Dimeric Barium β-Diketonate Complexes with Polydentate Amine Adducts: The Synthesis and Structural Characterization of $[Ba(THD)_2(L)]_2$ (L = Diethylenetriamine and Triethylenetetramine) Complex

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There has been a great deal of interest in the synthesis of alkaline earth metal β-diketonate complexes (particularly Ca, Sr and Ba), because they have been used as promising Metal Organic Chemical Vapor Deposition (MOCVD) precursors for perovskite metal oxides and ceramic superconductors.[1] A useful MOCVD precursor must have not only appropriate reactivity for the desired film growth process but also low volatility and stable vapor pressure characteristics.[2] Monomeric complexes are expected to exhibit enhanced volatility in comprarison to oligomeric complexes because of minimizing intermolecurlar solid-state interactions and connectivities. Barium bis (β-diketonate) complexes usually exist as tetramers in solid state and thus have relatively low volatility.[3] They also have unstable vapor pressure as a result of tendency to oligomerize. To circumvent this problem, recent research interests have been focused on the synthesis of barium precursors which have fluorinated β-diketonate ligands[4] or lewis base adduct complexes such as $[Ba(THD)_2(Et_2O)]_2$,[5] $Ba(THD)_2$(triglyme),[6] $Ba(THD)_2$(tetraglyme)[7] etc. (THD = 2,2,6,6-tetramethyl-3,5-heptanedionate). Fluorinated precursors such as $Ba(Hfa)_2$(tetraglyme)[8] (Hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentadionate) have superior volatility compared to that of nonfluorinated precursors. However, when they are empolyed as an MOCVD precursor, metal fluorides are usually deposited or fluoride contamination is unavoidable in final films. On the other hand, barium β-diketonate precursors with neutral lewis base adducts either decompose during vaporization or have low volatility. Because of the increased bacisity of amines compared to ethers, nitorgen donor ligands might be expected to make stronger bonds to barium diketonates than analogues oxygen-donor ligands. In this respect, when the polyamines were introduced as neutral ligands to metal diketonates, it is expected more stable thermal behavior of precursors than polyether adducts and simple monodentate lewis base adducts .

In this note, we report the synthesis and characterization of $[Ba(THD)_2(L)]_2$ (L = diethylenetriamine, triethylenetetramine) complexes which can be used as potential MOCVD precursors for high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ and ferroelectric $BaTiO_3$.

Experimental Section

All manipulations were performed using standard schelenk line techniques and under dinitrogen atmosphere. Tetrahydrofuran (THF) were distilled after being refluxed with sodium/benzophenone. Acetonitrile, n-pentane, n-hexane were distilled after being refluxed over CaH_2 befor use. Diethylenetriamine and triethylenetetramine (aldrich) were used as received. $Ba(thd)_2$ was prepared according to the literature method.[5]

$[Ba(THD)_2(diethylenetriamine)]_2$ (I). A 250 mL of schlenk flask was charged with 3 g of $Ba(thd)_2$ (5.95 mmol) and a stirring bar. To this flask 100 mL of THF was added *via* cannula and then 1.4 mL of diethylenetriamine (12.96 mmol) was injected slowly by a syringe with stirring at ambient temperature. The reaction mixtures were further stirred for 12h and filtered through fine porisity funnel. The solvent was removed by vacuum, then to the resulting oily crude pruducts 30 mL of acetonitrile was added, and stirred for 10 minutes. Finally white powders were isolated by filtration and dried under vacuum. Yield; 85%. Colorless crystals for single x-ray determination were grown from hot n-pentane solutions. mp 180-183, Calcd. For $Ba_2N_6O_8C_{52}H_{102}$: C, 51.44; H, 8.40; N, 6.92 Found. C, 51.35; H, 8.54; N, 6.86. FT-IR: ν (NH_2, NH); 3382, 3327 cm^{-1}, ν (C=O); 1593, 1590 cm^{-1}. ^1H NMR in d^6-Benzene: δ (C*H* in THD ligand); 5.744 (s, 1H), δ (CH_3 in THD ligand); 1.297 (s, 18H), δ (CH_2 in amine ligand); 2.503 (br, 2H), 2.278 (br, 2H), δ (NH_2, in amine ligand); 1.445 (br, 2H).

$[Ba(THD)_2(triethylenetetramine)]_2$ (II). A 250 mL of schlenk flask was charged with 3 g of $Ba(thd)_2$ (5.95 mmol) and a stirring bar. To this flask 100 mL of THF was added *via* cannula and then 1.8 mL of triethylenetetramine (12.09 mmol) was injected slowly by a syringe with stirring at ambient temperature. The reaction mixtures were further stirred for 12h and filtered through fine porisity funnel. The solvent was removed by vacuum, then to the resulting oily crude pruducts 30 mL of acetonitrile was added, stirred for 10 minutes. Finally white powders were isolated by filtration and dried under vacuum. Yield; 80%. Colorless crystals for single x-ray determination were grown from hot n-pentane solutions. mp 166-169, Calcd. For $Ba_2N_8O_8C_{56}H_{112}$: C, 51.72; H, 8.61; N, 8.61 Found. C, 51.76; H, 8.78; N, 8.62. FT-IR: ν (NH_2, NH); 3351, 3310, 3273 cm^{-1}, ν (C=O); 1579, 1568 cm^{-1}. ^1H NMR in d^6-Benzene: δ (C*H* in THD ligand); 5.82 (s, 1H), δ (CH_3 in THD ligand); 1.337 (s, 18H), δ (CH_2 in amine ligand); 2.416 (s, 2H), 2.253 (t, 4H), δ (NH_2, in amine ligand); 1.42 (br, 2H).

X-ray Crystallography. Single X-ray diffraction data for both crystals are presented in Table 1. Diffraction data were collected at ambient temperature on Bruker P4 four circle diffractometer using Mo-Kα radiation. Intensity data were collected by using a θ-2θ step scan technique and for all data sets the condition of the crystal was monitored by measuring 2 standard reflections. The solutions of both structures were carried out by a combination of heavy atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full matrix least squares methods was based on 8461 unique reflections (2θ = 45, $I > 2\sigma$) for I, and 4963 unique reflections (2θ = 45, $I > 2\sigma$) for II. Anisotropic temperature factors were used for all non-hydrogen atoms in I and II except one disordered carbon (C8A and C8B) for I which isotropic temperature factor was used. At the current stage of refinement on 705 parameters for I and 779 parameters for II with all atoms present in the asymmetric units, R = 0.054, Rw = 0.148 for I and R = 0.045, Rw = 0.117 for II.

Other physical measurements. ^{1}H NMR spectra (300 MHz) were obtained with Varian Gemini 300 spectrometer. Infrared spectra were measured with a Shimazu IR-470 spectrometer. CHN analyses were obtained with Thermoquest EA-1110 CHNS analyzer.

Results and Discussion

The dimeric species of $[Ba(THD)_2(L)]_2$ complexes can easily be obtained from the reaction shown in Eq. (1). The reaction of $Ba(THD)_2$ with 2 equivalent of diethylenetriamine in THF solution proceeds readily at ambient temperature, under N_2 atmosphere, to give colorless solution. The crude white product was redissolved in hot n-pentane and the volume of solution was reduced to one-half. Finally, colorless crystals of $[Ba(THD)_2(diethylenetriamine)]_2$ (I) was obtained from mother liquor. The $[Ba(THD)_2(triethylenetetramine)]_2$ (II) also could be isolated as colorless crystals in a similar method.

$$Ba(THD)_2 + L \rightarrow [Ba(THD)_2(L)]_2 \qquad (1)$$

L = diethylenetriamine, triethylenetetramine

The complexes of I and II are highly soluble in nonpolar hydrocarbon solvents such as n-pentane, n-hexane and in polar solvents like diethylether, THF and toluene but insoluble in CH_3CN or DMF. Both complexes are relatively stable in air but hygroscopic. The melting point of I and II is 180-183 °C and 166-169 °C, respectively, which is lower than that of $Ba(THD)_2$ (195-200 °C). Both complexes were characterized by IR, NMR, and elemental analysis.

The infrared spectrum of I and II exhibit the characteristic N-H stretching vibrational peaks from amine ligand at 3382, 3327 cm^{-1} in I, at 3351, 3310, 3273 cm^{-1} in II and the C=O stretching vibrational peaks from THD ligands at 1593, 1590 cm^{-1} in I, at 1579, 1570 cm^{-1} in II. ^{1}H NMR spectrum in C_6D_6 shows both complexes have $[Ba(THD)_2(L)]_n$ formula from 2 : 1 integral ratio between THD ligands and amine ligand.

Both complexes were structurally characterized in the solid state by the single-crystal X-ray diffraction method, and the ORTEP diagrams of I and II are shown in Figure 1 which reveals that both complexes are dimeric.

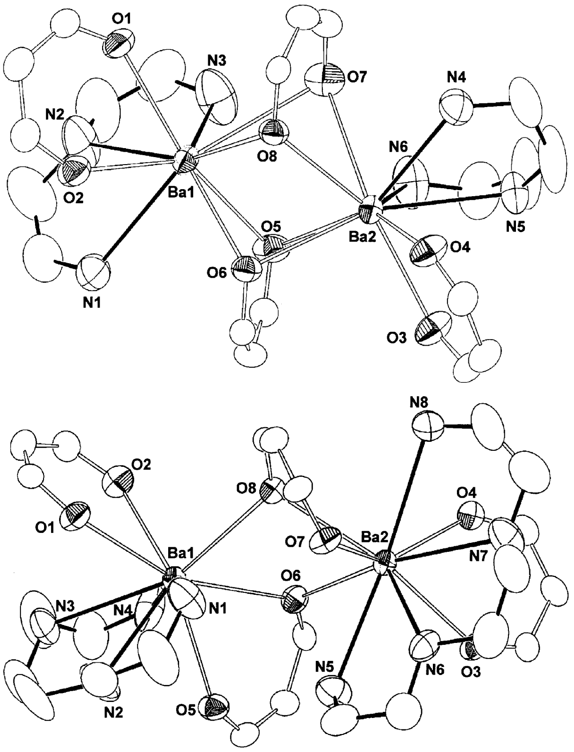

Figure 1. Structure and labeling of (a) $[Ba(THD)_2(diethylenetriamine)]_2$ (I) and (b) $[Ba(THD)_2(triethylenetetramine)]_2$(II). Thermal ellipsoids as drawn by ORTEP represent the 30% probability surfaces. Hydrogen atoms and ^{t}Bu carbon atoms in THD ligand have been omitted for clarity

The selected bond distances and angles of complex I and II are presented in Table 2.

In complexes I and II, each barium metal is a nine coordinate, with a distorted propellane fashion, where a terminal amine ligand and three THD ligands are coordinated to barium metal. In each complex, two barium atoms are bridged by two THD ligands, in which two amine ligands and two terminal THD ligands are coordinated as trans fashion. In the case of complex I, each barium atom is coordinated with three nitrogen atoms (Ba-N average 2.924 Å) from diethylenetriamine ligand and six oxygen atoms, two from the terminal THD ligand and four from the bridging THD ligands. On the other hand, each barium atom in complex II is coordinated with four nitrogen atoms (Ba-N average 2.95 Å) from triethylenetetramine and five oxygen atoms, two from the terminal THD ligand and three from the bridging THD ligand. The distances in bridging Ba-O_{thd}(average 2.906 Å in I and 2.842 Å in II) are significantly longer than those in terminal chelating ones (average 2.647 Å in I and 2.688 Å) as expected in both complexes. But two of four bridging Ba-O_{thd} distances in complex I are significantly long (Ba(1)-O(7); 3.173 Å, Ba(2)-(O(5); 3.240 Å), which indicates rather weak interaction. This tendency is more great in complex II, where no interaction between Ba(1)-O(7) and Ba(2)-(O(5) was observed. This is probably due to higher denticity of

Table 1. Crystallographic data for $[Ba(THD)_2(diethylenetriamine)]_2$ (I) and $[Ba(THD)_2(triethylenetetramine)]_2$ (II)

	I	II
formula	$Ba_2N_6O_8C_{52}H_{102}$	$Ba_2N_8O_8C_{56}H_{112}$
fw	1214.04	1300.18
crystal sys.	monoclinic	orthorhombic
space group	$P2_1/c$ (No.14)	P2(1)2(1)2(1) (No.19)
a, Å	22.880(3)	16.355(2)
b, Å	10.689(2)	19.412(3)
c, Å	28.354(4)	21.754(3)
α, deg	90	90
β, deg	109.16(1)	90
γ, deg	90	90
Z	4	8
V, $Å^3$	6550	6907
T, °C	20	20
λ, Å	0.71073	0.71073
ρ_{cacld}, g cm^{-3}	1.440	1.250
μ, cm^{-1}	1.256	1.183
R [a]	0.054	0.045
Rw [b]	0.148	0.117

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

amine ligand. Also, the slightly longer terminal chelating Ba-O distances in complex II than those for complex I reflect strong chelating effect of tetradentate triethylenetetramine ligand. These results show interesting feature that as the number of N atom donor in amine ligand is increased, the bonding between bridging THD ligand and barium metal is weakened.

The average Ba-N distances in complex I (2.924 Å) are slightly shorter than those for complex II (2.95 Å). However, in $Ba(THD)_2(TMEDA)_2$[9] complex, despite of higher basicity of TMEDA (N,N,N'N'-tetramethylethylenediamine) Ba-N distances (average 3.04 Å) are longer than those of complexes I and II. In this case, steric interactions between methyl groups on nitrogen atoms of TMEDA and t-butyl groups of THD ligands are more pronounced effect than basicity of amine ligand and thus Ba-N bond is weakened.

Further studies are in progress to derive monomeric barium precursors by reactions of both complexes with additional amine ligands or $Ba(THD)_2$ with other polyamine such as tetraethylenepentamine. Also thermal characteristics (volatility, stability, reactivity and decomposition) of I and II are currently under investigation in our laboratory.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes I, II

		I		II			
			Distance[a]				
Ba(1)-O(1)		2.653(5)		2.729(9)			
Ba(1)-O(2)		2.633(5)		2.659(10)			
Ba(2)-O(3)		2.642(5)		2.698(9)			
Ba(2)-O(4)		2.660(6)		2.668(10)			
			Ba-O in bridging position				
Ba(1)-O(5)	2.878(5)	Ba(2)-O(5)	3.240(6)	Ba(1)-O(5)	2.769(9)	Ba(2)-O(6)	3.005(9)
Ba(1)-O(6)	2.723(5)	Ba(2)-O(6)	2.747(5)	Ba(1)-O(6)	2.770(9)	Ba(2)-O(7)	2.815(9)
Ba(1)-O(7)	3.173(6)	Ba(2)-O(7)	2.946(6)	Ba(1)-O(8)	2.922(9)	Ba(2)-O(8)	2.772(8)
Ba(1)-O(8)	2.794(5)	Ba(2)-O(8)	2.750(5)				
Ba-N		2.924		2.95			
Range		2.874(8), 2.966(7)		2.875(12), 3.00(2)			
			Angles[a]				
O(2)-Ba(1)-O(1)		64.7(2)		63.6(3)			
O(3)-Ba(2)-O(4)		64.6(2)		63.6(3)			
Ba(1)-O(5)-Ba(2)		79.64(14)					
Ba(1)-O(6)-Ba(2)		91.81(14)		103.2(3)			
Ba(1)-O(7)-Ba(2)		79.79(14)					
Ba(1)-O(8)-Ba(2)		90.23(14)		105.3(3)			
N-Ba-N		58.7		58.2			
Range		58.5(2), 59.2(2)		57.5(4), 59.0(5)			
N(1)-Ba(1)-N(3)		102.6(3)		N(1)-Ba(1)-N(4)	159.8(6)		
N(4)-Ba(2)-N(6)		98.1(3)		N(5)-Ba(1)-N(8)	160.2(6)		

[a] Mean values of crystallographically independent, chemically equivalent structural parameters when more than two values are available. The number in parentheses represents the individual standard deviation.

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