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Volatile *N,N′*-dialkyl-β-dialdiminate complexes of magnesium and zinc as possible chemical vapor deposition precursors

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ABSTRACT

A series of volatile magnesium(II) and zinc(II) bis(β-dialdiminato) complexes (of stoichiometry $M[RN(CH)_3NR]_2$ where R = methyl, ethyl, isopropyl, or *tert*-butyl) have been prepared and investigated as potential precursors for the chemical vapor deposition of thin films. Several of the compounds have been characterized crystallographically; the metal centers adopt pseudo-tetrahedral geometries with the two ligands forming six-membered rings with the metal center. All eight compounds sublime cleanly both in vacuum and under 1 atm of N_2, and the most volatile compounds (those having *N*-methyl substituents) have vapor pressures of 1 Torr at 88 (Mg) and 90 °C (Zn). In general, metal complexes of *N,N′*-dialkyl-β-dialdiminate ligands are more volatile than their corresponding *N,N′*-dialkyl-β-diketiminate and *N,N*-dialkylamidinate analogues.

1. Introduction

β-Diketiminate (nacnac) groups are widely employed as ligands for metal centers; part of their popularity stems from the ability to tune their steric and electronic properties to suit the specific need [1–6]. As a result, they have been used for a variety of applications; in main group chemistry, for example, they can stabilize metals in unusually low oxidation states such as Mg^I, Al^I and Ga^I [4,7–10]. In transition metal chemistry, they serve as ancillary ligands for metals that are catalytically active for a variety of molecular transformations [11–13].

Closely related to the β-diketiminates are the β-dialdiminates, in which the imine carbon bears hydrogen atoms rather than other (usually organic) substituents (Fig. 1, $R^2 = R^4 = H$). Most of the known metal complexes of β-dialdiminate ligands bear aryl substituents on the two nitrogen atoms; in contrast, metal complexes of *N,N′*-dialkyl-β-dialdiminates have been little studied. A few *N,N′*-dialkyl-β-dialdiminate compounds of divalent Co, Ni, Cu, Zn and Pd are known in which the central methine position (R^3 in Fig. 1) is substituted with a nitro group [14,15]. In addition, there are some transition metal complexes of tetradentate ligands that incorporate *N,N′*-dialkyl-β-dialdiminate units [16–19]. None of these complexes, however, contains unsubstituted *N,N′*-dialkyl-β-dialdiminate ligands with small aliphatic alkyl groups on nitrogen.

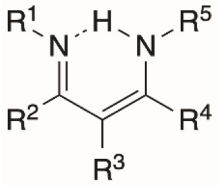

Fig. 1. A generic β-diimine.

Unlike amidinates, β-dialdiminates and β-diketiminates do not require large substituents on nitrogen to form monomeric bis-complexes (due to the longer backbone which leads to a larger ligand bite angle): for example, magnesium bis(amidinato) compounds have N-Mg-N angles of about 66° [20] whereas magnesium bis(β-diketiminato) complexes have N-Mg-N angles of about 100° [21]. Furthermore, because β-dialdiminate ligands have lower molecular weights than corresponding β-diketiminates (due to the lack of methyl substituents on the ligand backbone R^2 and R^4 positions), β-dialdiminates should form coordination complexes whose volatilities are greater than those of analogous β-diketiminate (and amidinate) ligands. As a result, β-dialdiminate complexes might serve as excellent precursors for the chemical vapor deposition (CVD) or atomic layer deposition (ALD) of thin films.

We have recently described the synthesis of *N,N′*-dialkyl-1,3-propanedialdiminium chlorides, *N,N′*-dialkyl-1,3-propanedialdimines, and lithium *N,N′*-dialkyl-1,3-propanedialdiminates, in which the *N*-alkyl groups are methyl, ethyl, isopropyl, or *tert*-butyl [22]. In the present paper, we make use of these reagents to prepare bis(β-dialdiminato) complexes of zinc and magnesium and test these hypotheses.

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2. Results and discussion

2.1. *Synthesis and Characterization of Bis(β-dialdiminato) Complexes of Magnesium(II) and Zinc(II)*

We have synthesized eight new bis(β-dialdiminato) compounds of stoichiometry $Mg[RN(CH)_3NR]_2$, **1a**-**1d**, and $Zn[RN(CH)_3NR]_2$, **2a**-**2d**, where R = (**a**) Me, (**b**) Et, (**c**) ^{i}Pr, or (**d**) ^{t}Bu. The compounds were prepared by one of three different synthetic routes (Scheme 1): (i) protonolysis of (*n*-butyl)(*sec*-butyl)magnesium with the neutral *N,N*′-dialkyl-1,3-propanedialdimine (**1b**, 72 %), (ii) salt metathesis from the metal halide and isolated samples of lithium *N,N*′-dialkyl-1,3-propanedialdiminate (**1a**, 20 %; **1c**, 80 %; **1d**, 26 %; **2d**, 29 %), or (iii) salt metathesis from the metal halide and sodium *N,N*′-dialkyl-1,3-propanedialdiminate prepared *in situ* from the *N,N*′-dialkyl-1,3-propanedialdiminium chloride and sodium ethoxide (**2a**, 70 %; **2b**, 79 %; **2c**, 88 %). The highest yielding and most convenient synthetic route depends on the choice of metal and the substituent on nitrogen.

All compounds can be isolated in moderate-to-good yields by sublimation, crystallization, or vacuum distillation. Compounds **1a**, **1d**, **2a**, **2b**, and **2d** are colorless solids, whereas compounds **1b**, **1c**, and **2c** are oils. The magnesium compounds decompose within minutes upon exposure to air or water. In contrast, the zinc compounds can be handled in air for at least an hour without decomposition, but over several hours to several days the solids discolor in air and agglomerate, presumably due to hydration or hydrolysis.

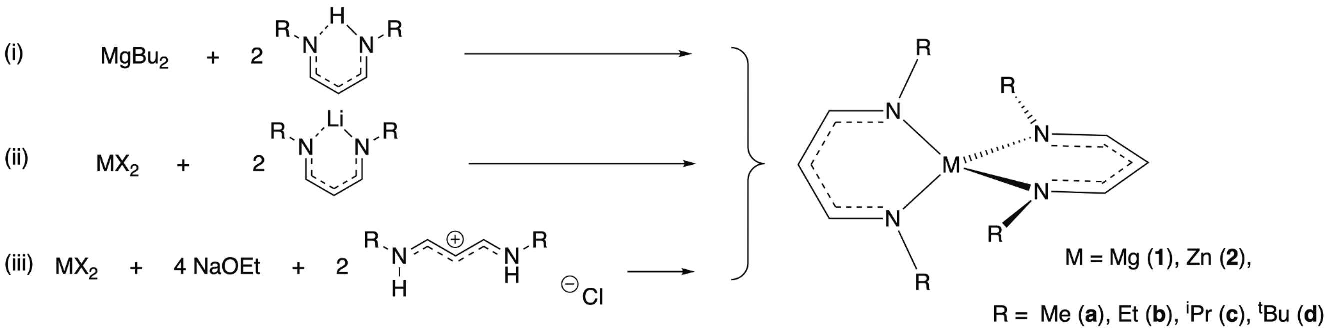
The IR spectra of compounds **1a**-**1d** and **2a**-**2d** show two strong peaks due to C=C and C=N stretching vibrations, one between 1589 and 1604 cm^{-1}, and a second between 1515 and 1522 cm^{-1}. The *N-tert*-butyl compounds **1d** and **2d** have an additional strong band at 1507 and 1506 cm^{-1}, respectively. The absorption bands in these regions are similar to those reported for *N*-alkyl β-diketiminato compounds of magnesium [21] and also for *N*-aryl β-diketiminato compounds of magnesium [23] and zinc [24,25], which generally feature a C=C/C=N stretching band between 1551 and 1594 cm^{-1}, and a second band between 1513 and 1524 cm^{-1}. UV–Vis data for the zinc compounds **2a**-**2d** as well as the neutral β-dialdimines can be found in the SI.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **1a**-**1d** and **2a**-**2d** (Fig. 2; Table S1.1 and S1.2) show nicely resolved resonances for the ligand backbone CH and *N*-alkyl groups, with chemical shifts that are similar to those seen for the lithium salts [22].

2.2. *Crystal Structures*

We have carried out X-ray crystallographic studies of the magnesium *N-tert*-butyl compound **1d** and all four zinc compounds **2a**-**2d**. Comparisons of their structures with those of similar reported compounds can be found in the Supplemental Information.

All five compounds are monomeric in the solid state and adopt pseudo-tetrahedral geometries about the metal center, as expected for these d^0 (Mg^{II}) and d^{10} (Zn^{II}) species (Figs. 3 and 4). The τ_4 values (a parameter that ranges from 1.00 for perfect tetrahedral geometry to zero



Scheme 1. Syntheses of the magnesium and zinc compounds presented here.

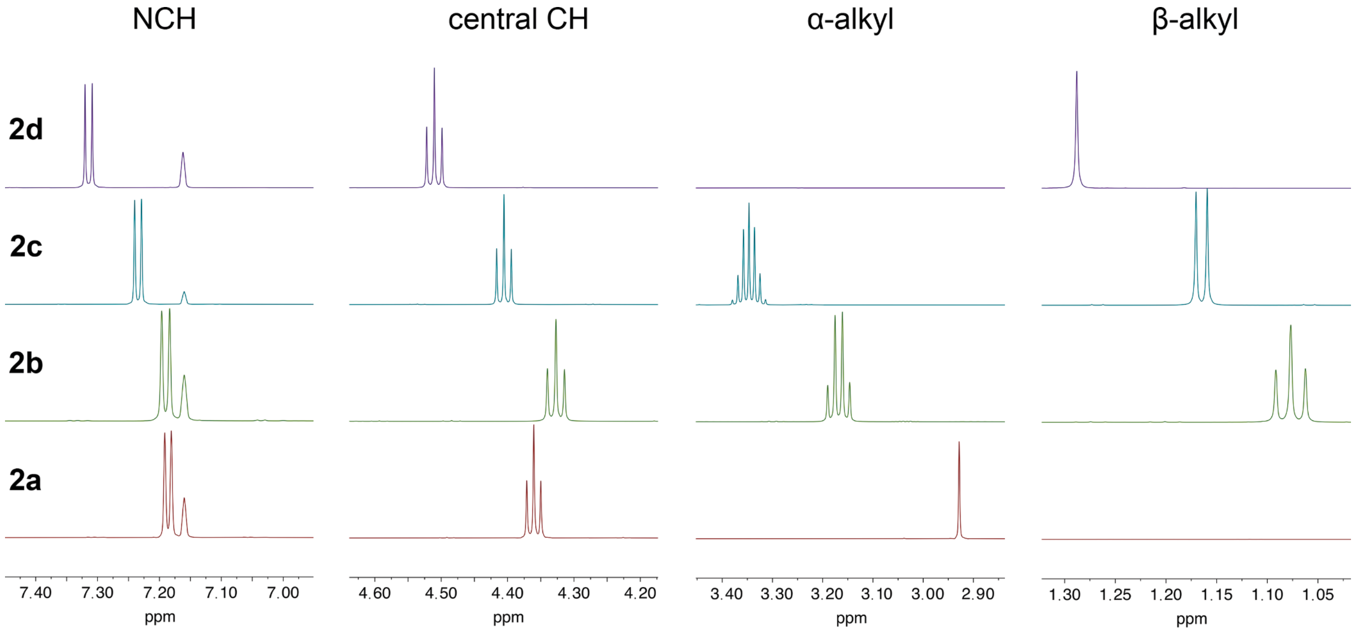


Fig. 2. ^{1}H NMR spectra of the zinc(II) compounds **2a**-**2d**. The peak at δ 7.16 is due to solvent.

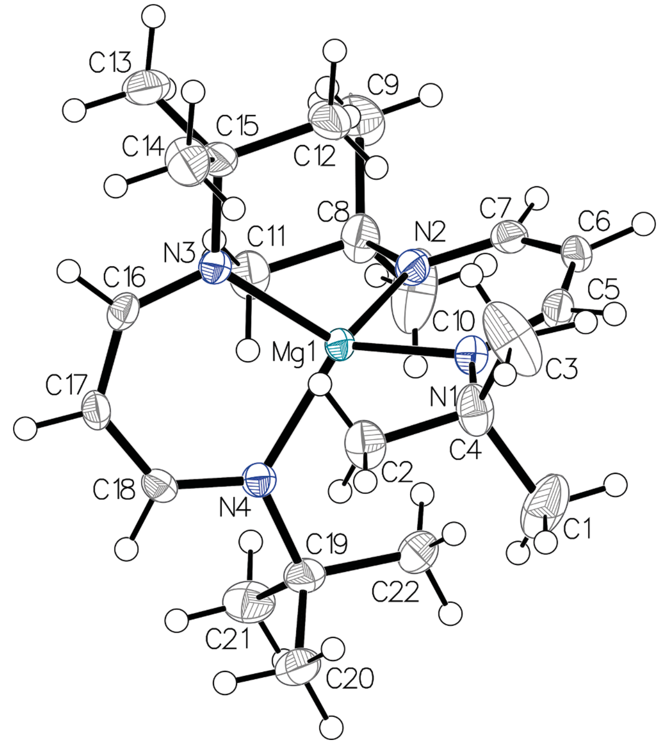


Fig. 3. Molecular structure of the magnesium compound **1d**. Thermal ellipsoids drawn at the 50% probability density level except for hydrogen atoms, which are represented by arbitrarily-sized spheres.

for perfect square-planar geometry) [26] are 0.84–0.92, and the dihedral angle between the two ligand planes ranges from 81.89(6) to 90° (Table 1). The π bonds in the planar NCCCN ligand backbones are delocalized, so that the two N═C distances are equal, as are the two C═C distances. For example, the zinc complex **2a** has N═C bond distances of 1.313(1) and 1.312(2) Å, and C═C distances of 1.395(2) and 1.396(2) Å, whereas the magnesium complex **1d** has N═C bond distances that range between 1.312(2) and 1.322(3) Å (with an average of 1.316 Å) and C═C distances that range between 1.394(3) and 1.399(3) Å (with an average value of 1.396 Å).

For the zinc compounds **2a**-**2d**, the average M−N bond distance increases slightly as the substituent on the nitrogen increases in steric bulk, from 1.987(1) and 1.990(1) Å in **2a** to 2.017(2) Å in **2d**. The magnesium compound **1d** has longer M−N bond distances that range between 2.073(2) to 2.081(2) Å (2.077 Å on average), despite having a slightly smaller ionic radius (0.60 Å for four-coordinate Zn^{II} vs. 0.57 Å for four-coordinate Mg^{II}) [27]. The distances suggest that the M−N bonds in the zinc complexes have a larger covalent character, which is expected from the relative electronegativities of Zn and Mg which are 1.6 and 1.2, respectively [28].

The ligand bite angle (defined as the N-M-N angle within a single 6-membered metal–ligand ring) also increases slightly as the substituent on nitrogen increases in steric bulk, from 96.26(4) and 96.25(4)° for **2a**, to 99.17(11)° for **2d**. For the magnesium compound **1d**, the ligand bite angles for the two ligands are 95.61(6) and 95.29(7)°, which are slightly smaller than that in the zinc analog **2d**, as expected from the somewhat longer Mg-N distances vs. the Zn-N distances in these two compounds.

2.3. Volatility Studies

Because these β-dialdiminate complexes are potential CVD precursors, we investigated their thermal properties by thermogravimetric analysis (TGA). All eight compounds **1a**-**1d** and **2a**-**2d** exhibit smooth volatilization curves, with no evidence of decomposition. The residual masses were < 1 % for the zinc compounds **2a**-**2d** and < 5 % for the magnesium compounds **1a**-**1d** (Figs. 5 and 6); the latter percentage is somewhat larger likely due to reaction with small amounts of atmospheric moisture during the sample loading process (See Experimental

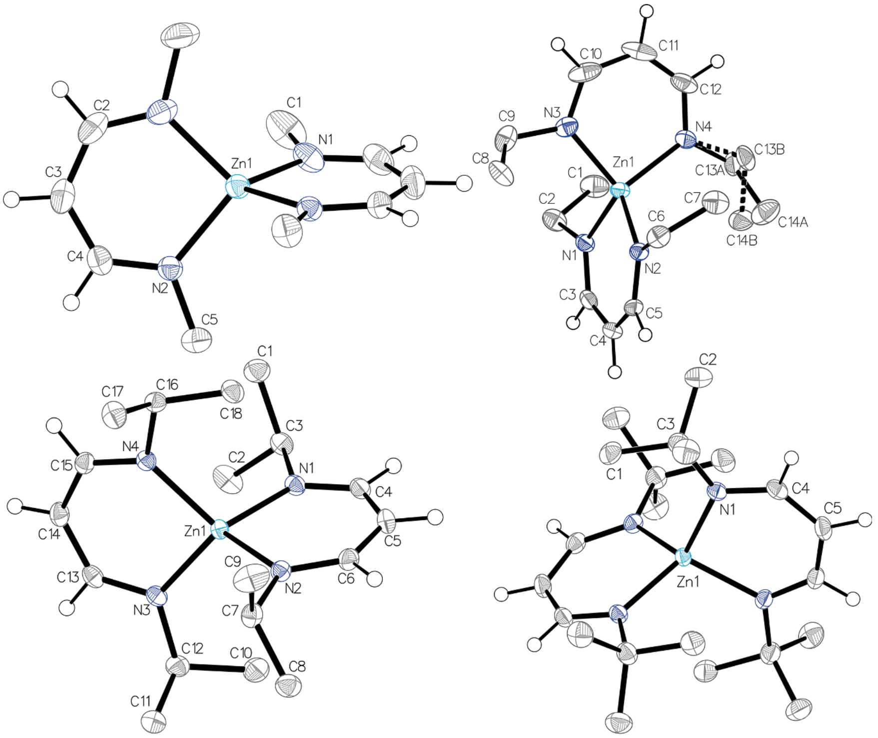


Fig. 4. Molecular structures of the zinc compounds **2a**-**2d**. Thermal ellipsoids drawn at the 50% probability density level except for hydrogen atoms, which are represented by arbitrarily-sized spheres. Hydrogen atoms on the alkyl arms have been omitted for clarity.

Table 1
Selected crystal structure parameters for compounds **1d** and **2a-2d**.

cmpd	τ_4	dihedral angle (°)	M—N (Å)	bite angle (°)
1d	0.88	89.49(6)	2.073(2) to 2.081(2)	95.61(6), 95.29(7)
2a	0.84	81.89(5)	1.990(1), 1.987(1)	96.25(4), 96.26(4)
2b	0.89	88.27(9), 88.29(8)	1.985(3) to 1.999(3)	97.0(1) to 97.6(1)
2c	0.89	86.92(3)	1.988(1) to 2.007(1)	97.53(4), 97.46(4)
2d	0.92	90	2.017(2)	99.2(1)

Section).

The temperature required to achieve 1 Torr of vapor pressure (a useful metric for CVD experiments) increases as expected with increasing molecular mass, being 88, 136, 144, and 165 °C for the magnesium methyl, ethyl, isopropyl, and *tert*-butyl compounds, respectively and 90, 109, 138, and 165 °C for the zinc methyl, ethyl, isopropyl, and *tert*-butyl compounds, respectively. The volatilization onset temperatures under 1 atm of N_2 also follows this same trend (see Table S3.1). For both the magnesium and zinc compounds, the volatilization enthalpies for the methyl, ethyl, and isopropyl compounds are all very similar (65–70 kJ/mol), whereas those for the *tert*-butyl compounds are larger (81 kJ/mol). All these values were measured by performing a series of isothermal experiments to obtain volatilization rates, which were then converted into vapor pressures [29].

The magnesium *N*-methyl compound is significantly more volatile than magnesium amidinates, which require bulky substituents on nitrogen such as *N-sec*-butyl or *N-tert*-butyl groups in order to be monomeric: the most volatile magnesium amidinate sublimes at 70 °C/0.05 Torr [20], vs. 40 °C/0.01 Torr for **1a**. In addition, the magnesium β-dialdiminate compounds **1c** and **1d** with R = isopropyl and *tert*-butyl are more volatile than the corresponding magnesium β-diketiminates with the same *N*-alkyl substituents [21], which sublime without decomposition at 104 °C/0.05 Torr and 160 °C/0.05 Torr, respectively [21]. Although sublimation conditions are at best only very roughly correlated with vapor pressures, we can say the following: generally the β-dialdiminato compounds reported here volatilize at lower temperatures than the β-diketiminato complexes with the same *N*-alkyl substituents.

Some zinc compounds of β-ketiminates (*N,O*-chelating ligands similar to β-diketiminates) have been employed as ALD precursors for the deposition of zinc oxide (ZnO); the most volatile of these (with an *n*-propyl substituent on nitrogen) begins to sublime at 94.6 °C under 1 atm of N_2 but does not finish subliming until 230 °C [30]. Thus, this compound is less volatile than the β-dialdiminato zinc compounds **2a** and **2b** described here, which finish subliming at the lower temperatures of 178 and 215 °C, respectively. The compounds reported here are also more volatile than zinc acetylacetonate [31], but are less volatile than diethylzinc, which is commonly used as a zinc CVD precursor [32]. Unlike dialkylzinc compounds, however, the β-dialdiminato zinc complexes reported here are not pyrophoric, and can be handled in air for several hours or more without decomposition.

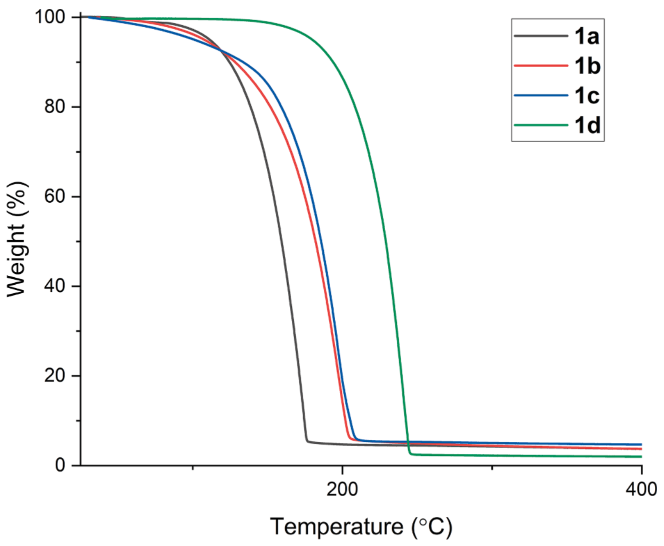


Fig. 5. TGA ramp experiments for the magnesium(II) compounds **1a-1d** under 1 atm of N_2; the heating rate was 10 °C/minute. For all four compounds the residual (unsublimed) mass is < 5 %.

3. Conclusions

Our studies show that metal complexes of *N,N′*-dialkyl-β-dialdiminate ligands are more volatile than their corresponding *N,N′*-dialkyl-β-diketiminate and *N,N*-dialkylamidinate analogues. There are two reasons for this greater volatility: (i) relative to β-diketiminates, the lower molecular weights of the β-dialdiminates reduce intermolecular attractions, and (ii) relative to amidinates (which form four-membered rings with metal centers) the large bite angles of the β-dialdiminate ligands (which form six-membered rings with metal centers) bring the steric bulk of the substituents on nitrogen closer to the metal, so that even small substituents are sufficient to prevent the formation of oligomers or polymers [33].

Studies of the use of these new compounds as CVD precursors will be reported separately.

4. Experimental Section

4.1. General Considerations

All operations were carried out in vacuum or under argon using standard Schlenk and glove box techniques unless otherwise stated. All glassware was oven dried before use. Solvents were distilled under nitrogen from sodium/benzophenone (pentane, diethyl ether, and THF), or magnesium/iodide (methanol) before use. Anhydrous metal halides ($ZnCl_2$, $MgBr_2$) were purchased from Sigma-Aldrich, Strem, or Alfa Aesar and used as received. *N,N′*-dialkyl-1,3-propanedialdiminium chlorides, *N,N′*-dialkyl-1,3-propanedialdimines, and lithium *N,N′*-dialkyl-1,3-propanedialdiminates were prepared by literature routes [22]. Deuterated benzene (Cambridge Isotope Laboratories) was distilled from calcium hydride and stored over vacuum-heated 3 Å molecular sieves (Alfa Aesar). All other compounds were purchased as reagent grade and used as received.

Elemental analyses were performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. FTIR spectra were acquired on a Thermo Nicolet IR200 spectrometer as Nujol mulls between KBr plates and processed using the Omnic software package. NMR spectra were recorded on a Varian Unity Inova 400 spectrometer at 9.4 T, a Varian Unity Inova 500NB spectrometer at 11.75 T, a Varian VXR 500 spectrometer with Unity Inova 500 console at 11.75 T, a Varian Unity Inova 500 spectrometer at 11.75 T, or a B600 Bruker NEO spectrometer at 14.1 T equipped with a Bruker Avance Neo console and 600-MHz, 5-mm, BBO-BB Prodigy CryoProbe. ^1H and ^{13}C NMR chemical shifts are reported in δ units, positive shifts indicating higher frequency relative to TMS, set by assigning appropriate shifts to residual solvent signals. Melting points and decomposition temperatures were determined in closed capillaries under argon on a Thomas-Hoover Unimelt apparatus. Thermogravimetric analysis was done on a TA instruments Q50 TGA.

In order to speed up the purification process, during distillations and sublimations we typically employed bath temperatures higher than those required to volatilize the compounds. We did not measure the temperature of the vapor during the distillations.

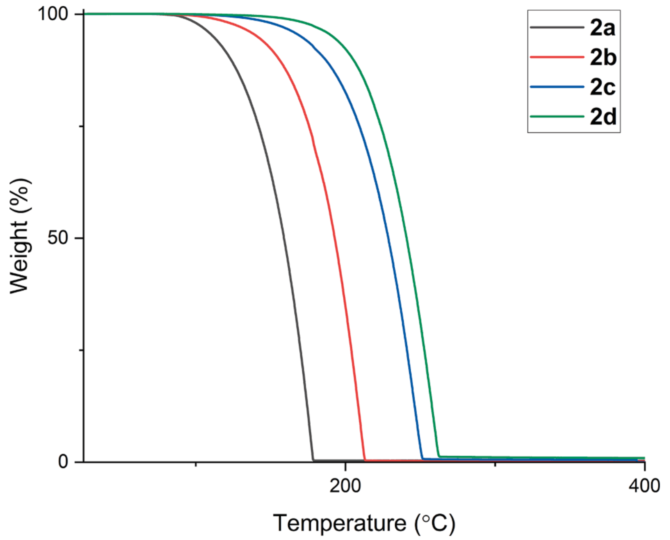


Fig. 6. TGA ramp experiments for the zinc(II) compounds **2a-2d** under 1 atm of N_2; the heating rate was 10 °C/minute. For all four compounds the residual (unsublimed) mass is < 1 %.

4.2. Bis(N,N′-dimethyl-1,3-propanedialdiminato)magnesium(II), 1a

To a suspension of $MgBr_2$ (0.19 g, 1.1 mmol) in diethyl ether (10 mL) at –78 °C was added a solution of lithium *N,N′*-dimethyl-1,3-propanedialdiminate (0.23 g, 2.2 mmol) in diethyl ether (30 mL), and the solution was allowed to warm slowly to room temperature with stirring over 12 hr. The reaction solution was evaporated to dryness in vacuum and the residue extracted with pentane (3 × 10 mL), and the resulting colorless extracts were filtered, combined, concentrated, and stored at –78 °C to yield colorless crystals which were sublimed at 40 °C and 10 mTorr to yield colorless crystals. Yield: 0.047 (20 %). M.p. 83 °C. Anal. Calc. for $C_{10}H_{18}N_4Mg$ (218.58): C, 54.9; H, 8.30; N, 25.6; found: C, 54.5; H, 8.20; N, 25.9. ^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 7.24 (d, $^3J_{HH} = 6$ Hz, 4H, N=CH), 4.44 (t, $^3J_{HH} = 6$ Hz, 2H, β-CH), 2.89 (s, CH_3). ^{13}C NMR (600 MHz, C_6D_6, 20 °C): δ 163.83 (s, N=CH), 87.34 (s, β-CH), 44.02 (s, CH_3). IR (KBr): 1596 (m), 1521 (s), 1400 (m), 1328 (m), 1129 (w), 1089 (w), 722 (m).

4.3. Bis(N,N′-diethyl-1,3-propanedialdiminato)magnesium(II), 1b

To a solution of *N,N′*-diethyl-1,3-propanedialdimine (0.54 g, 4.3 mmol) in diethyl ether (80 mL) at 0 °C was added *n*-butyl-*sec*-butylmagnesium (3.05 mL of a 0.7 M solution in hexanes, 2.1 mmol) slowly over 5 min. The solution was stirred at 0 °C for 10 min, then warmed to room temperature and stirred an additional 4.5 h. The reaction solution was evaporated to dryness in vacuum, the residue was extracted with pentane (3 × 10 mL), and the resulting colorless extracts were filtered, combined, and evaporated to dryness in vacuum. The resulting beige-colored residue was distilled in vacuum (5 mTorr; bath temperature 220 °C) to yield a yellow oil. Yield: 0.42 g (72 %). Anal. Calc. for $C_{14}H_{26}N_4Mg$ (274.69): C, 61.2; H, 9.54; N, 20.4; found: C, 60.9; H, 9.49; N, 20.4. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 7.23 (d, $^3J_{HH} = 6$ Hz, 4H, N=CH), 4.38 (t, $^3J_{HH} = 6$ Hz, 2H, β-CH), 3.15 (q, $^3J_{HH} = 7$ Hz, 8H, CH_2), 1.07 (t, $^3J_{HH} = 7$ Hz, 12H, CH_3). ^{13}C NMR (500 MHz, C_6D_6, 20 °C): δ 161.82 (s, N=CH), 86.87 (s, β-CH), 52.94 (s, CH_2), 17.97 (s, CH_3). IR (KBr): 1592 (s), 1519 (s), 1444 (s), 1332 (s), 1265 (s), 1138 (s), 1088 (w), 1038 (m), 779 (w), 722 (m).

4.4. Bis(N,N′-di(isopropyl)-1,3-propanedialdiminato)magnesium(II), 1c

To a suspension of $MgBr_2$ (0.36 g, 2.0 mmol) in diethyl ether (20 mL) at –78 °C was added a solution of lithium *N,N′*-di(isopropyl)-1,3-propanedialdiminate (0.65 g, 4.1 mmol) in diethyl ether (22 mL), and the solution was allowed to warm slowly to room temperature with stirring over 12 hr. The reaction solution was evaporated to dryness in vacuum, the residue was extracted with pentane (3 × 10 mL), and the resulting colorless extracts were filtered, combined, and evaporated to dryness in vacuum. The resulting yellow oil was vacuum distilled (5 mTorr, bath temperature 220 °C) to yield a yellow oil. Yield: 0.52 g (80 %). Anal. Calc. for $C_{18}H_{34}N_4Mg$ (330.79): C, 65.4; H, 10.4; N, 16.9; found: C, 65.2; H, 10.4; N, 17.6. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 7.25 (d, $^3J_{HH} = 7$ Hz, 4H, N=CH), 4.41 (t, $^3J_{HH} = 7$ Hz, 2H, β-CH), 3.26 (sept, $^3J_{HH} = 7$ Hz, 4H, N-CH), 1.17 (d, $^3J_{HH} = 7$ Hz, 24H, CH_3). ^{13}C NMR (500 MHz, C_6D_6, 20 °C): δ 160.07 (s, N=CH), 87.41 (s, β-CH), 56.94 (s, N-CH), 25.42 (s, CH_3). IR (KBr): 1588 (s), 1518 (s), 1336 (s), 1322 (s), 1293 (s), 1202 (m), 1145 (s), 1119 (m), 724 (m).

4.5. Bis(N,N′-di(tert-butyl)-1,3-propanedialdiminato)magnesium(II), 1d

To a suspension of $MgBr_2$ (0.10 g, 0.57 mmol) in diethyl ether (10 mL) was added a solution of lithium *N,N′*-di(*tert*-butyl)-1,3-propanedialdiminate (0.20 g, 1.1 mmol) in diethyl ether (15 mL), and the solution was stirred for 12 hr. The reaction solution was evaporated to dryness in vacuum and the residue extracted with pentane (2 × 10 mL), and the resulting colorless extracts were filtered, combined, concentrated, and stored at –20 °C to yield colorless crystals. Yield: 0.044 g (21 %). A second crop of crystals grown from the mother liquor yielded an additional 0.011 g, for a total yield of 0.055 g (26 %). M.p. 240 °C (discoloration from colorless to orange seen > 140 °C). Anal. Calc. for $C_{22}H_{42}N_4Mg$ (386.90): C, 68.3; H, 10.9; N, 14.5; found: C, 67.9; H, 10.9; N, 14.3. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 7.35 (d, $^3J_{HH} = 7$ Hz, 4H, N=CH), 4.52 (t, $^3J_{HH} = 7$ Hz, 2H, β-CH), 1.28 (s, 36H, CH_3). ^{13}C NMR (500 MHz, C_6D_6, 20 °C): δ 157.93 (s, N=CH), 87.71 (s, β-CH), 55.00 (s, N—C), 31.94 (s, CH_3). IR (KBr): 1589 (m), 1519 (s), 1507 (s), 1330 (s), 1243 (w), 1197 (m), 1174 (m), 927 (w), 730 (m).

4.6. Bis(N,N′-dimethyl-1,3-propanedialdiminato)zinc(II), 2a

To $ZnCl_2$ (0.16 g, 1.1 mmol), sodium ethoxide (0.32 g, 4.7 mmol), and *N,N′*-dimethyl-1,3-propanedialdiminium chloride (0.30 g, 2.3 mmol) was added dry methanol (7 mL), and the mixture was stirred for 65 h. The solution was evaporated to dryness in vacuum and extracted with pentane (2 × 10 mL); the resulting colorless extracts were filtered, combined, and evaporated to dryness in vacuum. The residue was sublimed at 40 °C and 10 mTorr to yield colorless crystals. Yield: 0.21 g (70 %). M.p. 90 °C. Anal. Calc. for $C_{10}H_{18}N_4Zn$ (259.67): C, 46.3; H, 6.99; N, 21.6; found: C, 46.3; H, 6.91; N, 21.7. ^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 7.19 (d, $^3J_{HH} = 6.4$ Hz, 4H, N=CH), 4.36 (t, $^3J_{HH} = 6.4$ Hz, 2H, β-CH), 2.93 (s, 12H, CH_3). ^{13}C NMR (600 MHz, C_6D_6, 20 °C): δ 161.81 (s, N=CH), 86.53 (s, β-CH), 45.32 (s, CH_3). IR (KBr): 1604 (s), 1522 (s), 1398 (m), 1332 (s), 1198 (w), 1131 (w), 1102 (w), 806 (w), 719 (m).

4.7. Bis(N,N′-diethyl-1,3-propanedialdiminato)zinc(II), 2b

To $ZnCl_2$ (0.15 g, 1.1 mmol), sodium ethoxide (0.31 g, 4.5 mmol), and *N,N′*-diethyl-1,3-propanedialdiminium chloride (0.36 g, 2.2 mmol) was added tetrahydrofuran (12 mL), and the mixture was stirred for 12 h. The solution was evaporated to dryness in vacuum and extracted with pentane (2 × 10 mL); the resulting extracts were filtered, combined, and evaporated to dryness in vacuum. The residue was sublimed at 65 °C and 10 mTorr to yield a colorless sublimate. Yield: 0.28 g (79 %). M.p. 41 °C. Anal. Calc. for $C_{14}H_{26}N_4Zn$ (315.772): C, 53.3; H, 8.30; N, 17.7; found: C, 53.3; H, 8.28; N, 17.6. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 7.19 (d, $^3J_{HH} = 6.6$ Hz, 4H, N=CH), 4.33 (t, $^3J_{HH} = 6.4$ Hz, 2H, β-CH), 3.17 (q, $^3J_{HH} = 7.4$ Hz, 8H, CH_2), 1.08 (t, $^3J_{HH} = 7.3$ Hz, 12H, CH_3). ^{13}C NMR (500 MHz, C_6D_6, 20 °C): δ 159.84 (s, N=CH), 86.11 (s, β-CH), 53.85 (s, CH_2), 17.39 (s, CH_3). IR (KBr): 1599 (s), 1519 (s), 1442 (m), 1336 (m), 1264 (m), 1140 (m), 1090 (w), 1041 (w), 980 (w), 854 (w), 777 (w), 720 (m).

4.8. Bis(N,N′-di(isopropyl)-1,3-propanedialdiminato)zinc(II), 2c

To $ZnCl_2$ (0.70, 5.1 mmol), sodium ethoxide (1.40 g, 20 mmol), and *N,N*′-di(isopropyl)-1,3-propanedialdiminium chloride (1.92 g, 10 mmol) was added tetrahydrofuran (60 mL), and the mixture was stirred for 65 hrs. The solution was evaporated to dryness in vacuum and extracted with pentane (3 × 10 mL); the resulting extracts were filtered, combined, and evaporated to dryness in vacuum. The resulting yellow oil was distilled in vacuum (5 mTorr; bath temperature 220 °C) to yield a yellow oil. Yield: 1.63 g (88 %). Anal. Calc. for $C_{18}H_{34}N_4Zn$ (371.88): C, 58.1; H, 9.22; N, 15.1; found: C, 58.3; H, 9.09; N, 15.1. ^1H NMR (600 MHz, C_6D_6, 20 °C): δ 7.24 (d, $^3J_{HH} = 7$ Hz, 4H, N=CH), 4.41 (t, $^3J_{HH} = 7$ Hz, 2H, β-CH), 3.35 (sept, $^3J_{HH} = 7$ Hz, 4H, N-CH), 1.17 (d, $^3J_{HH} = 7$ Hz, 24H, CH_3). ^{13}C NMR (600 MHz, C_6D_6, 20 °C): δ 158.13 (s, N=CH), 87.05 (s, β-CH), 57.06 (s, N-CH), 24.95 (s, CH_3). IR (KBr): 1593 (s), 1515 (s), 1383 (s), 1363 (m), 1339 (s), 1316 (m), 1293 (s), 1203 (m), 1144 (s), 1118 (m), 1033 (w), 1014 (w), 984 (w), 956 (w), 752 (w), 723 (m).

4.9. Bis(N,N′-di(tert-butyl)-1,3-propanedialdiminato)zinc(II), 2d

To a suspension of $ZnCl_2$ (0.15 g, 1.1 mmol) in diethyl ether (30 mL) at –78 °C was added a solution of lithium *N,N*′-di(*tert*-butyl)-1,3-propanedialdiminate (0.42 g, 2.2 mmol) in diethyl ether (20 mL), and the solution allowed to warm slowly to room temperature with stirring over 12 hr. The reaction solution was evaporated to dryness in vacuum, the residue was extracted with pentane (2 × 10 mL), and the resulting colorless extracts were filtered, combined, concentrated, and stored at –20 °C to yield colorless crystals. Yield: 0.096 g (20 %). A second crop of crystals grown from the mother liquor yielded an additional 0.039 g, for a total yield of 0.135 g (29 %). M.p. 242° (change from colorless to orange at ca. 140 °C). Anal. Calc. for $C_{22}H_{42}N_4Zn$ (427.98): C, 61.7; H, 9.89; N, 13.1; found: C, 61.9; H, 9.86; N, 13.0. ^1H NMR (600 MHz, C_6D_6, 20 °C): δ 7.32 (d, $^3J_{HH} = 7$ Hz, 4H, N=CH), 4.51 (t, $^3J_{HH} = 7$ Hz, 2H, β-CH), 1.29 (s, 36H, CH_3). ^{13}C NMR (600 MHz, C_6D_6, 20 °C): δ 156.39 (s, N=CH), 87.56 (s, β-CH), 56.03 (s, N—C), 31.89 (s, CH_3). IR (KBr): 1596 (m), 1520 (s), 1506 (m), 1362 (m), 1334 (s), 1243 (w), 1194 (m), 1174 (m), 930 (w), 731 (m).

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Claire E. Schmit: Writing – original draft, Investigation, Formal analysis. **Gregory S. Girolami:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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CCDC 2328701, 2328702, 2328703, 2328705, and 2328706 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

Author Contributions

All authors have given approval to the final version of the manuscript.

Appendix A. Supplementary data

^1H and ^{13}C NMR spectra, IR spectra, TGA data, crystallographic studies, and comparisons of structural features of interest for compounds **1a-1d** and **2a-2d**, and UV-Vis spectra for **2a-2d**. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2024.116985.

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