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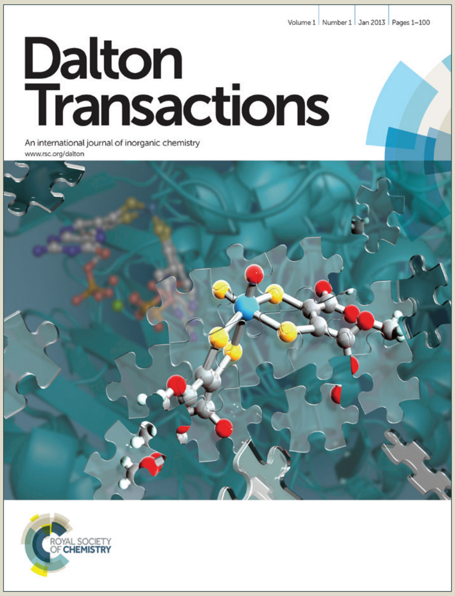

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New Heteroleptic Magnesium Complexes for MgO Thin Film Applications

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Novel heteroleptic magnesium complexes, $[Mg(dmamp)(acac)]_2$ (**1**), $[Mg(dmamp)(tmhd)]_2$ (**2**), $[Mg(dmamp)(tfac)]_2$ (**3**), and $[Mg(dmamp)(hfac)]_2$ (**4**), were successfully synthesized using dmamp and *β*-diketonate as ligands. The thermogravimetric analyses and volatile studies of the complexes show that the complexes, **2** and **4** display good volatility and thermal stability. The single crystal X-ray study of the complexes reveals that both the complexes **1** and **2** were crystalized in triclinic space group and as dimers, where magnesium atom is in a pentacoordinate state with distorted trigonal bipyramidal geometry.

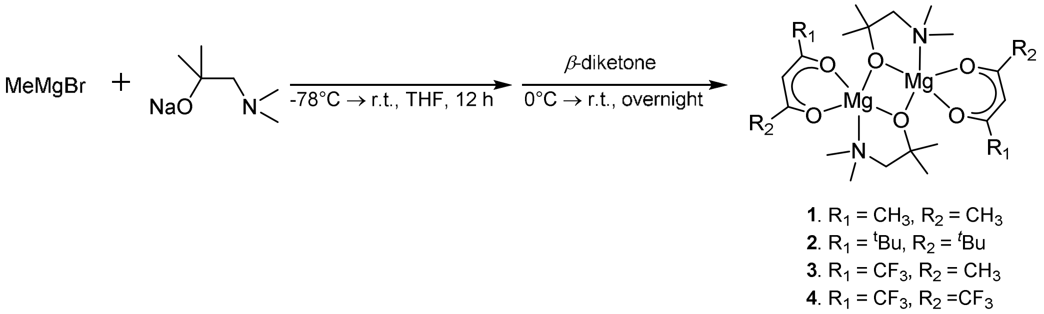
Introduction

Magnesium oxide thin films are attracting great scientific and technological interest due to their important applicative properties. Magnesium oxide, with a cubic crystalline structure, is characterized by remarkable chemical and thermal stability, a wide band gap (7.2 eV), and good electrical insulating properties. Therefore, MgO thin films are valuable candidates for the production of protective and barrier layers for various applications.[1]

Among the numerous methods used to deposit MgO thin films, metal–organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) are particularly attractive because they offer the potential for large-area growth with good control over composition, film uniformity, and excellent conformal step coverage on nonplanar device geometries.[2] However, the key to the successful growth of thin films using these techniques is the availability of highly volatile and thermally stable precursors. Various organometallic and coordination compounds of magnesium, including alkyls,[3] alkoxide,[4] carboxylates,[5] cyclopentadienyls,[6] chelating borohydrides[7] and *β*-diketonates,[8] have been used as magnesium oxide sources. Among these, the widely used *β*-diketonates complexes offer good thermal stability, volatility, and clean decomposition pathways. However, the high stability of *β*-diketonates compounds necessitates the use of harsh conditions, such as high temperatures, in order to deposit MgO thin films. The undesirable properties of other commonly used magnesium precursors such as, thermal instability, short shelf life, and low vapor pressures necessitate further research in this field.

Homoleptic precursors, wherein the magnesium ion is bonded to two identical ligands, have been commonly used to prepare MgO thin films; most of these compounds contain neutral coordinating ligands or solvent molecules[9] that are used to saturate the coordination sphere of the central magnesium ion. However, it may be difficult to control the desired reactivity and stability of the homoleptic magnesium precursor owing to the uniformity of the ligands, whereas a heteroleptic precursor with two different ligands attached to the metal center may provide us interesting alternatives to improve volatility, stability, and reactivity compared to their homoleptic counterparts. Our efforts have been concentrated on developing heteroleptic magnesium precursors to deliver better results by minimizing the shortcomings of the existing homoleptic complexes. These studies were supported by the recent publications,[10] which demonstrate the successful development and application of several heteroleptic precursors with improved performances.

In this study, we demonstrate the synthesis of new heteroleptic magnesium precursors by controlled two-step reactions using a combination of *β*-diketonate and aminoalkoxide ligands. The *β*-diketones used were acacH (acetylacetone), tmhdH (2,2,6,6-tetramethylheptan-3,5-dione), tfacH (trifluoroacetylacetone), and hfacH (hexafluoroacetylacetone), while dmampH (1-dimethylamino-2-methyl-2-propanol) was used as the aminoalcohol. The complexes $[Mg(dmamp)(acac)]_2$ (**1**), $[Mg(dmamp)(tmhd)]_2$ (**2**), $[Mg(dmamp)(tfac)]_2$ (**3**), and $[Mg(dmamp)(hfac)]_2$ (**4**) were synthesized, purified, and characterized by NMR, FT-IR, elemental analysis, and thermogravimetric analysis (TGA).



Scheme 1. Synthesis of Complex **1**-**4**.

The results obtained demonstrate the excellent thermal stability and volatility of these complexes especially **2** and **4** which display high volatility and stability.

Results and discussion

The new magnesium complexes were carefully prepared using Grignard reagent (MeMgBr) as shown in Scheme 1. In the first step MeMgBr was treated with one equivalent of the Na(dmamp), and reaction progress was monitored to completion through NMR analysis until all the aminoalkoxide was consumed. Next, the corresponding *β*-diketone was added and the resulting reaction mixture was stirred overnight at room temperature to afford the desired complexes. The final products [Mg(dmamp)(acac)]$_2$ (**1**), [Mg(dmamp)(tmhd)]$_2$ (**2**), [Mg(dmamp)(tfac)]$_2$ (**3**), and [Mg(dmamp)(hfac)]$_2$ (**4**) were purified by sublimation or by recrystallization from diethyl ether solution in moderate yields. We initially intended to isolate MeMg(dmamp) from the reaction between MeMgBr and Na(dmamp) and use this compound as an intermediate for the preparation of [Mg(dmamp)(*β*-diketonate)]$_2$. However, unlike the above mentioned reaction performed *in situ*, this method afforded several side products that were not identified nor purified by experimental methods. The novel magnesium complexes are air-sensitive, white solids at room temperature, which are quite soluble in organic solvents such as hexane, diethyl ether, toluene, and THF. Elemental analyses of the complexes demonstrates highly hygroscopic nature of the complexes.

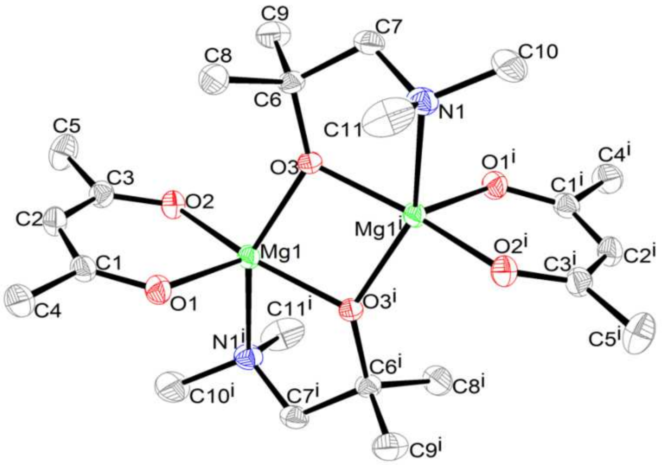


Figure 1. Crystal structure of complex **1**.

The X-ray quality crystals of complexes **1** and **2** were grown from saturated diethyl ether solutions at room temperature. The single crystal X-ray study of the complexes reveals that both the complexes **1** and **2** were crystalized as dimers in same triclinic space group (Table 1). Each of the magnesium metal centers in complexes **1** and **2**, which are isostructural, is bonded to one dmamp and one *β*-diketonate ligand (Fig. 1). The two dmamp alkoxide oxygen atoms bridge the pentacoordinate metal centers, each of which has distorted trigonal bipyramidal geometries. The Mg–O–Mg angles were found to be 99.70(6)° in **1** and 100.33(5)° in **2** (Table 2) which are comparable with those of oxygen bridged dimeric magnesium complexes like [Mg(L^2)$_2$]$_2$ (101.24(5)° and 100.70(5)°) and [MgCp(L^2)]$_2$ (98.72(4)°) (where L^2 = 4-(2,2-dimethyl hydrazino)-3-penten-2- onate).[11] However, the angles are larger than the bridging angles recorded in complexes [Mg$_2$(tmhd)$_4$] (87.4(3)°, 81.6(3)°, and 82.8(3)°),[12] and [L′MgOBu^n]$_2$ (94.23(1)°) (where L′ = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)-imino]pent-2-ene).[13] The distances between two Mg metal centers in **1** (3.0249(12) Å) and **2** (3.0293(11) Å) are shorter than that in [Mg(L^2)$_2$]$_2$ (3.1549(8) Å),[11] although they are comparable with those of [MgCp(L^2)]$_2$ (3.046(5) Å)[11] and [L′MgOBu^n]$_2$ (2.968(7) Å).[13] In complex **1**, oxygen atom of dmamp ligand (O3^i) and one oxygen atom of acac ligand (O2) occupy the axial positions with a O(2)–Mg(1)–O(3)^i bond angle of 156.87(6)°. The nitrogen atom of one dmamp group (N1^i), the oxygen atom of the neighboring dmamp group (O3), and one oxygen atom of acac ligand (O1) occupy equatorial sites around the central magnesium ion. The bond angles of O(3)–Mg(1)–O(1), O(3)–Mg(1)–N(1)^i, and O(1)–Mg(1)–N(1)′ are 114.06(6)°, 144.70(6)°, and 100.08(6)°, respectively, with sum of those angles equal to 358.84°, close to that of an idealized equatorial plane (360°). In complex **2**, oxygen atom of dmamp ligand (O3^i) and one oxygen atom of tmhd (O1) remain in axial positions, and O(1)–Mg(1)–O(3)^i bond angle is 157.00(5)°. Whereas, nitrogen atom of one dmamp group (N1^i), the oxygen atom of the neighboring dmamp group (O3), and one oxygen atom of tmhd (O2) are located in equatorial positions around the magnesium metal center. The bond angles of O(3)–Mg(1)–O(2), O(3)–Mg(1)–N(1)^i, and O(2)–Mg(1)–N(1)^i are 112.99(5)°, 145.60(5)°, and 99.46(5)°, respectively, again the sum of those angles (358.05°) close to an idealized equatorial plane (360°).

Table 1. Crystal Data and Data Collection Parameters for **1** and **2**.

Compound	1	2
Formula weight	479.20	647.51
T (K)	100(1)	100(1)
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	7.4739(2)	9.9012(3)
b (Å)	10.2275(3)	10.0337(4)
c (Å)	10.4806(3)	11.2703(4)
α (°)	106.722(2)	91.692(2)
β (°)	109.032(2)	108.897(2)
γ (°)	101.980(2)	108.191(2)
V (Å^3)	683.94(3)	995.68(6)
Z	1	1
$P_{\text{calcd.}}$ (Mg/m^3)	1.163	1.080
μ(mm^{-1})	0.123	0.100
F(000)	260	356
Crystal size (mm^3)	0.21 × 0.10 × 0.05	0.24 × 0.18 × 0.16
Theta range (°)	2.20 to 28.47	1.93 to 28.47
Index ranges	-9<=h<=9	$-13 \le h \le 13$
	-13<=k<=13	$-13 \le k \le 13$
	-14<=l<=14	$-15 \le l \le 15$
Total refl.	11843	25218
Indep. Refl. (R$_{\text{int}}$)	3330 (0.0220)	5019 (0.0480)
Parameters	145	199
GOF on F^2	1.059	1.048
R1 [I >2σ(I)]	0.0496	0.0505
wR2 [I >2σ(I)]	0.1463	0.1143

The ^{1}H NMR spectra of the complexes **1** to **4** show CH_3 on alkoxy carbon of dmamp ligand with signals at δ_H = 1.33, 1.31, 1.17, and 1.05 ppm, respectively (the corresponding signal for free dmampH appears at δ_H = 1.13 ppm). The upfield shifted signal in the spectrum of **4** may be caused by the higher number of fluorine atoms of hfac ligands attached to the same metal atom. The N(CH_3)$_2$ protons of the dmamp ligand for complexes **1** to **4** appear at δ_H = 2.10, 2.12, 2.01, and 1.93 ppm, respectively, which show upfield shift in peak positions with respect to dmampH (δ_H = 2.14 ppm). The β-CH protons of the diketonate ligands (acac, tmhd, tfac, and hfac) from compounds **1**-**4** appear at δ_H = 5.37, 5.82, 5.78, and 6.30 ppm, respectively, as singlets. The substantial deviation of these chemical shifts relative to those of free ligands, in addition to the absence of OH peaks from either dmampH or β-diketones (acacH, tmhdH, tfacH, and hfacH), confirm that the reactions were successful.

In order to get a clear idea about the structure of these complexes in solution, low temperature proton NMR analyses were carried out from 298K to 203K at ten different temperatures. For clarity, the β-diketonate peaks of the complexes were taken to explain the acquired data. The spectral data for the complexes **1** and **2** display no change in their spectra throughout the analyses. The methyl protons and β-CH protons appear as broad singlets in their respective spectra. This suggest that fluxional character of these molecules in solution even at low temperature with respect to the NMR time scale. The low temperature NMR spectra of the complex **3** and **4** give much clearer picture. In **3** the methyl protons of the tfac ligand which were observed as a broad singlet at room temperature, split into two equal singlets at 223K which then further split at lower temperatures. The β-CH protons of the tfac liand in **3** which is a broad singlet peak at room temperature separates into two singlets at 203K. The spectra of complex **4** display two distinct peaks for hfac β-CH protons from room temperature itself whereas, it appeared as singlet in benzene-d_6. The observed low temperature NMR data of the complexes clearly point towards the retention of dimeric structures in solution. In compounds **1** and **2** the presence of tmhd/acac ligands and site exchange reactions makes it difficult to distinguish between the CH_3 and β-CH protons whereas, in **3** and **4** the dimeric structure was much clear with identifiable peaks for each β-diketonate ligands.

Table 2. Selected bond lengths and bond angles of **1** and **2**.

	Compound 1	Compound 2
	Bond lengths (Å)	
Mg(1)-O(3)	1.9694(14)	1.9581(12)
Mg(1)-O(2)	2.0090(14)	1.9697(12)
Mg(1)-O(3)’	1.9880(14)	1.9866(11)
Mg(1)-O(1)	1.9914(14)	2.0092(12)
Mg(1)-N(1)’	2.2415(16)	2.2408(14)
Mg(1)…Mg(1)’	3.0249(12)	3.0293(11)
	Bond angles (°)	
O(3)-Mg(1)-O(2)	99.12(6)	112.99(5)
O(3)-Mg(1)-O(3)’	80.30(6)	79.67(5)
O(2)-Mg(1)-O(3)’	156.87(6)	111.27(5)
O(3)-Mg(1)-O(1)	114.06(6)	102.16(5)
O(2)-Mg(1)-O(1)	90.33(6)	89.36(5)
O(3)’-Mg(1)-O(1)	111.18(6)	157.00(5)
O(3)-Mg(1)-N(1)’	144.70(6)	145.60(5)
O(2)-Mg(1)-N(1)’	89.05(6)	99.46(5)
O(3)’-Mg(1)-N(1)’	79.17(6)	78.13(5)
O(1)-Mg(1)-N(1)’	100.08(6)	88.84(5)
Mg(1)-O(3)-Mg(1)’	99.70(6)	100.33(5)

Mass spectra of the complexes **1-4** display dominant peaks at m/z = 362, 222, and 123 for **1**, 530, 390 and 207 for **2**, 470, 330, and 177 for **3** and 578, 438, and 231 for **4** and each of these peaks corresponds to [{M(demamp)(β-diketonate)}$_2$-{dmamp}]$^+$, [M(β-diketonate)$_2$]$^+$, and [M(β-diketonate)]$^+$ respectively. These results confirm the formation of dimeric structures in all four complexes. The reason for fragmentation can be connected to the high sensitivity of these complexes to air and moisture.

Thermo-gravimetric analyses of the compounds **1** to **4** were conducted between room temperature to 800 °C (Fig. 2). Prior to analysis samplings were carried out in an argon filled glove box and data were collected under a constant flow of nitrogen to avoid any possible air contact. Complex **1** displays a 2.6% mass loss in 80–150 °C and complex **2** shows a 5.5% mass loss in 100–215 °C region which might be explained as evaporation of some trapped volatiles. Complex **1** exhibits a further mass loss of 70% in 150–340 °C region and a final residual mass of

16% at 800 °C. On the other hand, complex **2** displays a clean single-step mass loss of 89% at 150–335 °C region and a final nonvolatile residual mass of 5%. The TG plot of complex **3** shows several small steps from room temperature to 340 °C representing a combined mass loss of 64%, and a further mass loss of 4% was observed in **3** up to 800 °C. The TG plot of complex **4** shows a single step mass loss of 80% between room temperature and 255 °C, followed by a further mass loss of 8% up to 350 °C. Among the four magnesium complexes studied, compound **2** shows the lowest residue of 5% which is much lower than the calculated value 12.4% of MgO, meaning high volatility of **2**.

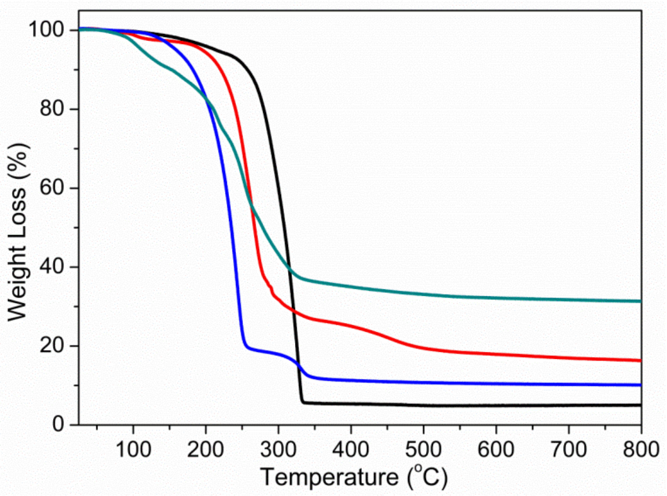


Figure 2. TGA plots of complexes **1-4**, red (**1**), black (**2**), green (**3**), blue (**4**).

The identities of all four complexes were confirmed by the spectroscopic and elemental analyses and the X-ray studies of **1** and **2** reveal their dimeric structures. Although repeated attempts to obtain suitable single crystals of **3** and **4** were unsuccessful, the similarity in ligands used in all four complexes led us to assume that the above complexes also exist as dimers. The absence of any coordinating solvent molecules and neutral ligands proposes that complexes **1** to **4** might function as stable magnesium precursors since the coordinating solvents and neutral ligands within such complexes tend to be the first to dissociate from the metals at elevated temperatures leading to the ligand rearrangement around the metal. The TG analyses for compounds **1**, **2,** and **4** display major single mass losses of 70, 89, and 80% up to 350 °C which indicate that they may act as potential precursors for magnesium oxide thin film deposition. The low amount of residue obtained in case of complex **2** reaffirms that this is a high potential precursor for MgO deposition. However, the TGA plot of **3** displays that mass loss occurs in several steps and yields a high amount of non-volatile residue, indicating its instability at higher temperatures. One possible reason for high amount of residue in the case of complex **3** can be the braking away of ligand fractions with temperatures which leaves magnesium oxide and carbon residues at the end. In order to reaffirm the volatility of the complexes **2** and **4**, sublimation tests were carried out under reduced pressure. At 0.5 Torr, compounds **2** and **4** exhibited good volatile character and sublimed at 80 °C and 90 °C, respectively. On the other hand, **1** and **3** were found to decompose at elevated temperature. FT-NMR, FT-IR and elemental analyses of sublimed samples of **2** and **4**, verified that these complexes had not undergone fragmentation during the sublimation process. The melting point of compound **2** (151 °C) which is higher than previously reported several ‘Mg(tmhd)$_2$’ complexes,[12,14] however its sublimation temperature (80 °C at 0.5 Torr) was much lower than that of previously reported [Mg$_2$(tmhd)$_4$] (120 °C at 0.2 Torr). This observation indicates that a decrease in sublimation temperature occurs when two of the tmhd ligands in [Mg$_2$(tmhd)$_4$] were replaced by dmamp ligand, supporting our argument that by selecting suitable ligands in a heteroleptic metal complex, we can improve the properties considerably from the corresponding homoleptic parent complexes.

Experimental

General

All manipulations were performed under a dry, oxygen-free atmosphere of nitrogen or argon using standard Schlenk techniques or a glove box. All solvents were purified using an Innovative Technology PS-MD-4 solvent purification system. The functionalized bidentate aminoalcohol 1-dimethylamino-2-methyl-2-propanol (dmampH), was synthesized by slightly modified literature method.[15] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 MHz FT-NMR spectrometer. All NMR samples were contained in sealed NMR tubes and referenced using benzene-d_6 as standard. VT-NMR spectra were recorded on a Bruker DPX 500 MHz FT-NMR spectrometer using toluene-d_8 as standard and solvent. Infrared spectra were obtained with a Nicolet NEXUS FT-IR spectrometer using a 4 mm KBr window or KBr pellet. The samples were prepared in a glove box. Elemental analyses were performed using a Thermoquest EA-1110 CHNS analyzer.

Thermal analyses of 1-4: Thermogravimetric and differential thermal analyses (TGA/DTA) for newly synthesized complexes were obtained using a Perkin-Elmer TGA7 apparatus. TGA data were obtained up to 800 °C with a heating rate of 10 °C/min under atmospheric pressure with N$_2$ as the carrier gas. TG sampling was carried out inside an argon-filled glove box to avoid contact with air.

Syntheses

Na(dmamp): First, dmampH (5.10 g, 43.5 mmol) was slowly added to a suspension of Na (1.00 g, 43.5 mmol) in hexane (50 mL) at 0 °C, the reaction mixture was then allowed to reflux overnight. After cooling to room temperature, the solvent was removed to obtain sodium 1-dimethylamino-2-methyl-2-propoxide (Na(dmamp)) as a white powder. Yield 4.40 g (73%). ^{1}H NMR (C_6D_6, 300 MHz): δ_H 1.23 (s, 6H, CCH_3), 2.24 (s, 8H, N$(CH_3)_2$ and CH_2).

$[Mg(dmamp)(acac)]_2$ (1): MeMgBr (3.0 M in diethyl ether, 2.39 mL, 7.18 mmol) was added to a solution of Na(dmamp) (1.00 g, 7.18 mmol) in THF at -78 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 12 h. Acetylacetone (acacH, 0.720 g, 7.18 mmol) was slowly added to the above mixture and stirring was continued for another 12 h. The reaction mixture was then dried from the volatiles and the resulted residue was then extracted into hexane, filtered to remove salts and the filtrate was concentrated *in vacuo* to afford the product as a white solid. Recrystallization from ether afforded the pure magnesium complex as colorless crystals. Yield: 1.40 g (69%); mp 136 °C. FTIR (ν_{max}/cm^{-1}) 2987m, 2972m, 2960m, 2917m, 2863m, 2833m, 2789w, 1609m, 1516m, 1470m, 1397m, 1360m, 1351m, 1296w, 1260m, 1227m, 1213m, 1195m, 1155m, 1126w, 1034m, 1019s, 996m, 955s, 922s, 904w, 841w, 802m, 767s, 657m, 620m, 555w, 529w, 489w, 453w. ^{1}H NMR (C_6D_6, 300.13 MHz): δ_H 1.33 (s, 6H, OC(C*H*$_3$)$_2$), 1.90 (s, 6H, C*H*$_3$C=O), 2.10 (s, 6H, N(C*H*$_3$)$_2$), 2.16 (s, 2H, CC*H*$_2$N), 5.37 (s, 1H, β-C*H*). ^{13}C NMR (C_6D_6, 75.04 MHz): δ_C 28.1 (2C, diketone α-C(*C*H$_3$)$_2$), 33.0 (2C, C(*C*H$_3$)$_2$), 47.2 (2C, N(*C*H$_3$)$_2$), 67.0 (1C, *C*(CH$_3$)$_2$), 72.8 (1C, C*C*H$_2$N), 100.2 (1C, β-*C*H), 191.5 (2C, diketone α-*C*). Anal. Calcd for $C_{11}H_{21}MgNO_3.1.5H_2O$: C, 52.20; H, 8.96; N, 5.53. Found: C, 51.77; H, 8.29; N, 5.06. EI-MS: *m/z* calc. for $[Mg(dmamp)(acac)]_2$: 479.60 $[M]^+$; found 362 $[\{Mg(dmamp)(acac)\}_2\text{-}\{dmamp\}]^+$, 222 $[Mg(acac)_2]^+$, 123 $[Mg(acac)]^+$.

$[Mg(dmamp)(tmhd)]_2$ (2): A similar procedure was followed as above and 2,2,6,6-tetramethylheptan-3,5-dione (tmhdH, 1.32 g, 7.18 mmol) was used as the β-diketonate ligand. The product was obtained as white solid and purified by sublimation under vacuum condition (80 °C/0.5 Torr). Yield: 1.40 g (61%); mp 151 °C. FTIR (ν_{max}/cm^{-1}) 2963s, 2864m, 2832m, 2790w, 1594s, 1581s, 1539m, 1509s, 1496m, 1454m, 1415s, 1355m, 1297w, 1247m, 1226m, 1214m, 1198m, 1182m, 1159m, 1139m, 1127w, 1034m, 1020m, 998m, 954w, 904w, 868m, 793m, 759w, 736w, 626m, 530w, 495w, 473w, 430w. ^{1}H NMR (C_6D_6, 300.13 MHz): δ_H 1.28 (s, 18H, ^{t}Bu), 1.31 (s, 6H, OC(C*H*$_3$)$_2$), 2.12 (s, 6H, N(C*H*$_3$)$_2$), 2.15 (s, 2H, CC*H*$_2$N), 5.82 (s, 1H, β-C*H*). ^{13}C NMR (C_6D_6, 75.04 MHz): δ_C 28.8 (6C, diketone α-CC(*C*H$_3$)$_3$), 32.9 (2C, C(*C*H$_3$)$_2$), 41.1 (2C, diketone α-C*C*(CH$_3$)$_3$), 47.3 (2C, N(*C*H$_3$)$_2$), 66.9 (1C, *C*(CH$_3$)$_2$), 72.9 (1C, C*C*H$_2$N), 89.8 (1C, β-*C*H), 201.1 (2C, diketone α-*C*). Anal. Calcd for $C_{17}H_{33}MgNO_3$: C, 63.07; H, 10.27; N, 4.33. Found: C, 62.45; H, 10.29; N, 4.11. EI-MS: *m/z* calc. for $[Mg(dmamp)(tmhd)]_2$: 647.52 $[M]^+$; found 530 $[\{Mg(dmamp)(tmhd)\}_2\text{-}\{dmamp\}]^+$, 390 $[Mg(tmhd)_2]^+$, 207 $[Mg(tmhd)]^+$.

$[Mg(dmamp)(tfac)]_2$ (3): A similar procedure as above was followed, and trifluoroacetylacetone (tfacH, 1.10 g, 7.18 mmol) was used as the β-diketonate ligand. The product was obtained as a yellow solid and recrystallization from ether afforded pure compound as colorless crystals. Yield: 1.34 g (54%); mp 211 °C. FTIR (ν_{max}/cm^{-1}) 3054w, 2966m, 2866m, 2837m, 2795w, 1695m, 1637s, 1521m, 1497m, 1457m, 1383w, 1361m, 1294s, 1265m, 1213m, 1188m, 1138s, 1029w, 1017w, 993m, 950w, 896w, 854w, 803w, 742m, 705m, 614w, 571w, 518w, 435w. ^{1}H NMR (C_6D_6, 300.13 MHz): δ_H 1.17 (s, 6H, OC(C*H*$_3$)$_2$), 1.73 (s, 3H, C*H*$_3$C=O), 2.01 (s, 6H, N(C*H*$_3$)$_2$), 2.32(s, 2H, CC*H*$_2$N), 5.78 (s, 1H, β-C*H*). ^{13}C NMR (C_6D_6, 75.04 MHz): δ_C 25.7 (1C, diketone α-C*C*H$_3$), 28.8 (2C, C(*C*H$_3$)$_2$), 47.1 (2C, N(*C*H$_3$)$_2$), 68.0 (1C, *C*(CH$_3$)$_2$), 95.6 (1C, C*C*H$_2$N), 117.9 (1C, β-*C*H), 121.7 (1C, diketone α-C*C*F$_3$), 171.6 (1C, diketone α-*C*CF$_3$), 199.6 (1C, diketone α-*C*CH$_3$). Anal. Calcd for $C_{11}H_{18}F_3MgNO_3.H_2O$: C, 43.67; H, 6.33; N, 4.63. Found: C, 43.58; H, 6.17; N, 4.23. EI-MS: *m/z* calc. for $[Mg(dmamp)(tfac)]_2$: 587.14 $[M]^+$; found 470 $[\{Mg(dmamp)(tfac)\}_2\text{-}\{dmamp\}]^+$, 330 $[Mg(tfac)_2]^+$, 177 $[Mg(tfac)]^+$.

$[Mg(dmamp)(hfac)]_2$ (4): A similar procedure as above was followed, and hexafluoroacetylacetone (hfacH, 1.49 g, 7.18 mmol) was used as the β-diketonate ligand. The product was obtained as a pale yellow solid and purified by sublimation under vacuum condition (90 °C/0.5 Torr). Yield: 1.10 g (44%); mp 179 °C. FTIR (ν_{max}/cm^{-1}) 2969m, 2872m, 2839m, 2797w, 1659s, 1555m, 1529m, 1515s, 1458m, 1409m, 1384w, 1357w, 1256s, 1208s, 1144s, 1029w, 1017w, 994m, 953m, 908w, 842w, 798m, 743m, 706m, 663m, 613m, 585m, 528m, 496w, 431w. ^{1}H NMR (C_6D_6, 300.13MHz): δ_H 1.05 (s, 6H, OC(C*H*$_3$)$_2$), 1.93 (s, 6H, N(C*H*$_3$)$_2$), 1.93(s, 2H, CC*H*$_2$N), 6.30 (s, 1H, β-C*H*). ^{13}C NMR (C_6D_6, 75.04 MHz): δ_C 25.4 (2C, C(*C*H$_3$)$_2$), 47.6 (2C, N(*C*H$_3$)$_2$), 68.5 (1C, *C*(CH$_3$)$_2$), 89.9 (1C, C*C*H$_2$N), 116.4 (1C, β-*C*H), 120.2 (2C, diketone α-C*C*F$_3$), 178.5 (2C, diketone α-*C*CF$_3$). Anal. Calcd for $C_{11}H_{15}F_6MgNO_3.2H_2O$: C, 36.14; H, 4.69; N, 3.83. Found: C, 36.00; H, 4.33; N, 3.32. EI-MS: *m/z* calc. for $[Mg(dmamp)(hfac)]_2$: 695.08 $[M]^+$; found 578 $[\{Mg(dmamp)(hfac)\}_2\text{-}\{dmamp\}]^+$, 438 $[Mg(hfac)_2]^+$, 231 $[Mg(hfac)]^+$.

X-ray Crystallography: Single crystals of **1** and **2** were grown from a diethyl ether solution at room temperature. A specimen of suitable size and quality was coated with Paratone oil and mounted onto a glass capillary. Reflection data were collected on a Bruker Apex II-CCD area detector diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The hemisphere of reflection data was collected as ω-scan frames with 0.3°/frame and an exposure time of 10 s/frame. Cell parameters were determined and refined by the SMART program.[16] Data reduction was performed using SAINTsoftware.[17] The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.[18] The structure was solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F2 using the SHELXTL/PC package.[19] Hydrogen atoms were placed at their geometrically calculated positions and were refined riding on the corresponding carbon atoms with isotropic thermal parameters.

CCDC-999419 (for **1**), and CCDC-999420 (for **2**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In summary, new heteroleptic magnesium complex combining dmamp and β-diketonate ligands were synthesized in two step reactions. Complexes **1** and **2** were characterized by single crystal X-ray studies and shown to exist as dimers wherein, pentacoordinate magnesium atoms adopt distorted trigonal bipyramidal geometries. The complexes are promising candidates for thin film applications as made evident by their volatility and thermogravimetric analyses. Among the complexes, **2** and **4** display good volatility and thermal stability. Complex **2** in particular, exhibits excellent thermal properties with clean single step TG curve and low non-volatile residual mass. Although it has a higher melting point, complex **2** has a low sublimation temperatures compared to $[Mg_2(tmhd)_4]$ complex. These results presented herein demonstrate the advantage of designing suitable heteroleptic complexes as metal oxide thin film precursors with improved physical and chemical properties. Studies are in progress on the application of these heteroleptic magnesium complexes (especially **2**) as possible precursors for the growth of magnesium oxide thin films using metal organic vapor deposition (MOCVD) or atomic layer deposition (ALD) techniques.

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Notes and references

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†Electronic Supplementary Information (ESI) available: VT-NMR spectra of complexes **1**-**4** were given. See DOI: 10.1039/b000000x/

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Graphical Abstract

Novel magnesium precursors for ALD/CVD process of MgO thin films were synthesized as heteroleptic complexes. These complexes show high volatility and good thermal properties which proved to be superior to those of homoleptic parent complexes.