$

chem formula	$[Ba_2(C_{11}H_{19}O_2)_4$ $(C_6H_{14}O_3)_2]$	fw	1276.088
cryst syst	triclinic	space group	$P\bar{1}$
a/Å	10.431(6)	b/Å	10.441(6)
c/Å	15.955(7)	α/deg	72.11(4)
β/deg	76.52(3)	γ/deg	84.33(3)
Z	1	V/Å^3	1607.39
D_c/g cm^{-3}	1.318	μ(Mo Kα)/cm^{-1}	12.7
T/K	150	θ range/deg	2.1–29.5
R^a	0.030	$R_w{}^b$	0.036

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

with rigorous exclusion of moisture and air. The solvent *n*-hexane was predried over 4A molecular sieves, distilled over sodium prior to use, and then stored over 4A molecular sieves under an atmosphere of nitrogen in a glass storage vessel fitted with a greaseless J. 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^{-1}. The NMR spectra were recorded on a JEOL GS 270 at 270 MHz in dry and oxygen-free C_6D_6 or dmso-d_6 as appropriate, using the protio impurities of the deuterated solvents as reference for ^{1}H NMR and ^{13}C NMR resonances of the solvent as a reference for ^{13}C NMR. Elemental analyses were performed by Butterworth Laboratories, and the compound was handled in an inert atmosphere. Mass spectroscopic data were obtained on a Kratos MS 30 by the Royal School of Pharmacy Mass Spectrometry Service, University of London. The melting point is an uncorrected value, with the sample sealed under argon.

Controlled thermal analysis of the complex was investigated using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by a Omni Pro 486DX-33 PC connected to a Rioch 1200 laser printer. The weight of the sample investigated was 19 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.

Chemicals. 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 was obtained from Inorgtech of Mildenhall, and diglyme, from Aldrich Chemicals. The barium ethoxide $[Ba(OEt)_2(EtOH)_4]_\infty$ was prepared according to a literature procedure.[14]

Synthesis of $[Ba(thd)_2(diglyme)]_2$. $[Ba_4(thd)_8]$ (2.01 g, 4.89 mmol) was weighed into a Schlenk tube and *n*-hexane (20 mL) added. To the resulting clear solution was added diglyme (1.1 mL, 4.90 mmol), and the reaction mixture was 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 (10 mL) and left to crystallize at –35 °C. Yield: 3.0 g, 85% based on barium. Anal. Calcd (found) for $C_{28}H_{50}O_7$-Ba: C, 52.89 (52.73); H, 7.92 (7.87). Mp: 93–95 °C. IR (Nujol; ν, cm^{-1}); 1588 (m), 1571 (m), 1535 (w), 1504 (m), 1356 (s), 1289 (w), 1272 (w), 1248 (m), 1223 (w), 1184 (w), 1126 (m), 1093 (m), 1066 (s), 1010 (w), 950 (w), 861 (w), 833 (w), 790 (m), 757 (w), 732 (m), 593 (m). ^{1}H NMR (270 MHz, 25 °C, C_6D_6): δ 1.28 (36H, s, Me), 3.17 (4H, m, OCH_2-b), 3.18 (6H, s, OCH_3), 3.20 (4H, m, OCH_2-a), 5.80 (4H, s, CH). $^{13}C\{^1H\}$ NMR (67.94 MHz, 25 °C, C_6D_6): δ 28.74 (s, Me), 41.84 (s, CMe_3), 58.13 (s, OMe), 69.41 (s, OCH_2-b), 71.14 (s, OCH_2-a), 89.05 (s, CH), 198.42 (s, CO). MS (EI positive ion): m/z 833 $[Ba_2(thd)_3]$, 448 $[Ba(thd)(Bu^tCOCHCOH)]$, 321 [Ba(thd)], 271 [Ba(diglyme)].

Single-Crystal X-ray Analysis. A summary of the crystallographic data for complex **1** is given in Table I. The X-ray measurements were made on a crystal mounted using silicone oil and transferred to a goniostat. The data were collected at 150 K on a Delft Instruments FAST TV area detector diffractometer equipped with a rotating anode FR591 generator (50 kV, 50 mA), a bufferboard and DEP image intensifier with Mo Kα radiation (λ = 0.710 69 Å, graphite monochromator), and an Oxford Cryostream low-temperature cooling system, controlled by a microVax 3200 and driven by MADNES software.[20] The orientation matrix and unit-cell parameters were determined via the ENDEX and REFINE routines of the MADONL software (the small-molecule version of MADNES), using 50 reflections from two 5° FIND rotation ranges separated by 90° around the ω axis, and subsequently refined during data processing using 250 reflections from each processed batch of data. Data evaluation was performed off-line on a Vax station 4000/60 clustered with the diffractometer driving computer with frames transfer and processing taking place simultaneously with data collection, the processing time not exceeding the exposure time. Slightly more than a hemisphere of data was collected (an ω rotation of 195° around an arbitrary axis at χ = 0° plus two complementary "cusps" of 70° each differing by 90° in φ at χ = 90°) with crystal-to-detector distance = 39.92 mm, detector swing angle = 24.97°, between frames increment = 0.20°, and exposure time = 10 s. The data were corrected for Lorentz and polarization effects and also for absorption using the program DIFABS,[21] adapted for FAST geometry.[22] The structure was solved via the Patterson and Fourier methods and refined (on F) by full-matrix least-squares procedures (SHELX-80),[23] with a unit weighting scheme which gave acceptable variance analyses. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms, isotropically.

Table II. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2 (×10^3) for $[Ba_2(thd)_4(diglyme)_2]$

	x	y	z	U_{eq}
Ba	–1106.3(3)	2861.6(3)	1109.4(2)	12.6(1)
O(1)	778(3)	1143(3)	1728(2)	21(1)
O(2)	–1941(3)	499(3)	2053(2)	25(1)
O(3)	–972(3)	3996(3)	2308(2)	22(1)
O(4)	–3346(3)	4029(3)	1687(2)	21(1)
O(5)	1351(3)	4105(3)	78(2)	22(1)
O(6)	253(3)	2185(3)	–452(2)	24(1)
O(7)	–2485(3)	2095(3)	–14(2)	29(1)
C(1)	2009(4)	–257(4)	2788(3)	19(2)
C(2)	708(4)	249(4)	2463(3)	16(1)
C(3)	–475(4)	–330(4)	3032(3)	18(1)
C(4)	–1709(4)	–163(4)	2819(3)	16(1)
C(5)	–2948(4)	–775(4)	3537(3)	22(2)
C(6)	1991(5)	130(6)	3641(4)	29(2)
C(7)	3188(5)	379(5)	2066(4)	25(2)
C(8)	2153(6)	–1790(5)	2999(4)	30(2)
C(9)	–2654(6)	–1554(6)	4460(3)	31(2)
C(10)	–3581(6)	–1697(6)	3181(4)	29(2)
C(11)	–3891(6)	410(6)	3635(5)	39(2)
C(12)	–1172(5)	4201(4)	3774(3)	22(2)
C(13)	–1781(4)	4186(4)	2982(3)	16(1)
C(14)	–3147(5)	4384(4)	3049(3)	18(1)
C(15)	–3851(4)	4341(4)	2401(3)	15(1)
C(16)	–5350(4)	4656(4)	2559(3)	19(1)
C(17)	–207(6)	5336(6)	3427(4)	32(2)
C(18)	–397(8)	2867(7)	4036(5)	47(3)
C(19)	–2169(6)	4381(6)	4596(4)	35(2)
C(20)	–5936(5)	4999(5)	3430(4)	28(2)
C(21)	–6040(5)	3441(6)	2555(5)	34(2)
C(22)	–5603(5)	5852(6)	1764(4)	33(2)
C(23)	1985(6)	4422(6)	696(4)	32(2)
C(24)	2144(5)	3142(5)	–316(3)	27(2)
C(25)	1462(5)	2815(5)	–949	29(2)
C(26)	–456(6)	1794(6)	–999(4)	33(2)
C(27)	–1688(6)	1128(5)	–396(4)	33(2)
C(28)	–3741(6)	1611(8)	470(4)	43(3)

All calculations were performed on a T800 transputer hosted by an IBM/AT personal computer. Final atomic parameters are given in Tables II and III; selected bond lengths and angles, in Table IV. The structure of a single molecule of the complex is shown in Figure 2.

Results and Discussion

The complex $[Ba(thd)_2(diglyme)]_2$ (**1**) was prepared via the reaction of $[Ba_4(thd)_8]$[18] and diglyme in *n*-hexane at ambient temperature in a yield of 85%. The product was obtained as a colorless crystalline solid, which was found to be air and moisture stable.

$$^1/_2[Ba_4(thd)_8] + 2CH_3OCH_2CH_2OCH_2CH_2OCH_3 \xrightarrow[\text{RT}]{n\text{-hexane}} [Ba(thd)_2(diglyme)]_2$$

Spectroscopic Data. The IR spectrum (Nujol mull) reveals only one clearly defined set of C=O and C=C stretches, possibly

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Table III. Hydrogen Fractional Atomic Coordinates (×10^4) and Isotropic Temperature Factors (Å^2 × 10^3) for [$Ba_2(thd)_4(diglyme)_2$]

	x	y	z	U_{iso}
H(3)	-415(47)	-911(49)	3471(34)	17(12)
H(6A)	1980(47)	1098(51)	3551(32)	20(12)
H(6B)	1241(58)	-150(55)	4154(39)	37(16)
H(6C)	2757(56)	-289(54)	3907(37)	36(15)
H(7A)	4063(53)	35(52)	2324(35)	32(14)
H(7B)	3005(55)	1335(60)	1941(38)	39(16)
H(7C)	3263(67)	91(69)	1578(48)	63(21)
H(8A)	2052(48)	-2012(48)	2471(34)	22(13)
H(8B)	3017(61)	-2037(57)	3100(40)	42(17)
H(8C)	1440(58)	-2262(57)	3484(39)	38(16)
H(9A)	-1951(53)	-2407(54)	4417(35)	31(14)
H(9B)	-2154(51)	-1072(51)	4681(34)	26(13)
H(9C)	-3462(59)	-1988(57)	4872(40)	41(16)
H(10A)	-3814(41)	-1234(42)	2644(30)	6(10)
H(10B)	-4333(61)	-1994(59)	3542(41)	40(17)
H(10C)	-2929(62)	-2456(63)	3111(41)	49(18)
H(11A)	-3541(56)	1005(59)	3859(39)	38(16)
H(11B)	-4128(58)	945(60)	3045(43)	44(17)
H(11C)	-4683(67)	42(63)	3982(45)	52(19)
H(14)	-3642(50)	4574(49)	3534(35)	25(13)
H(17A)	-621(57)	6185(61)	3254(39)	39(16)
H(17B)	380(72)	5261(72)	3806(51)	71(23)
H(17C)	461(55)	5173(53)	2953(39)	30(14)
H(18A)	151(64)	2766(63)	4522(45)	56(19)
H(18B)	297(61)	2602(60)	3540(42)	46(17)
H(18C)	-1112(60)	2226(59)	4264(40)	39(17)
H(19A)	-1775(50)	4408(50)	5085(35)	27(13)
H(19B)	-2702(56)	5286(58)	4448(38)	39(16)
H(19C)	-2778(53)	3633(55)	4873(36)	30(14)
H(20A)	-6951(50)	5341(49)	3515(33)	25(13)
H(20B)	-5555(58)	5748(62)	3486(40)	43(17)
H(20C)	-5900(70)	4204(75)	3960(50)	72(23)
H(21A)	-6875(69)	3770(66)	2549(44)	56(20)
H(21B)	-5690(71)	3160(72)	2058(52)	67(23)
H(21C)	-5906(71)	2781(76)	3029(52)	66(23)
H(22A)	-5259(48)	5614(47)	1151(34)	22(12)
H(22B)	-6684(52)	6180(50)	1871(34)	28(13)
H(22C)	-5157(64)	6575(66)	1718(44)	52(20)
H(23A)	1433(51)	4991(52)	921(34)	23(13)
H(23B)	2154(53)	3690(55)	1172(38)	31(14)
H(23C)	2855(58)	4941(56)	391(39)	39(16)
H(24A)	2246(48)	2309(49)	204(33)	23(13)
H(24B)	3072(66)	3441(64)	-637(45)	57(19)
H(25A)	2048(47)	2257(47)	-1274(33)	19(12)
H(25B)	1213(53)	3596(56)	-1410(38)	35(15)
H(26A)	54(49)	1182(50)	-1210(33)	20(12)
H(26B)	-731(52)	2605(55)	-1435(37)	32(14)
H(27A)	-1281(47)	363(48)	92(33)	21(12)
H(27B)	-2181(47)	802(47)	-797(33)	22(13)
H(28A)	-4322(73)	2275(75)	709(50)	66(23)
H(28B)	-4271(80)	1427(81)	93(56)	87(26)
H(28C)	-3615(71)	898(75)	909(52)	66(23)

Table IV. Selected Bond Lengths (Å) and Angles (deg) for [$Ba_2(thd)_4(diglyme)_2$][a]

O(1)–Ba	2.679(6)	O(2)–Ba	2.578(6)
O(3)–Ba	2.574(7)	O(4)–Ba	2.630(6)
O(5)–Ba	2.888(6)	O(5′)–Ba	3.173(6)
O(6)–Ba	2.819(6)	O(7)–Ba	2.870(7)
O(2)–Ba–O(1)	66.2(2)	O(3)–Ba–O(1)	86.2(2)
O(3)–Ba–O(2)	103.4(2)	O(4)–Ba–O(1)	141.0(1)
O(4)–Ba–O(2)	92.2(2)	O(4)–Ba–O(3)	66.9(2)
O(5)–Ba–O(1)	74.9(2)	O(5)–Ba–O(2)	138.4(1)
O(5)–Ba–O(3)	87.5(2)	O(5)–Ba–O(4)	128.4(2)
O(5′)–Ba–O(1)	138.0(2)	O(5′)–Ba–O(2)	155.8(2)
O(5′)–Ba–O(3)	82.2(2)	O(5′)–Ba–O(4)	68.1(2)
O(5′)–Ba–O(5)	64.4(2)	O(6)–Ba–O(1)	78.1(2)
O(6)–Ba–O(2)	97.6(2)	O(6)–Ba–O(3)	146.0(1)
O(6)–Ba–O(4)	139.1(1)	O(6)–Ba–O(5)	59.4(2)
O(6)–Ba–O(5′)	89.4(2)	O(7)–Ba–O(1)	116.8(2)
O(7)–Ba–O(2)	76.0(2)	O(7)–Ba–O(3)	152.9(1)
O(7)–Ba–O(4)	86.1(2)	O(7)–Ba–O(5)	111.2(2)
O(7)–Ba–O(5′)	88.4(2)	O(7)–Ba–O(6)	58.5(2)
Ba–O(5)–Ba′	115.6(3)	C(2)–O(1)–Ba	129.2(4)
C(4)–O(2)–Ba	126.0(4)	C(13)–O(3)–Ba	133.9(3)
C(15)–O(4)–Ba	134.4(3)	C(23)–O(5)–Ba	107.3(3)
C(24)–O(5)–Ba	107.7(3)	C(24)–O(5)–C(23)	110.3(5)
C(25)–O(6)–Ba	119.5(4)	C(26)–O(6)–Ba	120.5(4)
C(26)–O(6)–C(25)	113.2(5)	C(27)–O(7)–Ba	109.1(4)
C(28)–O(7)–Ba	111.1(5)	C(28)–O(7)–C(27)	112.4(6)

[a] The primed atoms belong to one and the same dimer and are related to the unprimed ones by the symmetry operation (−x, 1 − y, −z).

indicative of only one thd ligand environment. On exposure of the sample to air for several days, the IR spectrum remains unchanged. These results may be contrasted with those for the parent complex [$Ba_4(thd)_8$], for which several bands are observed in the IR spectra, strongly indicative of the differing coordination modes of the thd ligands found in this complex.[18]

The solution spectroscopic studies (^{1}H and ^{13}C NMR) at 25 °C in C_6D_6 show characteristic signals for only one thd and one diglyme environment. These spectra are in accord with the solid-state structure of the dimer, which has an inversion center, with one unique diglyme ligand and the two independent thd ligands in similar environments. A shift downfield is observed for the diglyme methylene signals in both the ^{1}H and ^{13}C NMR spectra on coordination to the barium atom. The spectroscopic data clearly rule out the possibility of coordinated OH or H_2O groups, which is in accord with the solid-state structure, and emphasizes that the use of rigorous Schlenk techniques under an argon atmosphere will yield anhydrous products.

This complex exhibits excellent solubility in a wide range of aliphatic (*n*-hexane), aromatic (e.g. benzene and toluene), and coordinating solvents (e.g. dmso and thf) and excellent stability to both moisture and oxygen. Thus water coordination is less likely to result. In line with these properties, there is a substantial reduction in the melting point of this complex (93–95 °C), which may be contrasted with that of the tetrameric parent material [$Ba_4(thd)_8$]: 194–197 °C.[18] This is excellent evidence for a lack of strong intermolecular interactions in [$Ba(thd)_2(diglyme)]_2$, as were recently shown to be present in the homoleptic complex, and is in accord with previous results on [$Ba(thd)_2$(tetraglyme)].[6]

The mass spectroscopic data reveal the highest mass ion to be a dimeric unadducted species [$Ba(thd)_3]^+$ (m/z 833). Other monomeric barium thd species, e.g. [Ba(thd)(Bu^{t}COCHCOH)]$^+$ (448 amu) and [Ba(thd)]$^+$ (321 amu), and [Ba(diglyme)]$^{2+}$ (271 amu) are also present. There are evidently several different pathways operating in the gas phase, i.e. loss of glyme to yield a [$M_2L_3]^+$ and [ML]$^+$ species and also loss of the β-diketonates to yield [Ba(glyme)]$^+$. Fragmentation of thd ligands with loss of Bu^t groups has been previously observed by other workers.[5,6]

Physical Properties. In good agreement with the mass spectroscopic data, the complex decomposes under high-vacuum sublimation at 105 °C and 10^{-3} Torr. The resulting white solid was found to be [$Ba_4(thd)_8$], which is found to be presubliming at ~100 °C lower than if unadducted. The instability of the material in the gas phase is most likely due to the weak binding of the diglyme and the ready ease of association of [$Ba(thd)_2$] fragments to yield the oligomeric species [$Ba_4(thd)_8$].

Thermogravimetric analysis (TGA) has found extensive use especially where a study of weight loss versus temperature may yield valuable information on thermal behavior of materials over a wide temperature range.

The differential scanning calorimetry curve for complex **1** reveals a sharp melting point endotherm at 108.14 °C (−30.80 mcal/mg) and two further isotherms, the first at 219.71 °C (−3.98 mcal/mg) and the second at 393.24 °C (−7.21 mcal/mg). The first of these two isotherms is presumably due to the loss of the glyme, and the second is assigned to the sublimation end point of [$Ba(thd)_2]_4$. The TGA curve of complex **1** has two steps (see Figure 1); the first starts at ~120 °C and is essentially complete by 220 °C and represents the loss of the diglyme ligand (found 21.6%, expected 21.4%).

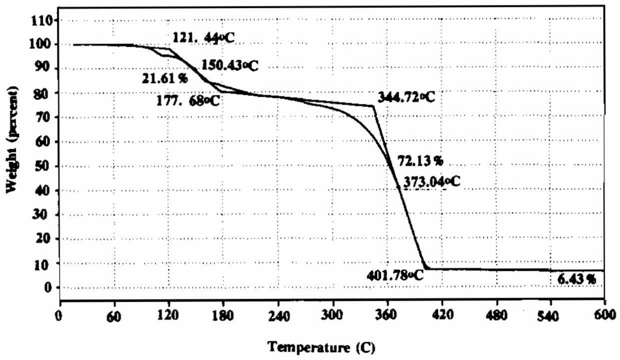

Figure 1. Thermogravimetric analysis of $[Ba(thd)_2(diglyme)]_2$ (**1**) under nitrogen gas flow.

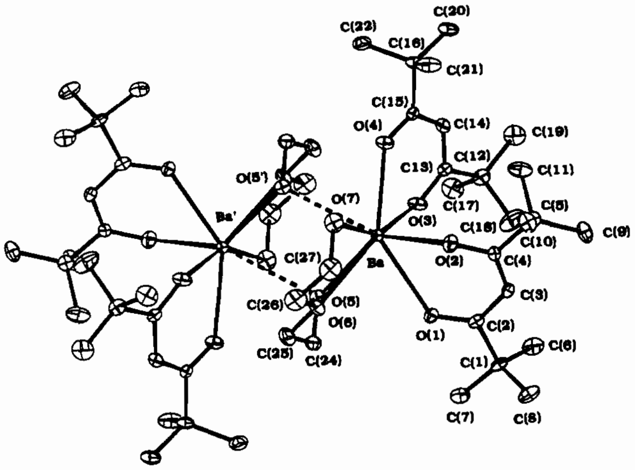

Figure 2. Structure of the centrosymmetric dimer $[Ba(thd)_2(diglyme)]_2$ (**1**) showing the atom-numbering scheme. The hydrogen atoms and terminal methyl groups of the diglyme ligand have been omitted for clarity.

This leaves the $[Ba(thd)_2]_4$ complex intact, which sublimes between 240 and 402 °C.[24] However, the volatility of this material is not as high as that of the recently characterized barium β-diketonates,[8] with a $T_{50\%} = 365$ °C. The residue level is far lower (6.43% residue at 400 °C) and compares very favorably with previous studies on pure $[Ba_4(thd)_8]$ by Yuhya et al. (25% residue at 500 °C)[25] and Cho et al.[26] (41% residue at 500 °C).[13] The TGA data for the complex clearly reveal that the diglyme compound does not sublime intact, which is in accord with the sublimation data.

X-ray Structure of $[Ba(thd)_2(diglyme)]_2$. In the solid state (see Figure 2) this complex exists as discrete centrosymmetric dimers, with a distorted square antiprismatic (eight-coordinate) geometry at each barium metal center. The complex possesses the stoichiometry $[Ba_2(thd)_4(L)_2]$, which may be compared with that of the recently characterized dimeric barium β-diketonate species "lightly stabilized" by the monodentate Lewis bases ammonia[17] and diethyl ether.[16] In striking contrast to these Lewis-base-adducted barium thd dimers, it may be noted that the thd ligands in the present compound do not bridge between the metal centers in this complex. Instead the diglyme ligand is found to bind in an unusual mode. The barium atom is coordinated by O(5), O(6), and O(7) of the diglyme in a classical chelating manner, with Ba–O distances of 2.888(6), 2.819(6), and 2.870(7) Å, with an average $Ba–O_{glyme}$ distance of 2.859(6) Å. The terminal oxygen of the diglyme chain O(5) also binds to the second barium with a Ba–O distance of 3.173(6) Å, thus bringing the two barium atoms closer together. This mode of bonding is we believe unprecedented for diglyme (or any glyme), which is normally observed either chelating in a classical manner or alternatively acting as a monodentate or bidentate ligand with a dangling chain end. There are only a few examples of purely bridging μ_2-thf and μ_2-OEt_2 ligands known.[27]

The O–Ba–O angle for O(7)–Ba–O(6) is 58.5(2)°, similar to that found for O(6)–Ba–O(5) of 59.4(2)° in the trischelating component of the diglyme. If we consider the bridging coordination mode, we find an expansion of the angles O(6)–Ba–O(5′) and O(7)–Ba–O(5′) to 89.4(2) and 88.4(2)°, respectively, as might be expected, given the distortion experienced at O(5) and O(5′); and the Ba–O(5)–Ba′ bridge angle is 64.4(2)°. The bridging interaction of the glyme ligand also maximizes the coordination number of the barium atoms, and they thus achieve a higher coordination number than would be the case if it had been a purely monomeric complex.

The Ba···Ba distance in this complex of 5.130(2) Å is relatively long, as might be expected when compared with that of the recently structurally characterized tetrameric species $[Ba_4(thd)_8]$[11,18] (4.152(5) Å), which contains bridging thd ligands that tend to pull the metal centers closer together. This Ba···Ba distance may be contrasted with those of the recently structurally characterized thd dimers, 3.83 Å,[16,17] a barium siloxide trimer, 3.93 Å,[28] a pentameric barium aggregate, 3.96 Å,[9] and a hexameric complex, 3.98 Å.[9]

The four thd β-diketonate ligands bond to the barium atoms in a classical chelating mode with the following Ba–O distances: O(1), 2.679(6); O(2), 2.578(6); O(3), 2.574(7); O(4), 2.630(6) Å. These are, as expected, approximately 0.25 Å shorter than the $Ba–O_{diglyme}$ distances. There is also a small amount of asymmetry in their bonding to the barium metal centers. The average thd Ba–O distance of 2.615(6) Å and the O–Ba–O angle of 66.6(2)° are very similar to those in the recently reported dimeric complex $[Ba(thd)_2(Et_2O)]_2$, 2.578(5) Å and 66.7(2)°. A further contrast may also be made with $[Ba(hfa)_2(18\text{-crown-}6)]$, having a $Ba–O_{hfa}$ distance of 2.82 Å and an O–Ba–O angle of 61.2(3)°.[7]

It is also of interest to note that the two thd ligands chelated to each barium show large deviations from planarity (atomic deviations up to 0.072(1) Å from the mean plane of OCCCO) and significant buckling about the O- - -O axis [dihedral angles of 33.7(5)° between the Ba–O(1)–O(2) and O(1)–C(2)–C(3)–C(4)–O(2) planes and 20.4(5)° between the Ba–O(3)–O(4) and O(3)–C(13)–C(14)–C(15)–O(4) planes]. These results suggest considerable flexibility of the thd ligands when chelated to a metal center and may be attributed to several inter-ligand steric interactions between the thd oxygens and diglyme CH_2/CH_3 groups. In particular the nonbonded contacts O(1)- - -H(24A)/C(24) of 2.56(5)/3.356(8) Å, O(2)- - -H(28C) (terminal methyl of diglyme ligand) of 2.73(7)/3.352(8) Å, O(3)- - -H(25B)/C(25′) of 2.50(5)/3.433(8) Å, and O(4)- - -H(24B)/C(24′) of 2.66(7)/3.251(8) Å are fairly short and would contribute toward the nonplanarity and folding nature of the thd ligands observed in the complex.

These observations demonstrate that multidonor chelating Lewis bases such as glymes readily add to oligomeric barium β-diketonates and cleave them to yield smaller species, which are generally either dimers, as here, or highly soluble monomers with ligands such as tetraglyme.[6] The Lewis base used in this study is bound sufficiently strongly to reduce aggregation, but unfortunately it is far too labile (presumably due either to the relatively weak Ba–O bonds or to steric crowding) to give volatile adducted

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species. One may possibly envisage that a more compact multidentate ether such as dimethoxyethane (dme) would lead to more thermally robust complexes. An important advantage of the use of such multidentate ligands arises from entropic effects (ring formation) and also their ability to coordinatively saturate the large group IIA metal barium, thus resulting in an air- and a moisture-stable material. This route also yields oxo and hydroxo free products, an important prerequisite for a reproducible route to such materials.

Not only should careful design of such molecular precursors reap great benefit to metal–oxygen-based chemistry, but also one can envisage the use of **1** as a template for further reactivity with other rare earth β-diketonates to yield a new range of stabilized mixed-metal β-diketonates.

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Supplementary Material Available: Listings of crystal data, anisotropic thermal parameters, complete bond lengths and angles, and selected nonbonded contacts and a DSC plot of compound **1** (11 pages). Ordering information is given on any current masthead page.