

Novel Volatile Heteroleptic Barium Complexes Using Tetradentate Ligand and β -Diketonato Ligand

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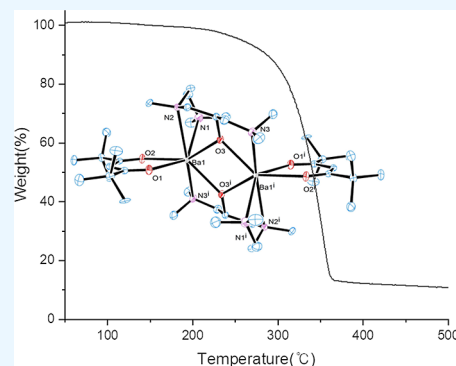


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ABSTRACT: Novel barium heteroleptic complexes were synthesized through the substitution of the bis(trimethylsilyl)amide of $\text{Ba}(\text{btsa})_2 \cdot 2\text{DME}$ with aminoalkoxide and β -diketonate ligands. Compounds $[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ (1) and $[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$ (2) were obtained and analyzed through Fourier transform infrared spectroscopy, nuclear magnetic resonance, thermogravimetric analysis, and elemental analysis (ddemapH = 1-(dimethylamino)-5-((2-(dimethylamino)ethyl) (methyl)amino)pentan-3-ol and ddemmpH = 1-(dimethylamino)-5-((2-(dimethylamino)ethyl) (methyl)amino)-3-methylpentan-3-ol). In single-crystal X-ray crystallography, complex 1 exhibited a dimeric structure with μ_2 -O bonds of the ddemap ligand. All complexes exhibited high volatility and could be sublimed under reduced pressure (0.5 Torr) at 160 °C, indicating that these complexes are promising candidates as atomic layer deposition or chemical vapor deposition precursors for the growth of barium-containing thin films.



INTRODUCTION

Heavier alkaline-earth metal compounds containing calcium, strontium, and barium are key components of magneto-resistive, ferroelectric, and piezoelectric materials for dynamic random access memory, a precursor for thin-film growth, organic synthesis, and electrically tunable microwave devices.^{1–15} In particular, electroceramics containing barium oxide (BaO) and transition-metal oxides such as BaTiO_3 , BaSrTiO_3 , and Y-doped BaZrO_3 exhibit high dielectric constants and high proton conductivity.^{16–21}

Therefore, they are commonly used in low-temperature superconductors, solar cells, high-k capacitors, and fuel cells. For the aforementioned applications, the fabrication of thin films containing these structures is required, which can be deposited using chemical vapor-phase methods such as metal–organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD). During these processes, it is essential to use precursor compounds with appropriate volatility and thermal stability.

However, the synthesis of barium complexes as CVD/ALD precursors is often limited by poor volatility and thermal stability owing to the formation of oligomeric structures as a result of their large atomic radius, high coordination sphere, and low oxidation number. To prevent the formation of oligomeric compounds, sterically bulky ligands or neural ligands such as tetraethylene glycol dimethyl ethereal (tetraglyme), tetramethylethylenediamine, β -diketonates, and cyclopentadienyl groups have been used to synthesize volatile Ba precursors with saturated metal centers. Precursors such as $\text{Ba}(\beta\text{-diketonate})_2(\text{glyme})$, $\text{Ba}(\text{thd})_2$, $\text{Ba}(\text{Me}_5\text{C}_5)_2$, Ba

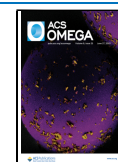
($^{\text{Pr}}\text{Me}_4\text{C}_5$)₂, and $\text{Ba}(^{\text{t}}\text{Bu}_3\text{C}_5\text{H}_2)_2$ have been reported to be volatile.^{22–29}

However, there have been challenges such as the instability of the β -diketonate precursors at their evaporation temperatures and the extreme sensitivity of cyclopentadienyl complexes to air (oxygen) and moisture.³⁰ To address these challenges, we synthesized heteroleptic precursors, where the central atom is bonded to different types of ligands such as multidentate aminoalkoxy ligands and β -diketonate ligands, which have a distinct advantage of having a different dissociation pattern for each ligand and might be useful in the development of thin films. Recently, we reported the synthesis of heteroleptic Sr complexes, which exhibited a saturated metal center and improved volatility and thermal stability.^{9,31} Among these complexes, a heteroleptic strontium complex with amino alkoxide ligand ($[\text{Sr}(\text{demamp})(\text{tmhd})]_2$) was used as the ALD precursor to fabricate thin films. Based on the results of our previous study, we conducted further research on heteroleptic Ba precursors using aminoalkoxides and β -diketonate ligands. Complexes $[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$ and $[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ were prepared through the in situ reaction of barium bis(trimethylsilyl)amides $[\text{Ba}(\text{btsa})_2 \cdot 2\text{DME}]$ (Scheme 1). All compounds were characterized

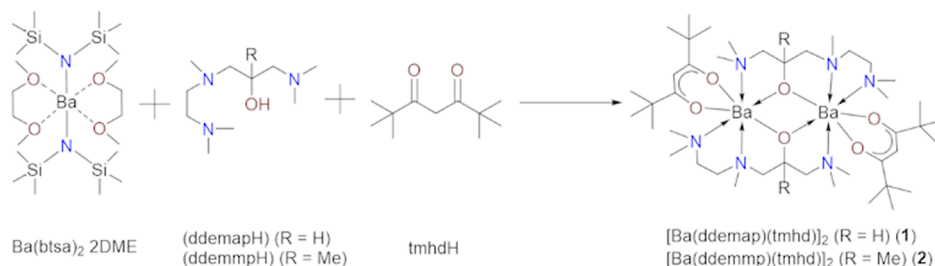
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Scheme 1. Synthesis of Complexes 1 and 2



through Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR) spectroscopy. Additionally, the molecular structure of complex **1** was characterized via X-ray crystallography.

EXPERIMENTAL SECTION

General Remarks. NMR spectra were recorded using a Bruker 500 MHz spectrometer (^1H) and a Bruker 500 MHz spectrometer (^{13}C) with C_6D_6 as the solvent and reference, respectively. Infrared (IR) spectra were obtained using a Nicolet Nexus FT-IR spectrophotometer. EA was performed using a Thermo Scientific OEA Flash 2000 analyzer. TGAs were conducted using a SETARAM 92–18 TG-DTA instrument with a constant flow of nitrogen (500 mL/min) throughout the experiment under inert conditions.

$\text{Ba}[\text{N}(\text{SiMe}_3)]_2 \cdot 2\text{DME}$ was prepared according to previously reported method.³² All reactions were performed under inert dry conditions in an argon-filled glovebox. Hexane was purified using an innovative technology PS-MD-4 solvent-purification system. All other chemicals were purchased from Aldrich and Alfa Aesar without further purification. The melting point was measured using a Stuart SMP40 automatic melting point apparatus.

ddemapH: dimethyl amine solution [2.0 M in tetrahydrofuran (THF)/50 mL, 0.1 mol] was added dropwise at 0°C with constant stirring to 40% ethanol solution of epichlorohydrin (9.2 g, 0.1 mol) in a three-necked flask fitted with a reflux condenser. After the addition, the reaction mixture was warmed to room temperature and stirring was continued for another 6 h. Then, trimethylethane-1,2-diamine (10.2 g, 0.1 mol) was added to the reaction mixture, which was then refluxed for 12 h. After the volatiles and solvent (ethanol and THF) were removed, the product was extracted with methylene chloride three times. The solvent was removed, and the crude product was distilled (110 $^\circ\text{C}/0.5$ Torr) to obtain a colorless liquid (10 g, 50%). ^1H NMR (500 MHz, C_6D_6): δ 2.05 (s, 6H, $(\text{CH}_3)_2\text{NCH}_2$), 2.20–2.45 (m, br, 8H, NCH_2CH , CHCH_2N , NCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}$), 2.13 (s, 6H, $(\text{CH}_3)_2\text{NCH}_2$), 2.15 (s, 3H, CH_3NCH_2), 3.84 (m, 1H, CH_2CHCH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 44.0 ($(\text{CH}_3)_2\text{NCH}_2$), 45.4 (CH_3NCH_2), 46.3 ($(\text{CH}_3)_2\text{NCH}_2$), 56.0 (NCH_2CH_2), 57.8 (NCH_2CH), 62.1 (CH_2CHCH_2), 64.3 (CH_2CHCH_2), and 67.1 (CH_2CHCH_2) ppm.

ddemmpH: dimethyl amine solution (2.0 M in THF/50 mL, 0.1 mol) was added dropwise at 0°C with constant stirring to 40% ethanol solution of 2-(chloromethyl)-2-methyloxirane (10 g, 0.1 mol) in a three-necked flask fitted with a reflux condenser. After the addition, the reaction mixture was warmed to room temperature and stirring was continued for another 6 h. Then, trimethylethane-1,2-diamine (10.2 g, 0.1

mol) was added to the reaction mixture, which was then refluxed for 12 h. After the volatiles and solvent (ethanol and THF) were removed, the product was extracted with methylene chloride three times. The solvent was removed, and the crude product was distilled (110 $^\circ\text{C}/0.5$ Torr) to obtain a colorless liquid (12 g, 60%). ^1H NMR (500 MHz, C_6D_6): δ = 1.24 (s, 3H, CH_3CCH_2), 2.02 (s, 6H, $(\text{CH}_3)_2\text{NCH}_2$), 2.08–2.62 (m, br, 8H, NCH_2CH , CHCH_2N , NCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}$), 2.27 (s, 3H, CH_3NCH_2), 2.30 (s, 6H, $(\text{CH}_3)_2\text{NCH}_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 26.0 (CH_3CCH_2), 45.1 ($(\text{CH}_3)_2\text{NCH}_2$), 46.9 (CH_3NCH), 48.2 ($(\text{CH}_3)_2\text{NCH}_2$), 57.7 (NCH_2CH_2), 58.1 (NCH_2CH), 65.6 (CH_2CHCH_2), 68.3 (CH_2CHCH_2), and 73.0 (CH_2CHCH_2) ppm.

General Procedure of the Synthesis of $[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ and $[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$. A hexane solution (10 mL) containing aminoalcohol ligands, ddemapH or ddemmpH, was added dropwise to a solution of $\text{Ba}[(\text{btsa})_2 \cdot 2\text{DME}]$ in hexane (20 mL) at room temperature with constant stirring. After stirring for 20 min at room temperature, 2,2,6,6-tetramethyl-3,5-heptadione (tmhdH) was added to the reaction mixture and stirred for another 15 h at room temperature. Subsequently, the mixture was filtered and the volatiles were removed in vacuo to obtain the product as a white solid. X-ray-quality crystals were grown from a saturated solution in toluene at -30°C .

$[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$ (1). $\text{Ba}(\text{btsa})_2 \cdot 2\text{DME}$ (0.64 g, 1.0 mmol), ddemmpH (0.20 g, 1.0 mmol), and tmhdH (0.18, 1.0 mmol) were used. Yield: 0.38 g (82%). mp > 200 $^\circ\text{C}$. ^1H NMR (500 MHz, C_6D_6): δ 1.35 (s, 18H, $(\text{CH}_3)_3\text{CCH}$), 1.85–2.66 (m, br, 8H, NCH_2CH , CHCH_2N , NCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}$), 2.13 (s, 3H, CH_3NCH_2), 2.17 (s, 6H, $(\text{CH}_3)_2\text{NCH}_2$), 2.33 (s, 6H, $\text{CH}_2\text{N}(\text{CH}_3)_2$), 4.34 (s, 1H, CH_2CHCH_2), and 5.81 (s, 1H, CCHC) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 29.3 ($(\text{CH}_3)_3\text{CCO}$), 41.1 ($(\text{CH}_3)_3\text{CCO}$), 41.3 ($(\text{CH}_3)_2\text{NCH}_2$), 44.7 (CH_3NCH_2), 57.4 ($(\text{CH}_3)_2\text{NCH}_2$), 67.4 (NCH_2CH_2), 68.9 (OCCH_2), 69.3 (NCH_2CH), 72.7 (CHCH_2N), 87.1 (CH_2CHCH_2), and 197.0 (COCHCO) ppm. FT-IR (KBr, cm^{-1}) = 2949 (s), 2898 (m), 2820(s), 2790(s), 1602 (s), 1576 (m), 1473 (m), 1455 (s), 1419 (s), 1356 (m), 1182 (m), 1144 (m), 1039 (w), and 863 (w). $\text{C}_{42}\text{H}_{86}\text{N}_6\text{O}_6\text{Ba}_2$ (1045.82) Calcd: C, 48.23; H, 8.29; N, 8.04. Found: C, 47.78; H, 8.59; N, 7.99.

$[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ (2). $\text{Ba}(\text{btsa})_2 \cdot 2\text{DME}$ (0.64 g, 1.0 mmol), ddemapH (0.22 g, 1.0 mmol), and tmhdH (0.18, 1.0 mmol) were used. Yield: 0.41 g (85%). mp > 200 $^\circ\text{C}$. ^1H NMR (500 MHz, C_6D_6): δ 1.35 (s, 18H, $(\text{CH}_3)_3\text{CCH}$), 1.40 (s, 3H, CH_3CCH_2), 2.11–2.43 (m, br, 8H, NCH_2CH , CHCH_2N , NCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{N}$), 2.19 (s, br, 3H, CH_3NCH_2), 2.26 (s, br, 6H, $(\text{CH}_3)_2\text{NCH}_2$), 2.28 (s, 6H, $\text{CH}_2\text{N}(\text{CH}_3)_2$) and 5.81 (s, 1H, CCHC) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 29.3

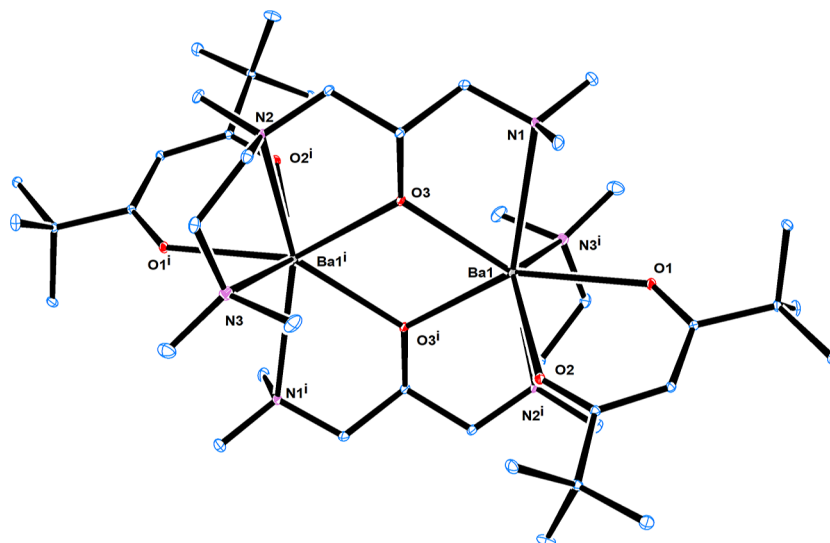


Figure 1. Oak Ridge Thermal Ellipsoid Plot drawing of the crystal structure of $[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ (**1**). The ellipsoids represent a probability of 30%.

$(\text{CH}_3)_3\text{CCO}$), 41.2 $(\text{CH}_3)_3\text{CCO}$), 45.4 $(\text{CH}_3\text{CCH}_2)$, 46.3 $(\text{CH}_3)_2\text{NCH}_2$), 48.4 $(\text{CH}_3\text{NCH}_2)$, 58.1 $(\text{CH}_2\text{NCH}_3)$, 71.6 (OCCH_3) , 74.2 $(\text{CH}_2\text{CCH}_2)$, 75.6 $(\text{CH}_2\text{CCH}_2)$, 87.1 $(\text{CH}_2\text{CHCH}_2)$, and 197.0 (COCHCO) ppm. FT-IR (KBr, cm^{-1}) = 2949 (s), 2898 (m), 2861 (m), 2820 (m), 2790 (m), 1602 (s), 1576 (m), 1505 (m), 1473 (m), 1455 (s), 1419 (s), 1356 (m), 1182 (m), 1144 (m), 1039 (w), 960 (w), and 863 (w). $\text{C}_{43}\text{H}_{88}\text{N}_6\text{O}_6\text{Ba}_2$ (1059.85) Calcd: C, 48.73; H, 8.37; N, 7.93. Found: C, 47.95; H, 8.60; N, 7.99.

Crystallography. A single crystal of **1** was grown through slow evaporation from a saturated solution of hexane in a glovebox at room temperature. Specimens of suitable size and quality were coated with paratone oil and mounted onto a glass capillary. Reflection data were collected using a Bruker Apex II-CCD area detector diffractometer with graphite-monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The cell parameters were determined and refined using the SMART program, and data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using the SADABS program. The structures were determined using direct methods, and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F2 using the SHELXTL/PC package. The hydrogen atoms were placed at their geometrically calculated positions and refined based on the corresponding carbon atoms with isotropic thermal parameters. The supplementary crystallographic data used in this study can be found at the Cambridge Crystallographic Data Centre (CCDC):2258733 (complex **1**). These data can be obtained free of charge from the CCDC.

RESULTS AND DISCUSSION

We have previously reported that the heteroleptic strontium complex $[\text{Sr}(\text{tmtad})(\text{tmhd})]_2$ with tmtad and tmhd as the coordinating bulky ligands saturates the metal center³⁰ (tmtadH = 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecan-7-ol). This complex exhibited a dimeric structure with a nonbonding amine group in its crystal structure and volatile properties. Based on these results, we conducted further research to prepare barium precursors with penta- and

tetradentate ligands, where only barium compounds using tetradentate ligands were synthesized as the desired products.

The simple preparation of $[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ and $[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$ complexes was conducted by a controlled in situ reaction using barium bis(trimethylsilyl)-amide $[\text{Ba}(\text{btsa})_2 \cdot 2\text{DME}]$ and appropriate ligands, such as ddemapH, ddemmpH, and tmhdH, to yield the desired products, $[\text{Ba}(\text{ddemap})(\text{tmhd})]_2$ (**1**) and $[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$ (**2**) (Scheme 1). All complexes were obtained in moderate yields of 80–90% as a white powder and purified through recrystallization from saturated hexane solution at $-30 \text{ }^\circ\text{C}$ or sublimation ($160 \text{ }^\circ\text{C}/0.5 \text{ Torr}$). In single X-ray crystallography, complex **1** exhibited a fully saturated dimeric structure without a nonbonding amine group. The ^1H NMR spectra of complexes **1** and **2** in the benzene- d_6 solution exhibited a downfield shift of the two amino groups $[-\text{N}(\text{CH}_3)_2]$ compared to the free ligands $[\text{CCH}_2\text{N}(\text{CH}_3)_2]$ and the absence of the btsa peak (Figures S1–S4), where ^1H NMR spectra of complex **2** exhibited broad peaks. The FT-IR spectra of all complexes indicated the absence of Si– CH_3 rocking vibration and –NH peaks from the btsa group; however, they exhibited peaks for C=O stretching in coordinated β -diketonate at 1602 and 1602 cm^{-1} , respectively, indicating that the reaction proceeded successfully (Figures S5 and S6).

Crystallography. The single-crystal X-ray study revealed that complex **1** crystallizes in the triclinic space group and exists as a dimer with an alkoxy oxygen bridging the two barium atoms in the complex through μ_2 -O bonding. In complex **1**, each of the metal centers is fully saturated by four oxygen atoms and three nitrogen atoms from the ddemap and one tmhd ligand, exhibiting a distorted capped trigonal prismatic structure, which is similar to the result of a previous report $[\text{Ba}(\text{tmtad})(\text{tmhd})]_2$ (Figure 1).³⁰ The distance between the two barium atoms in complex **1** is 4.112(8) \AA , which is shorter than that of $[\text{Ba}(\text{demamp})(\text{btsa})]_2$ [4.134(2) \AA].⁹ The reason for the reduced intermetal distance may be attributed to the replacement of the sterically bulky btsa group with a more compact tmhd group and ddemap ligand that includes an additional amine group. On average, the distance between the metal centers and the μ_2 -bridging alkoxy oxygen

atoms is 2.587 Å, which is slightly longer than the corresponding distance in $[\text{Ba}(\text{demamp})(\text{btsa})]_2$ (2.558 Å) (Table 1). The average bond lengths of Ba–N and Ba–O were 2.951 and 2.625 Å, respectively, and the bridging angle of Ba–O–Ba was 105.59 (7)°.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

bond lengths (Å)	1	bond angles (°)	1
Ba1–O3	2.588(2)	O3 ⁱ –Ba1–O3	74.41(7)
Ba1–O3 ⁱ	2.585(2)	O3 ⁱ –Ba1–N2 ⁱ	61.63(7)
Ba1–O1	2.638(2)	N2 ⁱ –Ba1–N3 ⁱ	61.78(8)
Ba1–O2	2.603(2)	O3–Ba1–N1	60.98(7)
Ba1–N2 ⁱ	2.928(3)	O1–Ba1–O2	65.82(7)
Ba1–N3 ⁱ	2.959(3)	Ba1–O3–Ba1 ⁱ	105.59(7)
Ba1–N1	2.969(3)		
Ba1–Ba1 ⁱ	4.112(8)		

Thermogravimetric Analysis. TGA of complexes 1 and 2 was conducted from room temperature to 500 °C (Figure 2)

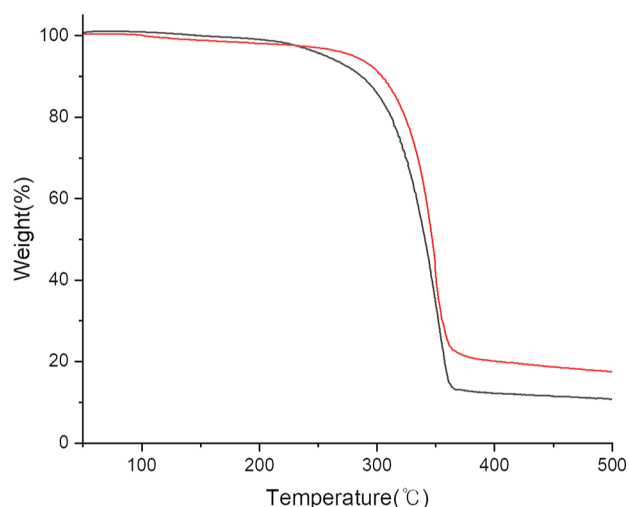


Figure 2. TGA plot of complexes 1 (black) and 2 (red).

Prior to this, sampling was conducted in an argon-filled glovebox, and data were collected under a constant flow of nitrogen to avoid any air contact. Complexes 1 and 2 exhibited 2% weight loss before reaching 250 °C. This mass loss can be explained by the evaporation of hexane from the sample. All compounds displayed clean one-step curves with 87% and 81% mass losses in the temperature range of 250–365 °C, where residual masses of 11% and 17% were observed, respectively. The residual masses of complexes 1 and 2 are comparable to those of BaO and BaCO₃ (calcd. 14% and 18%). All compounds exhibited high volatility and a low amount of nonvolatile residues. The sublimation tests of complexes 1 and 2 were performed under 0.5 Torr (160 °C), where the yields of sublimed products were in the range of 80–90%.

CONCLUSIONS

In this study, we successfully synthesized and characterized novel heteroleptic barium complexes; $[\text{Ba}(\text{ddemmp})(\text{tmhd})]_2$ (1) and $[\text{Ba}(\text{demamp})(\text{tmhd})]_2$ (2). All complexes were obtained as white crystalline powders, where complex 1 exhibited a dimeric structure with a μ_2 -bridging alkoxide

oxygen and distorted capped trigonal prismatic geometry in single-crystal X-ray crystallography. All the complexes are promising candidates for thin-film applications, as evidenced by their volatility and TGA results. These compounds exhibited a clean single-step TG curve and low nonvolatile residue and were sublimed at 0.5 Torr (160 °C). These results indicate the advantage of designing suitable heteroleptic complexes with fully saturated metal centers..

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c01697>.

Crystallographic data and data collection parameters for 1 (CIF)

Data collection parameters for complexes 1, DSC data of complexes 1 and 2, and NMR spectrum of complexes 1 and 2 (PDF)

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Notes

The authors declare no competing financial interest.

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