Mononuclear Barium Diketonate Polyamine Adducts. Synthesis, Structures, and Use in MOCVD of Barium Titanate

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Mononuclear barium β-diketonate Lewis base adducts have been synthesized by reaction of Ba(thd)$_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) with polyamines 1,1,4,7,7-pentamethyldiethylenetriamine (pmdt) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (hmtt). The adducts [Ba(thd)$_2$(pmdt)] (**I**) and [Ba(thd)$_2$(hmtt)] (**II**) have been characterized by NMR spectroscopy, elemental analyses and single-crystal X-ray diffraction. Compound **I** crystallizes in the space group $P2_1/c$ with a = 10.577(3) Å, b = 23.547(7) Å, c = 15.963(5) Å, β = 105.21(2)°, and Z = 4. Compound **II** crystallizes in the space group $P2_1/c$ with a = 10.833(6) Å, b = 20.442(12) Å, c = 19.404(9) Å, β = 104.35(4)°, and Z = 4. The adducts are seven- and eight-coordinate, respectively, with all nitrogen atoms of the polyamine bound to a single barium center. Compound **I** has been used for thin-film growth of BaTiO$_3$ which has revealed that, compared to Ba(thd)$_2$(tetraglyme), the polyamine adduct allows a larger temperature window for effective vapor transport.

Introduction

Numerous reports have been published over the past few years as a result of attempts to synthesize volatile barium compounds, suitable for chemical vapor deposition of barium-containing ferroelectrics and high-T_c superconducting oxides. Since the tendency for barium to attain high coordination numbers often yields multinuclear aggregates having limited volatility, a common strategy has been the synthesis of barium compounds with a high degree of steric saturation.

The air stability and moderate volatility of Ba(thd)$_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) have made it the most widely used barium source in MOCVD. Nevertheless, its vapor transport behavior is strongly dependent on synthesis conditions and purity of the compound. The determination that "Ba(thd)$_2$" is tetrameric in the solid state[1] and associated in the gas phase as well[2] has made it clear that some method of inhibiting molecular aggregation is required to enhance volatility and permit reproducible control over metal delivery rates.

Addition of polyethers to group IIA diketonates has proven to be effective in reducing aggregation through coordinative saturation. For example, Ba(thd)$_2$(tetraglyme) is a crystalline colorless solid which is monomeric in the solid state.[3] Although the nuclearity has been minimized in this compound, the tetraglyme dissociates upon attempted sublimation of the solid; a problem which is common to many Lewis base adducts of barium diketonates.

Nitrogen-donor ligands might be expected to make stronger bonds to barium diketonates than analogous oxygen-donor ligands, due to the increased basicity of amines compared to ethers. Ammonia, simple amines (NMe$_3$, NEt$_3$, pyridine) and even diamines (H$_2$NC$_2$H$_4$NH$_2$, Me$_2$NC$_2$H$_4$NMe$_2$) have been reported to cause a decrease in the melting and sublimation temperatures of barium diketonates,[4] but the adducts do not have stable vapor pressures due to dissociation of the amine upon vaporization. Furthermore, with the exception of [Ba(thd)$_2$(NH$_3$)$_2$]$_2$,[5] adducts which have coordinated amines have not been structurally characterized.[6]

We report here the reactions of Ba(thd)$_2$ with 1,1,4,7,7-pentamethyldiethylenetriamine (pmdt) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (hmtt), to form the adducts Ba(thd)$_2$(pmdt) (**I**) and Ba(thd)$_2$(hmtt) (**II**). By way of comparison to the polyether complexes, these polyamine ligands represent the fully N-methylated amine analogs of diglyme and triglyme, respectively.

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Table 1. Crystallographic Data for I and II

	I	II
	(a) Crystal Parameters	
formula	$C_{31}H_{61}BaN_3O_4$	$C_{34}H_{68}BaN_4O_4$
formula weight	677.2	734.2
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	10.577(3)	10.833(6)
b, Å	23.547(7)	20.442(12)
c, Å	15.963(5)	19.404(9)
β, deg	105.21(2)	104.35(4)
V, Å^3	3836.3(19)	4163(4)
Z	4	4
cryst color	colorless	colorless
D(calc), g cm^3	1.172	1.172
μ(Mo Kα), cm^{-1}	10.67	9.89
temp, K	298	240
T(max)/*T*(min)	0.62/0.50	0.93/0.82
	(b) Data Collection	
diffractometer	Siemens P4	
monochromator	graphite	
radiation	Mo Kα (λ = 0.710 73 Å)	
2*θ* scan range, deg	4–55	4–48
data collected (*h*, *k*, *l*)	±13, +30, +20	±12, +23, +21
rflns collected	9106	6752
indpt rflns	8796	6537
indpt obsvd rflns $F_o \geq 4\sigma(F_o)$	5258	3888
	(c) Refinement	
R(*F*),^{a} %	5.06	6.73
R(*wF*),^{a} %	6.67	7.62
Δ/σ(max)	0.06	0.08
$\Delta(\varrho)$, e Å^{-3}	0.69	0.64
N_o/N_v	15.0	10.1
GOF	1.09	1.34

^{a} $R = \Sigma\Delta/\Sigma(F_o)$; $R(\mathrm{w}) = \Sigma\Delta w^{1/2}/\Sigma(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

Experimental Section

General Techniques. Reactions were performed under dinitrogen in anhydrous pentane or hexane as the solvent. Ba(thd)$_2$ was synthesized by anhydrous methods. NMR spectra were recorded at room temperature in benzene-d_6 on an IBM WP200SY spectrometer and peaks referenced to the protio impurity in the solvent at δ 7.15. Elemental analyses were performed by Galbraith Laboratories Inc, Knoxville, TN.

Syntheses. *Ba(thd)$_2$(pmdt) (I)*: To 1.0 g (2.0 mmol) of Ba(thd)$_2$ suspended in 10 mL of pentane was added 0.41 mL (2.0 mmol) of *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (Aldrich Chemical Co.). This completely dissolved the starting material within a few minutes. Upon removal of solvent, a crystalline colorless solid was obtained. ^{1}H NMR: δ 5.83 (s, 2H); δ 1.32 (s, 3.6 H) (thd resonances), δ 2.55 (br); δ 2.25 (s, 12H); δ 1.94 (s, 3H); δ 1.89 (br) (coordinated pmdt resonances). Anal. Calcd (found) for $BaC_{31}H_{61}N_3O_4$: C, 54.98% (54.06%); H, 9.08% (9.11%); N, 6.21% (5.88%).

Ba(thd)$_2$(hmtt) (II): To 1.0 g (2.0 mmol) of Ba(thd)$_2$ suspended in 10 mL of hexanes was added 0.54 mL (2.0 mmol) of 1,1,4,7,10,10-hexamethyltriethylenetetramine (Aldrich Chemical Co.). The starting material dissolved completely within a few minutes. Upon concentrating the solution under nitrogen purge and cooling, a crystalline colorless solid was obtained. ^{1}H NMR: δ 5.84 (s, 2H); δ 1.35 (s, 36H) (thd resonances), δ 2.61 (br); δ 2.17 (s, 12H); δ 2.08 (s, 6H); δ 1.70 (br) (coordinated hmtt resonances). Anal. Calcd (found) for $BaC_{34}H_{68}N_4O_4$: C, 55.62% (55.25%); H, 9.33% (9.38%); N, 7.63% (7.59%).

Crystallographic Structure Determination for I and II. In each case X-ray-quality crystals were obtained by slow concentration of a pentane solution of the adduct. Crystallographic data are collected in Table 1. Both crystals were mounted on glass fibers with epoxy cement and found to have 2/*m* Laue symmetry. Systematic absences in the data uniquely indicated the appropriate space group as $P2_1/c$. The data were corrected for absorption by empirical methods. The structures were solved by Patterson methods and completed from subsequent difference maps. In both cases, methyl groups forming one of the *tert*-butyl groups were disordered over two half-occupancy (refined) sites: C(20), C(21), and C(22) in **I** and C(9), C(10) and C(11) in **II**, and their primed counterparts. Except for the disordered atoms, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. All computations used versions of SHELXTL-PC (G. Sheldrick, Siemens XRD, Madison, WI).

MOCVD of $BaTiO_3$. Preliminary film growth experiments were performed in a 2 in. reactor previously described,[7] in order to compare the properties of $BaTiO_3$ films derived from both Ba(thd)$_2$(pmdt) (**I**) and the previously used compound, Ba(thd)$_2$(tetraglyme). The titanium source was $Ti(OCH(CH_3)_2)_2(thd)_2$. In each case the barium and titanium precursors were combined, dissolved in isopropyl alcohol and delivered to the reactor as single solutions. Film compositions were measured by both XRF and EDX spectroscopy; film thicknesses were measured optically.

Results and Discussion

The synthesis of mononuclear barium complexes has invariably required the presence of neutral donor atoms to satisfy the high coordination numbers demanded by barium. An additional requirement for thermal stability and volatility of the complex is that the neutral donor remain attached to the metal during vaporization. This has precluded the use of many common Lewis bases, which easily dissociate from complexes such as Ba(thd)$_2$ at temperatures significantly lower than are required to break the cohesive forces of the condensed phase. Attempts to circumvent this problem by incorporation of additional donor atoms within the covalently bound ligands have met with some success,[8] but the compounds still exhibit thermal instability. Our research has recently focussed on increasing the bond strength of neutral donor ligands to barium β-diketonates using basic polyamine functionalities.

Syntheses of the two adducts, Ba(thd)$_2$(pmdt) (**I**) and Ba(thd)$_2$(hmtt) (**II**), were accomplished by straightforward addition of the polyamines to [Ba(thd)$_2$]$_4$. The coordination of polyamine is immediately observed by a marked increase in solubility of the Ba(thd)$_2$, as the tetrameric starting material is broken down. Both compounds were studied by single-crystal X-ray diffraction to ascertain the nuclearity of the products and the function of the polyamine ligands.

The X-ray structure of Ba(thd)$_2$(pmdt) (**I**) is shown in Figure 1. Selected distances and angles appear in Table 2. The barium ion is seven-coordinate, having all three nitrogen atoms of the polyamine coordinated to the metal center in a meridional fashion between the diketonate ligands. The distances from Ba to each of the thd oxygen atoms are similar (average 2.62 Å), as are the Ba–N bond distances (average 2.97 Å), with the distance of the "internal" nitrogen (N2) being only slightly longer than the others. The methyl groups on the polyamine are clearly oriented to minimize steric interactions with the *tert*-butyl groups of the thd ligands.

The X-ray structure of Ba(thd)$_2$(hmtt) (**II**) is shown in Figure 2; selected distances and angles are given in Table 2. The metal center is eight-coordinate, with all four nitrogen atoms of the polyamine bound to barium.

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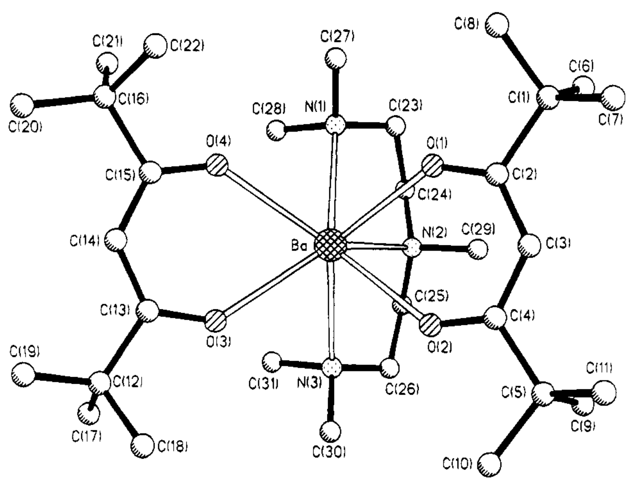

Figure 1. Molecular structure of Ba(thd)$_2$(pmdt) (**I**). Hydrogen atoms are omitted for clarity.

Table 2. Bond Distances and Angles for I and II

	I	II
(a) Bond Distances (Å)		
Ba–O(1)	2.616(5)	2.610(7)
Ba–O(2)	2.617(4)	2.680(8)
Ba–O(3)	2.633(5)	2.723(7)
Ba–O(4)	2.630(5)	2.584(9)
Ba–N(1)	2.949(6)	2.974(13)
Ba–N(2)	3.004(6)	3.048(13)
Ba–N(3)	2.965(8)	2.939(11)
Ba–N(4)		2.983(10)
(b) Bond Angles (deg)		
O(1)–Ba–O(2)	65.8(1)	64.8(2)
O(1)–Ba–O(3)	133.0(2)	140.3(2)
O(1)–Ba–O(4)	95.9(2)	86.2(3)
O(1)–Ba–N(1)	80.0(2)	77.2(3)
O(1)–Ba–N(2)	91.5(2)	84.3(3)
O(1)–Ba–N(3)	135.1(2)	135.5(3)
O(1)–Ba–N(4)		131.5(3)
O(2)–Ba–O(3)	95.6(1)	152.8(2)
O(2)–Ba–O(4)	133.2(2)	119.4(3)
O(2)–Ba–N(1)	135.0(2)	128.3(3)
O(2)–Ba–N(2)	91.7(2)	81.0(3)
O(2)–Ba–N(3)	80.4(2)	82.2(3)
O(2)–Ba–N(4)		79.0(3)
O(3)–Ba–O(4)	65.0(1)	64.8(2)
O(3)–Ba–N(1)	129.4(2)	76.4(3)
O(3)–Ba–N(2)	133.5(2)	107.5(3)
O(3)–Ba–N(3)	76.4(2)	80.1(3)
O(3)–Ba–N(4)		74.7(2)
O(4)–Ba–N(1)	76.2(2)	90.0(3)
O(4)–Ba–N(2)	133.2(2)	150.6(3)
O(4)–Ba–N(3)	128.9(2)	137.5(3)
O(4)–Ba–N(4)		84.7(3)
N(1)–Ba–N(2)	59.7(2)	60.8(3)
N(1)–Ba–N(3)	107.9(2)	104.7(3)
N(1)–Ba–N(4)		150.0(3)
N(2)–Ba–N(3)	70.5(2)	60.9(3)
N(2)–Ba–N(4)		122.0(3)
N(3)–Ba–N(4)		62.7(3)

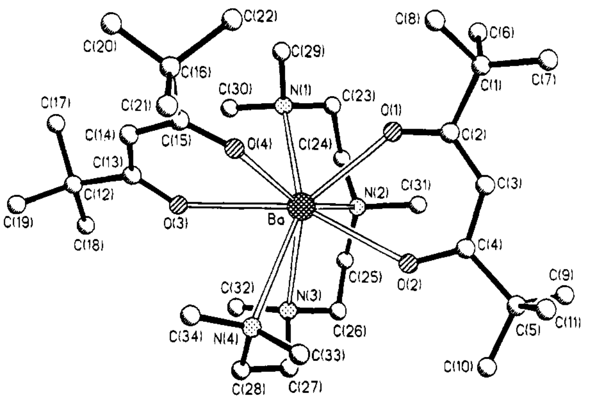

Figure 2. Molecular structure of Ba(thd)$_2$(hmtt) (**II**). Hydrogen atoms are omitted for clarity.

Compared to the structure of **I**, the increase in denticity has opened up the angle between the thd ligands, accompanied by a twist of the ligands with respect to each other {O(1)–Ba–O(4) = 95.9° in **I** and 86.2° in **II**; O(2)–Ba–O(3) = 95.6° in **I** and 152.8° in **II**}. This feature is also observed in the polyether analog, Ba(thd)$_2$(triglyme).[9] Note that the hmtt ligand is substantially folded about the equator of the coordination sphere and is bound such that the methyl groups on the nonterminal amino groups extend in opposite directions. Again it is clear that steric repulsions between methyl groups on the polyamine and *tert*-butyl groups on the thd ligands are being minimized.

An interesting feature of this structure which is not present in related polyether adducts is the effect that increased steric congestion has on the Ba–O bond distances. Although the Ba–N distances are rather consistent (within 3σ), between 2.986 and 3.060 Å, each of the thd ligands is involved in one shorter bond (2.61 and 2.58 Å) and one longer bond (2.68 and 2.72 Å, respectively) to the barium atom. As expected, the longer bonds are those which are closest to the steric influence of the coordinated polyamine. Although it is tempting to suggest that an electronic adaptation to the steric congestion has occurred, other distances within the thd ligands remain consistent with the more common delocalized diketonate bonding.

The ^{1}H NMR spectra of the compounds suggest fluxionality in benzene solution at room temperature, as the thd methyl groups appear as a sharp singlet in each case. Two singlets are observed for the terminal- and nonterminal-amino methyl groups, respectively, with the expected integration in each case. The ethylene proton resonances of the coordinated polyamine are broad and unresolved in both spectra, again indicative of fluxional processes in solution.

Having characterized these adducts, it was also of interest to compare the relative affinities of polyethers and polyamines toward Ba(thd)$_2$. NMR was used to monitor the effect of adding excess tetraglyme to a solution of Ba(thd)$_2$(hmtt). No ligand exchange was observed over 22 h, consistent with the expected greater basicity of the polyamine. On the other hand, addition of hmtt to a solution of Ba(thd)$_2$(tetraglyme) immediately produced free tetraglyme and Ba(thd)$_2$(hmtt).

The greater basicity of the polyamines was indeed found to enhance vapor transport of Ba(thd)$_2$, although **I** and **II** both exhibited dissociation of the polyamine ligand during sublimation. Nevertheless, this is unlike Ba(thd)$_2$(tetraglyme), which dissociates tetraglyme at 110 °C (0.1 Torr) *without* transport of Ba(thd)$_2$. For compound **II**, sublimation with decomposition was observed in the temperature range 95–120 °C (50 mTorr), with a very slow rate of sublimation at the bottom of this range and substantial polyamine dissociation at higher temperatures. Under the same pressure, compound **I** sublimed over a slightly higher temperature range (120–150 °C), again with loss of

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[9] Drake, S. R.; Miller, S. A. S.; Williams, D. J. *Inorg. Chem.* **1993**, *32*, 3227.

polyamine. This behavior suggests that the thermal stability of Ba(thd)$_2$(hmtt) is lower than that of Ba(thd)$_2$(pmdt), probably due to the steric effects noted in the molecular structure of **II**.

Both compounds are considerably more soluble in nonpolar solvents than the parent, Ba(thd)$_2$, and therefore we are assessing the use of these polyamines in solution-delivery techniques[10] for MOCVD of BaTiO$_3$ and Ba$_x$Sr$_{1-x}$TiO$_3$. Preliminary film growth experiments were performed in a 2 in. reactor, comparing the properties of BaTiO$_3$ films derived from both Ba(thd)$_2$(pmdt) and Ba(thd)$_2$(tetraglyme). The pmdt adduct was selected because its thermal stability was better than that of the hmtt adduct.

The film growth experiments revealed that similar growth rates and compositions were obtained using either Ba(thd)$_2$(pmdt) or Ba(thd)$_2$(tetraglyme) under conditions that were optimized for the tetraglyme adduct. A substantial difference was observed, however, when the wall temperature of the reactor lowered by 80 °C. The growth rate and film composition using the pmdt adduct remained virtually the same, while the growth rate using the tetraglyme adduct decreased by approximately 40% and the barium content in the film decreased by approximately 50%. These results are significant because of the difficulty in maintaining all surfaces downstream of the vaporization zone at temperatures within the narrow window where typical barium precursors neither decompose nor condense. Improvements in precursor volatility, such as demonstrated by these adducts, relax reactor design constraints and enhance CVD process reproducibility.

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Supplementary Material Available: Perspective drawings of **I** and **II** showing thermal ellipsoids, including idealized hydrogen atoms; accompanying tables of bond lengths and angles, atomic coordinates and displacement parameters and calculated hydrogen atom positions (28 pages); list of observed and calculated structure factors for **I** and **II** (35 pages). Ordering information is given on any current masthead page.

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