Ancillary Ligand Effect on the Properties of "Mg(thd)₂" and Crystal Structures of [Mg(thd)₂(ethylenediamine)]₂, [Mg(thd)₂(tmeda)], and [Mg(thd)₂(trien)][1]

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Complexes [Mg(thd)₂(A)] (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione; A = ethylenediamine, en (**2**); N,N′-dimethylethylenediamine, dmeda (**3**); N,N′-diethylethylenediamine, deeda (**4**); N,N,N′,N′-tetramethylethylenediamine, tmeda (**5**); diethylenetriamine, dien (**6**); triethylenetetra-amine, trien (**7**); 1,2-ethanediol (**8**)) and [Mg(thd)₂(EtOH)]₂(1,3-propanediol) (**9**) were prepared and characterized by NMR spectroscopy, mass spectrometry, and thermal analysis. Crystal structures of compounds **2**, **5**, and **7** are presented. In all structures, Mg exhibits distorted six-coordination, with four shorter distances between Mg and keto-oxygens and two longer distances between Mg and nitrogen atoms (**2**, **5**, **7**). The structure of **2** consists of two monomeric complexes which form an asymmetric unit. The structure of **7** is similar to **2**, but the trien molecule has coordinated through one terminal and one vicinal N atom to Mg. All complexes containing amines evaporated almost completely, but the complex **8**, which contained 1,2-ethanediol, was thermally unstable and decomposed when heated. At temperatures below the dissociation temperature, all adducts of diamines appeared to evaporate intact.

Introduction

The development of volatile compounds of alkaline earth metals has recently attracted much attention because of the need for these compounds as precursors for the preparation of thin films by chemical gas phase methods (e.g., MOCVD and ALD). Many technologically interesting thin film materials, such as superconductors and luminescent materials, contain these metals.[2−6] The most common volatile precursors for the deposition of alkaline earth metals are β-diketonates,[5] while others are alkoxides, amides, and cyclopentadienyls.[5]

The factors affecting volatility are molecular weight and interactive forces between molecules. The best volatility is achieved when the size of the molecules is as small as possible (monomeric complexes are preferred) and the forces between molecules are minimal. Oligomerization is undesirable. In the β-diketonates of the alkaline earth metals, the diketonato ligands coordinate to the metal through the two oxygen atoms, forming a chelate structure that contains aromatic features. Because the oxidation state is +2, the resulting coordination number in a monomeric chelate is four. However, alkaline earth metals, because of their size, prefer higher coordination numbers, and to compensate for the coordination unsaturation, the compounds either oligomerize or add neutral solvent or impurity molecules to the coordination sphere. Further reactions may occur if water is coordinated.

The usual means for avoiding oligomerization is to use larger sterically demanding β-diketonato ligands or to add ancillary coordinating Lewis base molecules. Sterically demanding ligands prevent oligomerization by making the vacant coordination sites at the metal center inaccessible to other ligands in the system. Ancillary Lewis base molecules prevent the oligomerization by satisfying the coordination sphere of the metal center with species that will not further react in the complex. There are several reports of Ca, Sr, and Ba β-diketones with polydentate ancillary ligands.[5] In some cases, though without success, a β-diketonato[7] or β-ketoiminato[8] ligand itself has been functionalized with side chains containing donor atoms.

The Mg^{2+} ion is much smaller (0.72 Å)[9] than the heavier counterparts of the alkaline earth group (Ca^{2+}, 1.00; Sr^{2+}, 1.18; Ba^{2+}, 1.35 Å),[9] and thus, it is easier to achieve coordinative saturation with Mg^{2+}. The most usual coordination number in Mg complexes is 6, while 8−12 coordination is observed with larger alkaline earth metals.[5] However, like the heavier alkaline earth elements, magnesium tends to form oligomeric β-diketonate complexes ([$Mg_3(acac)_6$][10] and [$Mg_2(thd)_4$][11]) which are reactive with small Lewis base molecules such as H_2O. This is reflected in the dissimilar properties reported for "Mg(thd)₂" when different methods of synthesis and purification are used.[11−15]

Magnesium β-diketonates with coordinated neutral ligands have been reported earlier by Dwyer,[16] Fenton,[17] Arunasalam

(1) Hthd = 2, 2, 6, 6,-tetramethylheptane-3,5-dione, tmeda = N, N, N′,N′-tetramethylethylenediamine, trien = triethylenetetra-amine, dmeda = N,N′-dimethylethylenediamine, deeda = N,N′-diethylethylenediamine, dien = diethylenetriamine, Hacac = pentane-2,4-dione, Hfod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione, Hhfpd = 1,1,1,5,5,5-hexafluoropentane-2,-dione, Htod = 2,2,6,6-tetramethyl-octane-3,5-dione, H3hd = 2,2,6-trimethylheptane-3,5-dione, dbeda = N,N′-dibutylethylenediamine, dheda = N,N′-dihexylethylenediamine.
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et al.,[18] and Gordon et al.[19] However, the crystal structures of the complexes are unknown and thermal properties are reported only for Mg(fod)$_2$(triglyme),[18] Mg(hfpd)$_2$(heptaglyme),[18] and Mg(β-dik)$_2$A (β-dik = thd, tod, 3hd; A = dbeda, dheda).[1,19]

In this work we investigated the effect of ancillary ligands on the structural and thermal properties of "Mg(thd)$_2$". We describe the synthesis and properties of several [Mg(thd)$_2$(A)] complexes in which A is a neutral Lewis base ligand, and we present the detailed crystal structures of [Mg(thd)$_2$(ethylene-diamine)]$_2$ (**2**), [Mg(thd)$_2$(tmeda)] (**5**), and [Mg(thd)$_2$(trien)] (**7**).

Experimental Section

General methods. Starting materials for the synthesis of [Mg$_2$(thd)$_4$] **1** were used as received. Amines for adduct syntheses were dried over KOH and distilled before use. 1,2-Ethanediol and 1,3-propanediol were distilled before use and stored over molecular sieves. Because of possible adduct formation and decomposition of **1**, all manipulations after drying and sublimation of the product were made under dry conditions using standard glovebox and Schlenk techniques. Ethanol (>99.6%) used for adduct preparation and crystallization was further dried with magnesium. Melting points were recorded with an electro-thermal melting point apparatus using capillaries open to air. Elemental analyses (CHN) were performed in the trace element laboratory at the University of Oulu. The NMR spectra were recorded on a Varian Gemini 2000 spectrometer at ambient temperature. Chemical shifts referenced to tetramethylsilane are given in ppm. Mass spectra were recorded with a JEOL JMS-SX102 operating in electron impact mode (70 eV) using a direct insertion probe and a temperature range of 50−200 °C. A Mettler Toledo TA8000 system equipped with a TGA850 thermobalance was used for thermal analyses (TG and SDTA) of the samples under flowing nitrogen atmosphere. In dynamic experiments, the samples weighed between 10 and 11 mg and the heating rate was 10 °C min^{-1}. In isothermal mass change determinations, sample sizes were approximately 20 mg. Samples were heated at constant temperature for 20 min. Then the temperature was increased 40 °C, and the isothermal stage was repeated. Sublimation experiments were done under reduced pressure with a Büchi TO-51 sublimator instrument. The sublimed products were collected from the surface of the coldfinger.

Synthesis of [Mg$_2$(thd)$_4$] (1). The complex was prepared in aqueous medium by the method of Schwarberg and Sievers.[12] After synthesis, the crude product was dried in a vacuum in the presence of P$_2$O$_5$ for 15−20 h and purified by sublimation at approximately 120 °C/0.2 mbar. Sublimation resulted in clear or white glasslike material on the coldfinger of the sublimator. The product was collected in a glovebox and stored under argon. Yield after sublimation was 40−71%. Mp 122−126 °C. Anal. Calcd. for MgC$_{22}$H$_{38}$O$_4$ (390.85): C, 67.61; H, 9.80. Found: C, 67.25; H, 10.47. ^{1}H NMR (CDCl$_3$) δ 1.09 (36H, m, CH$_3$), 5.65 (2H, s, CH). ^{13}C{^{1}H} NMR 28.27 (CH$_3$), 28.42 (CH$_3$), 28.83 (CH$_3$), 40.96 (C(CH$_3$)), 91.80 (CH), 201.43 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 207 [Mg(thd)]$^+$.

General synthesis of Mg(thd)$_2$A (2−8). [Mg$_2$(thd)$_4$] was weighed into a Schlenk tube and dissolved in dry ethanol or hexane. The amine or diol was added to the resulting clear solution. After addition, the solution was stirred for 2 h at room temperature. Product crystals were obtained by evaporating part of the solvent and allowing the crystal-

lization process to proceed at +4 °C. After collection and washing of the crystals with a small amount of solvent, they were dried in a vacuum for several hours. A total of 100% yield was achieved if the solvent was simply evaporated away. Crystals suitable for X-ray analysis were obtained after slow evaporation of the solvent in the glovebox.

[Mg(thd)$_2$(ethylenediamine)] (2). Mp 152 °C. Anal. Calcd for MgC$_{24}$H$_{46}$O$_4$N$_2$ (450,95): C, 63.92; H, 10.28; N, 6.21. Found: C, 63.49; H, 10.28; N, 6.21. ^{1}H NMR (CDCl$_3$) δ 1.06 (36H, s, CH$_3$), 1.68 (4H, s, br, NH$_2$), 2.82 (4H, s, CH$_2$), 5.49 (2H, s, CH). ^{13}C{^{1}H} NMR 28.49 (CH$_3$), 40.61 (C(CH$_3$)), 40.85 (CH$_2$N), 87.96 (CH), 200.11 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 450 [Mg(thd)$_2$-(en)]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 267 [Mg(thd)(en)]$^+$, 207 [Mg(thd)]$^+$.

[Mg(thd)$_2$(dmeda)] (3). The complex was synthesized in two ways, the general way described above and in situ. In the in situ synthesis, Mg(thd)$_2$ was prepared in aqueous medium by the reported method.[12] After filtering, the white solid was removed to hexane in which it did not dissolve. An equivalent molar amount of amine was added and the solution was stirred with the solid. All of the white solid dissolved, and the water phase was extracted. Hexane was evaporated leaving the product Mg(thd)$_2$(dmeda). Analysis of complexes prepared in the two different ways gave exactly the same results. Mp 89 °C. Anal. Calcd for MgC$_{26}$H$_{50}$O$_4$N$_2$ (479.00): C, 65.19; H, 10.52; N, 5.85. Found: C, 65.28; H, 11.36; N, 5.87. ^{1}H NMR (CDCl$_3$) δ 1.06 (36H, s, CH$_3$), 1.59 (2H, s, br, NH), 2.35 (6H, d, NCH$_3$), 2.72 (4H, s, CH$_2$), 5.44 (2H, s, CH). ^{13}C{^{1}H} NMR 28.48 (CH$_3$), 35.24 (NCH$_3$), 40.63 (C(CH$_3$)), 49.48 (CH$_2$N), 87.57 (CH), 199.86 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 478 [Mg(thd)$_2$(dmeda)]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 295 [Mg-(thd)(dmeda)]$^+$, 207 [Mg(thd)]$^+$.

[Mg(thd)$_2$(deeda)] (4). Mp 110 °C. Anal. Calcd for MgC$_{28}$H$_{54}$O$_4$N$_2$ (507.06): C, 66.33; H, 10.73; N, 5.52. Found: C, 66.38; H, 11.46; N, 5.57. ^{1}H NMR (CDCl$_3$) δ 1.05 (36H, s, CH$_3$), 1.10 (6H, t, CH$_3$), 2.68 (4H, kvart, CH$_2$), 2.77 (4H, s, CH$_2$), 5.43 (2H, s, CH). ^{13}C{^{1}H} NMR 14.08 (CH$_3$), 28.45 (CH$_3$), 40.55 (C(CH$_3$)), 43.20 (CH$_2$N), 87.56 (CH), 199.87 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 506 [Mg(thd)$_2$(deeda)]$^+$, 449 [Mg(thd)$_2$(deeda) − EtNHCH$_3$]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 323 [Mg-(thd)(deeda)]$^+$, 207 [Mg(thd)]$^+$.

[Mg(thd)$_2$(tmeda)] (5). Mp 152 °C. Anal. Calcd for MgC$_{28}$H$_{54}$O$_4$N$_2$ (507.06): C, 66.33; H, 10.73; N, 5.52. Found: C, 66.33; H, 11.45; N, 5.59. ^{1}H NMR (CDCl$_3$) δ 1.05 (36H, s, CH$_3$), 2.25 (12H, m, CH$_3$), 2.50 (4H, m, CH$_2$), 5.41 (2H, s, CH). ^{13}C{^{1}H} NMR 28.45 (CH$_3$), 40.57 (C(CH$_3$)), 46.47 (CH$_3$N), 56.41 (CH$_2$N), 87.23 (CH), 199.36 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 506 [Mg(thd)$_2$-(tmeda)]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 323 [Mg(thd)(tmeda)]$^+$, 207 [Mg(thd)]$^+$.

[Mg(thd)$_2$(dien)] (6). Mp 99 °C. Anal. Calcd for MgC$_{26}$H$_{51}$O$_4$N$_3$ (494.02): C, 63.21; H, 10.41; N, 8.51. Found: C, 63.11; H, 11.08; N, 8.55. ^{1}H NMR (CDCl$_3$) δ 1.05 (36H, s, CH$_3$), 2.06 (4H, s, br, NH$_2$), 2.80 (8H, 2*t, CH$_2$N), 5.46 (2H, s, CH). ^{13}C{^{1}H} NMR 28.47 (CH$_3$), 39.38 (C(CH$_3$)), 40.60 (CH$_2$NH$_2$), 50.59 (CH$_2$NH), 87.98 (CH), 200.03 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 493 [Mg(thd)$_2$(dien)]$^+$, 390 [HMg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 333 [Mg-(thd)$_2$ − tBu]$^+$, 310 [Mg(thd)(dien)]$^+$, 207 [Mg(thd)]$^+$.

[Mg(thd)$_2$(trien)] (7). Mp 75 °C. Anal. Calcd for MgC$_{28}$H$_{56}$O$_4$N$_4$ (537.09): C, 62.62; H, 10.51; N, 10.43. Found: C, 62.86; H, 10.21; N, 9.34. ^{1}H NMR (CDCl$_3$) δ 1.04 (36H, s, CH$_3$), 2.74 (12H, 2*m, CH$_2$), 5.45 (2H, s, CH). ^{13}C{^{1}H} NMR 28.49 (CH$_3$), 39.32 (CH$_2$N), 40.58 (C(CH$_3$)), 47.09 (CH$_2$N), 49.64 (CH$_2$N), 87.91 (CH), 199.87 (CO). MS (EI, 70 eV) m/z 597 [Mg$_2$(thd)$_3$]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg(thd)$_2$ − Me]$^+$, 353 [Mg(thd)(trien)]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 207 [Mg(thd)]$^+$.

[Mg(thd)$_2$(1,2-ethanediol)] (8). Mp 134−150 °C. Anal. Calcd. for MgC$_{24}$H$_{44}$O$_6$ (452.93): C, 63.65; H, 9.79. Found: C, 61.82; H, 10.38. ^{1}H NMR (CDCl$_3$) δ 1.15 (36H, m, CH$_3$), 3.65 (4H, m, CH$_2$), 5.62 (2H, s, CH). ^{13}C{^{1}H} NMR 27.00, 28.00, 28,50 (CH$_3$), 40.86 (C(CH$_3$)$_3$), 63.87 (CH$_2$O, gl), 89.68, 90.85 (CH), 201.75 (CO). MS (EI, 70 eV) m/z 780 [Mg$_2$(thd)$_4$]$^+$, 597 [Mg$_2$(thd)$_3$]$^+$, 390 [Mg(thd)$_2$]$^+$, 375 [Mg-(thd)$_2$ − Me]$^+$, 333 [Mg(thd)$_2$ − tBu]$^+$, 207 [Mg(thd)]$^+$.

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[Mg(thd)₂(EtOH)]₂(1,3-propanediol) (9). The goal was to synthesize 1,3-propanediol adduct. However, although the preparation was carried out like just as for the other adducts, the product was not [Mg(thd)₂(1,3-propanediol)] but {[Mg(thd)₂(EtOH)]₂(1,3-propanediol)}. Mp 92−98 °C. Anal. Calcd. for $Mg_2C_{51}H_{92}O_{12}$ (945.917): C, 64.76; H, 9.80. Found: C, 62.39; H, 10.35. ¹H NMR (CDCl₃) δ 1.15 (m, CH₃), 2.54 (br s, CH₂), 3.75 (m, CH₂), 4.84 (br s, 5.68 (2H, m, CH). ¹³C-{¹H} NMR 18.23 (CH₃, EtOH), 27.51, 28.35, 28.86 (CH₃), 32.63 (CH₂, prd), 40.75 (C(CH₃)₃), 58.45 (CH₂O, EtOH), 62.82, 64.18 (CH₂O, prd), 89.93, 90.84 (CH), 200.32 (CO). MS (EI, 70 eV) m/z 780 [Mg₂(thd)₄]⁺, 597 [Mg₂(thd)₃]⁺, 390 [Mg₂(thd)₂]⁺, 375 [Mg(thd)₂ − Me]⁺, 333 [Mg(thd)₂ − tBu]⁺, 207 [Mg(thd)]⁺.

Single-Crystal X-ray Structure Determination. Single crystals suitable for X-ray diffraction were obtained for complexes **2**, **5**, **7**, **8**, and **9**. The crystals were mounted on a glass fiber with use of the viscous oil-drop method at 193 K.[20] The measurements were performed on a four-circle Rigaku AFC-7S diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Unit cell parameters were determined by centering the 25 reflections found by the search method. Data collections were done with the ω-2θ-scan method, and intensities were extracted by applying the Lehmann−Larsen method[21] included in the diffractometer control software.[22] Three standard reflections for each compound were recorded after every 200 collected reflections. No decay was observed for any crystal, but about 1% random intensity fluctuations were found in test reflections. Intensities were corrected for Lorentz and polarization effects, and space groups were determined using the TEXSAN program.[23] Absorption was checked using the empirical Ψ-scan method, but no corrections were applied because there were only small variations in the relative transmission scaled to T_{max} = 1.0; the smallest T_{min} = 0.987 was for compound **8**. Structures were solved with the SIR92[24] or SHELXS program, and further refinements were carried out using the SHELXL-97[25] software package. Illustrations were produced by the SHELXTL-PC[26] program.

Results and Discussion

Synthesis. Complex [Mg₂(thd)₄] was prepared by the previously reported method.[12] The purification procedure, characteristics, and structure of the synthesized complex have recently been published by Hatanpää et al.[11]

The complexes [Mg(thd)₂(A)] (**2**−**8**) (A = ethylenediamine, dmeda, deeda, tmeda, dien, trien, or 1,2-ethanediol) were synthesized via the reaction of [Mg₂(thd)₄] with an equimolar amount of A in absolute ethanol at ambient temperature. Amine adducts were also synthesized in hexane, but products were the same as those prepared in ethanol. Darr et al.[27] have earlier reported the formation of tight cation−anion pair β-diketonate complexes with protonated amine ligands for the larger alkaline earth metals and fluorinated β-diketonate ligands when ethanol was used as solvent, but we did not observe such complexes for Mg(thd)₂ in our work. It was possible to increase the yields of the synthesis close to 100% simply by evaporating all the solvent. When the added neutral Lewis base molecule was 1,3-propanediol and the product was allowed to crystallize slowly,
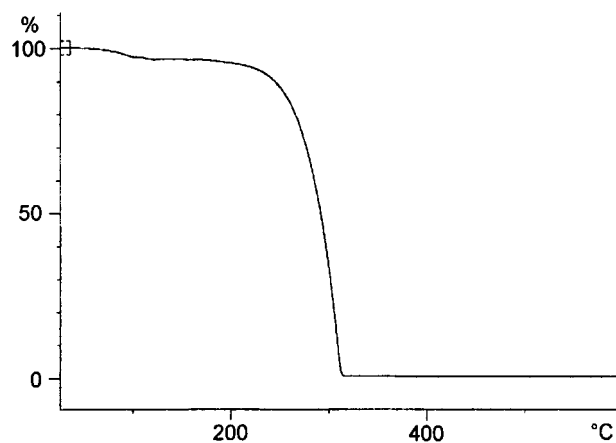
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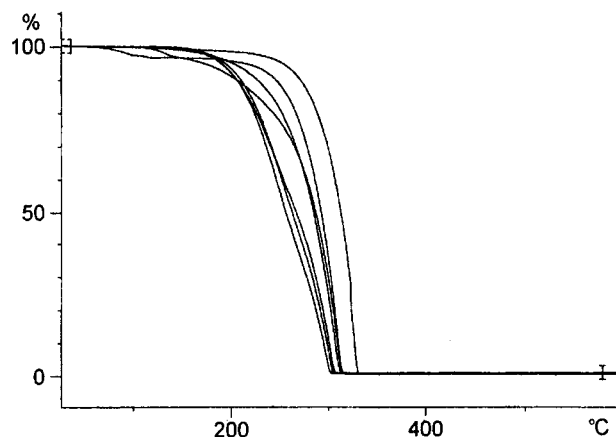
Figure 1. TG curve of [Mg₂(thd)₄] **1**.

Figure 2. TG curves of complexes **1**−**7**. Curves from left to right at 50% weight level: **3**, **4**, **5**, **6**, **2**, **1**, and **7**.

complex [Mg(thd)₂(EtOH)]₂(1,3-propanediol) (**9**) formed. Thus 1,3-propanediol seems to be less willing than amines or 1,2-ethanediol to replace all EtOH in the coordination sphere of magnesium. If the complexes had been prepared in some noncoordinating solvent, the incorporation of EtOH might have been prevented.

The Mg(thd)₂(dmeda) (**3**) was also prepared in situ. The raw product from the Mg(thd)₂ synthesis, which was insoluble in hexane, was stirred with hexane containing an equivalent amount of the amine. When the complex Mg(thd)₂(dmeda) formed, it dissolved in hexane and a small amount of water or ethanol or both was extracted. The water/ethanol phase was removed and the hexane evaporated, leaving behind the pure product. The formation of a water/ethanol phase suggests that the raw product from the Mg(thd)₂ synthesis is in fact a water/ethanol adduct, and when amine is added it replaces the coordinated water/ethanol. The described in situ route probably could be used with suitable adduct-forming ligands for other metals, too.

Melting points of the complexes were varied from much lower to much higher than that of pure [Mg₂(thd)₄]. No clear relations between melting points and crystal structures were evident. Crystals for X-ray analysis were grown by slowly evaporating the solvent in inert gas atmosphere. Suitable crystals were obtained for **2**, **5**, **7**, **8**, and **9**.

Thermal Analyses. Figure 1 presents the TG curve of [Mg₂(thd)₄] **1** separately. TG curves of complexes **1**−**7** are presented in Figure 2. Adducts **2**−**6** evaporate almost completely at lower temperatures than does pure [Mg₂(thd)₄], leaving less than 1% residue. Adduct of trien, **7**, evaporates at slightly higher temperature, also leaving less than 1% residue. Figure 3 shows
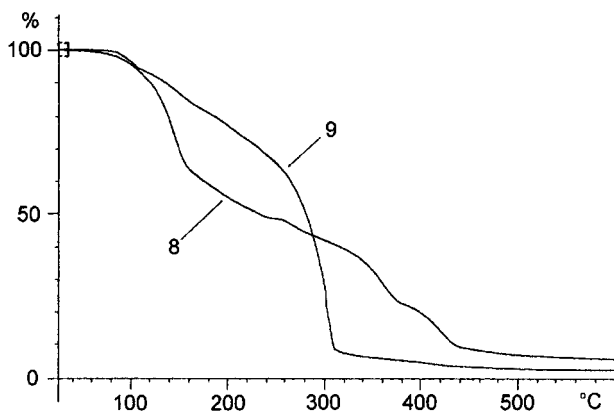
Figure 3. TG curves of complexes **8** and **9**.

Table 1. Data from the Sublimation Experiments

complex	T [°C]	p [mbar]	composition of condensed phase
1	120−130	0.20	noncrystalline **1**
2	100−110	0.20	**2**
3	75−85	0.18	**3**
4	90−100	0.21	**4**
5	110−130	0.19	**5**
6	110−130	1.20	dissociates
7	145−170	0.30	[Mg(thd)₂]₂(trien)?

the TG curves for **8** and **9**. As can be seen, complexes **8** and **9**, which have diols as ancillary ligands, are thermally unstable. Complex **8** begins to lose weight almost immediately when heated, and it leaves a residue of 5.41%. Complex **9** has slightly different TG curve, and it evidently decomposes less than does complex **8**, leaving a residue of 2.17%. The behavior of complexes **8** and **9** may be explained in terms of hydrolyzation reactions. There is hydrogen bonding in the crystal structure of **8**, which probably promotes thermal hydrolyzation.

It is also observed (more clearly from the DTG curve) that the evaporation processes of diamine adducts contain two overlapping steps, the first step associated with the evaporation of amine and the second with the evaporation of [Mg₂(thd)₄] dimer. The fact that, according to both the TG and DTG curves, adducts of dien and trien evaporate in one step does not prove that they evaporate as complete molecules, for it is quite possible that separate thd complex [Mg₂(thd)₄] and amine evaporate separately in exactly the same temperature range.

SDTA curves recorded simultaneously with the TG curves showed endothermic maxima assigned for melting and different evaporation steps.

The dynamic TG measurements likewise do not reveal whether the adducts sublime intact at temperatures lower than the temperature of dissociation in normal or reduced pressure. These lower temperatures were investigated by isothermal sublimation experiments followed by analysis of the sublimation products (mp, TG/SDTA, NMR, and elemental analysis). Experiments on the amine adducts performed under reduced pressure (Table 1) showed all adducts of diamines to sublime with their composition and structure intact. This finding suggests that, under the right conditions, complexes with diamine may sublime without decomposition. The experiments also revealed that the dien adduct partially dissociates when sublimed. The sublimation probably results in a mixture of [Mg₂(thd)₄] and [Mg(thd)₂(dien)]. A third observation was that the trien adduct partially dissociates and undergoes a change in crystal structure when sublimed (mp 75 → 186 °C). In the new structure, the trien molecule may be binding together two Mg(thd)₂ units.
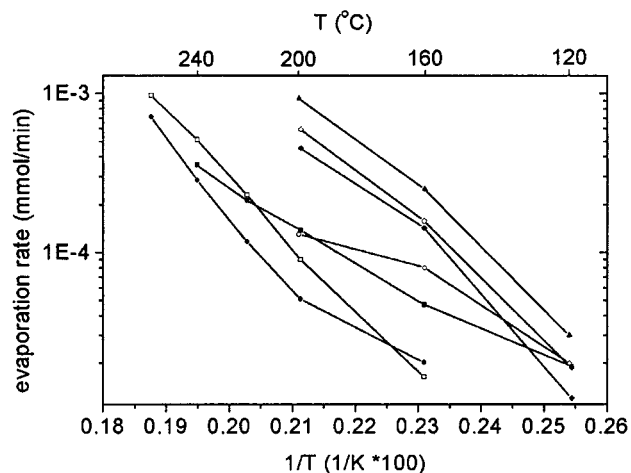

Figure 4. Evaporation rates (mmol/min) of complexes **1**−**7** as a function of $1/T$ (1/K). Curves from top to bottom at 160 °C: **4**, **3**, **5**, **2**, **6**, **7**, **1**.

Isothermal TG experiments were made for amine adducts in order to obtain information on evaporation rates and mass transport at different temperatures. The results of these experiments are shown in Figure 4, where evaporation rate (mmol/min) in logarithmic scale is represented as a function of $1/T$. It is presumed that the evaporating species are monomeric complexes. Linearity of these plots indicates pure sublimation, that is, evaporation in the absence of thermal decomposition or dissociation of the neutral ligand. Deviations from linearity at low temperatures probably are due to moisture or to excess of adduct-forming amine in the samples, while deviations at high temperatures are due to decomposition or dissociation of the complexes. Because deviations from linearity were not detected in the temperature range observed (Figure 4) and the sublimation products of the diamine adducts still contain the amine, the conclusion is that these complexes are evaporated intact.

Mass Spectra. The mass spectra of pure [Mg₂(thd)₄] and adducts are very similar. The most intense peak in all the mass spectra is at m/z 333, due to [Mg(thd)₂ − C(CH₃)₃]⁺. Small peaks assigned to dimeric species [Mg₂(thd)₄]⁺ (m/z 780) and [Mg₂(thd)₃]⁺ (m/z 597) are present in all spectra except the spectrum of **7**. Besides these peaks, peaks originating from Mg(thd)₂ and thd fragments are seen. Molecular ion [Mg(thd)₂-(A)]⁺ is observed in the spectra of **2**−**6** and fragment ion [Mg(thd)(A)]⁺ in the spectra of **2**−**7**. Neither ion is observed for **8** and **9**. The presence of molecular ions in the mass spectra of amine adducts confirms that these molecules really do exist in gas phase and supports the conclusions drawn from thermal analysis. The fact that oligomeric species are observed also does not prove that dissociation of adduct would neccessarily occur when the complexes are evaporated. The dissociation is most probably caused by the electron ionization used in the mass spectrometer.

NMR Spectra. ¹H NMR spectra of the amine adducts (**2**−**7**), show two unsplitt peaks originating from the methyl and methine protons of the thd ligand. Both peaks are shifted to higher field relative to the spectra of free Hthd and **1**. In the ¹H NMR spectrum of **1**, the peak at 1.09 originating from the methyl protons of the thd ligands is split to 5, while the peak at 5.65 originating from the methine protons is not split. The observed splitting is probably due to the dimeric structure of the complex. Peaks originating from the protons of the amines in the spectra of **2**−**7** are mainly shifted to a lower field, and the shapes are changed relative to those of the free amines. Loss of sharpness in the shape of the peaks is common. In the ¹H

Table 2. Crystal Data and Structure Refinement for Compounds **2**, **5**, and **7**

identification code	**2**	**5**	**7**
chemical formula	$C_{24}H_{46}MgN_2O_4$	$C_{28}H_{54}MgN_2O_4$	$C_{28}H_{56}MgN_4O_4$
formula weight	450.94	507.04	537.08
temperature, °C	−80(2)	−80(2)	−80(2)
λ (Mo Kα), Å	0.71073	0.71073	0.71073
space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$
a, Å	10.372(2)	10.091(4)	15.246(3)
b, Å	14.790(3)	19.133(5)	10.850(2)
c, Å	19.588(4)	17.021(5)	20.882(4)
α, deg	93.08(3)	90	90
β, deg	91.45(3)	93.250(5)	105.06(3)
γ, deg	107.44(3)	90	90
V (Å^3)	2859.9(10)	3281.0(18)	3335.6(11)
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.047	1.026	1.069
μ, cm^{-1}	0.89	0.84	0.88
R^a	0.0701	0.0759	0.1110
$R_w{}^b$	0.1697	0.2059	0.3076

$^a R = \sum ||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

NMR spectrum of complexes **8** and **9,** broad multiplets are observed for protons of both the thd and diol ligands. The overlapping of the peaks makes interpretation difficult.

The proton decoupled ^{13}C spectrum of **1** shows three peaks originating from the methyl carbons and just one peak each from the other kinds of carbon atoms (see Experimental Section). The three peaks originating from the methyl carbons indicate that there are three different chemical environments around the methyl groups. In the ^{1}H decoupled ^{13}C spectra of the amine adducts (**2**−**7**), in turn, only one peak originating from each kind of thd carbon is observed, implying that, in the monomeric complexes, in accordance with the pmr results, the methyl groups of the thd ligands experience similar chemical environments. The different carbon atoms of the amine ligand likewise give only one peak each. For complexes **8** and **9**, several peaks originating from methyl and methine carbons of thd are seen.

Single-Crystal X-ray Structures. A summary of data collection and the crystal structure determination is presented in Table 2 for crystals of **2**, **5**, and **7**. Figures 5, 6, 7, 8, and 9 show structures and atomic labeling for complexes **2**, **5**, **7**, **8**, and **9**, and tables 3, 4, and 5 show the selected interatomic distances and bond angles for complexes **2**, **5**, and **7**, respectively. Though data collections took place at 193 K, the diffraction results show large thermal displacement parameters and disorder, especially at the *tert*-butyl groups. This also increases the *R*-factor, and, in the following, numerical values are discussed only for structures with the conventional *R*-factor for observed reflections less than 10% (complexes **2** and **5**). The other results nevertheless reveal the structures of the molecules and can be used to explain some of the properties of the complexes. Hydrogen bonding in the structure of complex **8**, for example, may explain the thermal instability of the complex. Because of low precision, structures of complexes **8** and **9** are presented only in figures.[28]

Complexes with amines coordinated to Mg (**2**, **5**, **7**) formed monomeric structures, while complex **8** formed a structure with hydrogen bonding, and complex **9** is dimeric. All β-diketonato ligands in all complexes studied are bidentately coordinated to

(28) Crystal data for **8**: space group C 121 (no.), with $a = 24.305(5)$ Å, $b = 11.247(5)$ Å, $c = 9.570(5)$ Å, $\beta = 100.000(5)°$, $\gamma = 90°$, $V = 2576.3(18)$ Å^3, $Z = 2$, and $\rho_{calc} = 1.168$ g cm^{-3}. Crystal data for **9**: space group Cc, with $a = 14.413(3)$ Å, $b = 15.039(3)$ Å, $c = 28.024(6)$ Å, $\alpha = 90°$, $\beta = 90.79(3)°$, $\gamma = 90°$, $V = 6074(2)$ Å^3, $Z = 8$, and $\rho_{calc} = 0.982$ g cm^{-3}

Table 3. Selected Bond Lengths [Å] and Angles [deg] for [Mg(thd)$_2$(en)]$_2$, **2**

Mg(1)−O(11)	2.032(3)	O(21)−Mg(1)−N(12)	90.08(11)
Mg(1)−O(12)	2.034(3)	O(22)−Mg(1)−N(11)	93.66(12)
Mg(1)−O(21)	2.051(3)	O(11)−Mg(1)−N(11)	165.26(12)
Mg(1)−O(22)	2.019(3)	O(12)−Mg(1)−N(11)	80.53(12)
Mg(1)−N(11)	2.246(3)	O(21)−Mg(1)−N(11)	92.06(12)
Mg(1)−N(12)	2.208(3)	N(12)−Mg(1)−N(11)	77.96(11)
Mg(2)−O(31)	2.015(3)	O(31)−Mg(2)−O(41)	96.53(11)
Mg(2)−O(32)	2.055(3)	O(31)−Mg(2)−O(42)	91.09(11)
Mg(2)−O(41)	2.021(3)	O(41)−Mg(2)−O(42)	86.33(10)
Mg(2)−O(42)	2.046(3)	O(31)−Mg(2)−O(32)	86.33(11)
Mg(2)−N(21)	2.250(3)	O(41)−Mg(2)−O(32)	100.24(11)
Mg(2)−N(22)	2.201(3)	O(42)−Mg(2)−O(32)	173.17(11)
O(22)−Mg(1)−O(11)	92.95(11)	O(31)−Mg(2)−N(22)	167.32(13)
O(22)−Mg(1)−O(12)	91.76(11)	O(41)−Mg(2)−N(22)	96.13(11)
O(11)−Mg(1)−O(12)	86.11(11)	O(42)−Mg(2)−N(22)	90.56(11)
O(22)−Mg(1)−O(21)	86.06(11)	O(32)−Mg(2)−N(22)	90.59(11)
O(11)−Mg(1)−O(21)	101.53(11)	O(31)−Mg(2)−N(21)	90.06(13)
O(12)−Mg(1)−O(21)	172.15(12)	O(41)−Mg(2)−N(21)	166.70(12)
O(22)−Mg(1)−N(12)	170.65(12)	O(42)−Mg(2)−N(21)	82.00(12)
O(11)−Mg(1)−N(12)	96.16(11)	O(32)−Mg(2)−N(21)	91.67(12)
O(12)−Mg(1)−N(12)	90.93(11)	N(22)−Mg(2)−N(21)	77.72(13)

Table 4. Selected Bond Lengths [Å] and Angles [deg] for [Mg(thd)$_2$(tmeda)], **5**

Mg−O(22)	1.990(2)	O(11)−Mg−O(21)	175.48(8)
Mg−O(12)	2.000(2)	O(22)−Mg−N(1)	168.27(11)
Mg−O(11)	2.015(2)	O(12)−Mg−N(1)	91.84(10)
Mg−O(21)	2.0188(19)	O(11)−Mg−N(1)	92.53(9)
Mg−N(1)	2.261(2)	O(21)−Mg−N(1)	90.06(9)
Mg−N(2)	2.292(3)	O(22)−Mg−N(2)	89.79(10)
O(22)−Mg−O(12)	99.33(9)	O(12)−Mg−N(2)	170.49(11)
O(22)−Mg−O(11)	91.75(8)	O(11)−Mg−N(2)	90.72(10)
O(12)−Mg−O(11)	86.36(8)	O(21)−Mg−N(2)	93.41(10)
O(22)−Mg−O(21)	86.42(8)	N(1)−Mg−N(2)	79.24(11)
O(12)−Mg−O(21)	89.85(8)		

Table 5. Selected Bond Lengths [Å] and Angles [deg] for [Mg(thd)$_2$(trien)], **7**

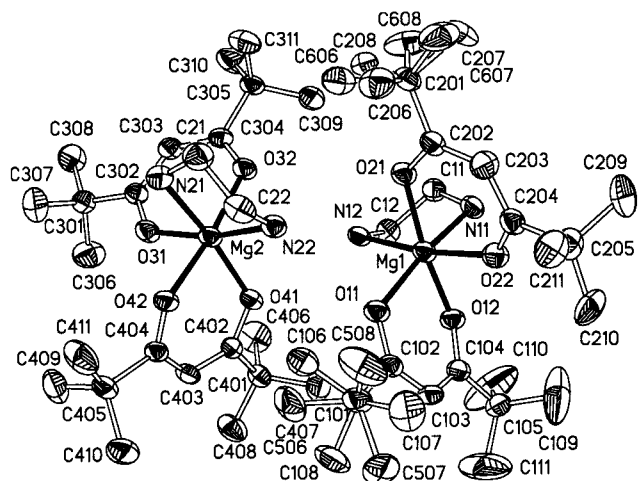|			
Mg−O(22)	2.014(7)	O(21)−Mg−O(12)	177.0(2)
Mg−O(11)	2.040(5)	O(22)−Mg−N(1)	169.2(2)
Mg−O(21)	2.060(7)	O(11)−Mg−N(1)	94.3(2)
Mg−O(12)	2.060(6)	O(21)−Mg−N(1)	87.9(3)
Mg−N(1)	2.187(7)	O(12)−Mg−N(1)	93.1(3)
Mg−N(2)	2.254(6)	O(22)−Mg−N(2)	91.3(2)
O(22)−Mg−O(11)	95.7(2)	O(11)−Mg−N(2)	169.8(3)
O(22)−Mg−O(21)	87.0(3)	O(21)−Mg−N(2)	90.1(2)
O(11)−Mg−O(21)	97.7(2)	O(12)−Mg−N(2)	87.3(2)
O(22)−Mg−O(12)	91.5(2)	N(1)−Mg−N(2)	79.2(2)
O(11)−Mg−O(12)	85.1(2)		

Mg. In dimeric complex **1**, three of the four thd ligands are acting as bridging ligands.[11] In all complexes studied, the coordination polyhedron around the Mg ions is a distorted octahedron where the distances from Mg to the N atoms in cis-positions are, as is normal,[10,11,29] slightly longer than to the keto O atoms of thd (see Tables 3−5). The coordination planes around Mg with nitrogen atoms or hydroxylic oxygen atoms and two keto oxygen atoms are regarded as basal planes. For all thd ions, one oxygen atom belongs to this basal plane and the other oxygen atoms are in apical positions, and their distances to Mg are longer than those on the basal plane.

While all the diamine adducts of Mg(thd)$_2$ studied are monomeric, the analogous complexes of heavier group 2 elements seem to be dimers as shown by the structrue of [Ba-(thd)$_2$(NH$_3$)$_2$]$_2$.[30] Because of the larger size of these elements, coordinative saturation is not achieved in monomeric complex

(29) Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr.* **1973**, *B29*, 1289.

(30) Rees, W. S., Jr.; Carris, M. W.; Hesse, W. *Inorg. Chem.* **1991**, *30*, 4479.

Figure 5. Structure of two monomeric molecules in the asymmetric unit for **2** with atom labels. The thermal ellipsoids are drawn at the 30% probability level. Rotational disorder of *tert*-butyl moieties at *C*101 and *C*201 are drawn showing the atoms with the occupancy factor 0.5 for each methyl group. Hydrogen atoms are omitted for clarity.
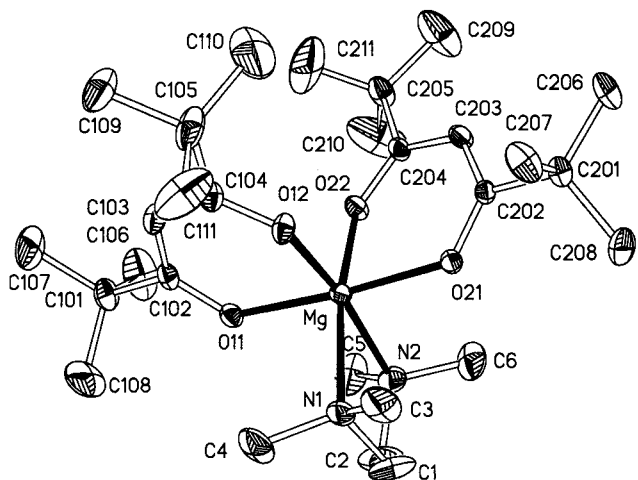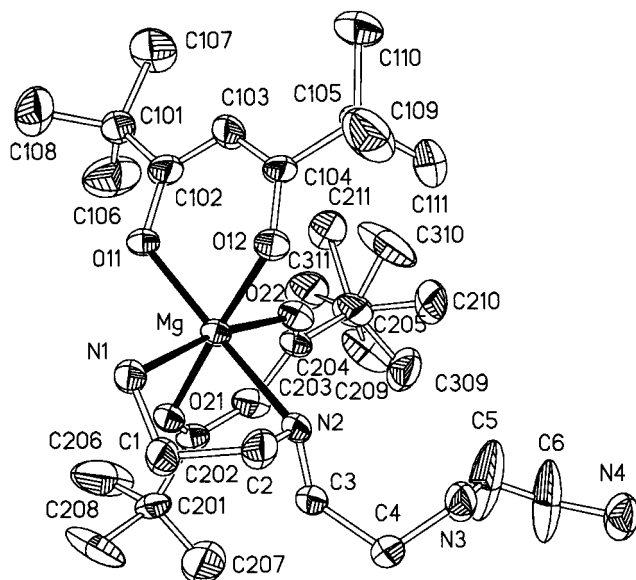

Figure 6. Structure of **5** with atom labels. The thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

in which the coordination number of the metal would only be 6. However, when two diamines coordinate to barium, coordinative saturation is achieved (CN = 8) so that monomeric coplexes may form as shown by the structure of [Ba(thd)$_2$-(tmeda)$_2$].[31]

In crystals of **2**, the asymmetric unit contains two nearly identical six-coordinated monomeric Mg complexes, where two thd ions and one ethylenediamine molecule are coordinated octahedrally to each Mg ion (Figure 5). The Mg−O distances (2.015−2.055 Å) and typically slightly longer Mg−N distances (2.201−2.250 Å) are normal. This structure also shows typical disorder at some *tert*-butyl moieties, but the refinement converges to a reasonable *R* value for this type of compound.

Complex **5** (Figure 6) is a monomer where Mg−O distances are nearly equal, from 1.999(2) to 2.019(2) Å, and Mg−N distances are about 0.25 Å longer. The Mg−N distances are the longest for the complexes studied, perhaps this can be due to steric inhibition and the weaker donor power of the ligand relative to primary and secondary diamines.

Likewise, the structure of the complex **7** (Figure 7) is monomeric and it shows similar features—shorter Mg−O and

(31) Labrize, F.; Hubert-Pfalzgraf, L. G.; Vaissermann, J.; Knobler, C. B. *Polyhedron* **1996**, *15*, 577.

Figure 7. Structure of **7** with atom labels. The thermal ellipsoids are drawn at 30% probability level. Rotational disorder of a *tert*-butyl moiety at *C*205 is drawn showing the atoms with occupancy factor 0.5 for the methyl group. Hydrogen atoms are omitted for clarity.
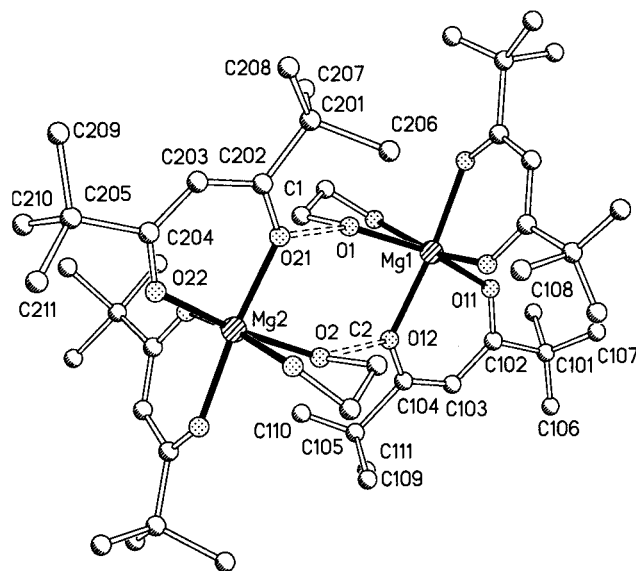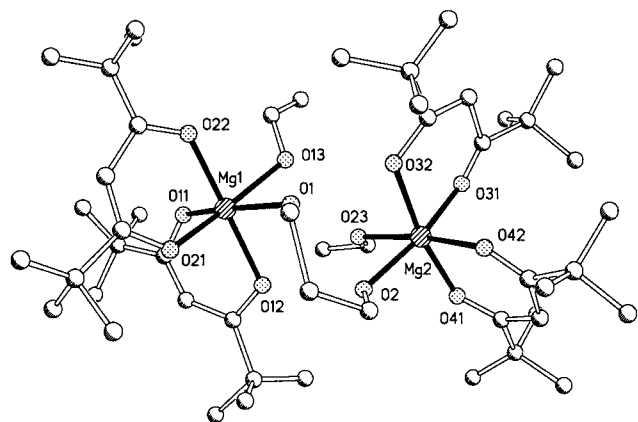

Figure 8. Structure of **8** where the asymmetric unit consists of two molecule halves, which are separately labeled. Many thermal displacement parameter values were nonpositive definite, so the atoms are drawn as circles. Dotted lines show the hydrogen bond distances between the hydroxyl groups and keto oxygen atoms. Hydrogen atoms are omitted for clarity.

longer Mg−N distances—to the other Mg complexes, where keto-oxygen atoms form short bonds and nitrogen atoms form considerably longer bonds (Tables 3−5). Only two of the four nitrogen atoms are coordinated to magnesium. The free NH$_2$ group of the trien molecule stretches to the distance of 3.766 Å from the Mg ion of the neighboring molecule in the *b*-axis direction (Figure 10).

The structures of compounds **8** and **9** also were determined.[28] However, the data are of low quality, so the results are only indicative. For this reason only graphic results showing one orientation of disorder is presented for each of the compounds (Figures 8 and 9). In the structure of compound **8** a hydrogen bond network, connecting pairwise two keto-oxygens and two hydroxylic groups, forms one-dimensional chains through the

Figure 9. Structure of the dimeric complex **9**. Owing to the large thermal displacement parameter values, atoms are shown as circles. The disordered 1,3-propanediol molecule acts as bridge between Mg ions and only one position is shown. Hydrogen atoms are omitted for clarity.
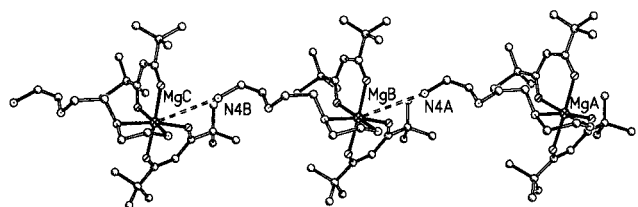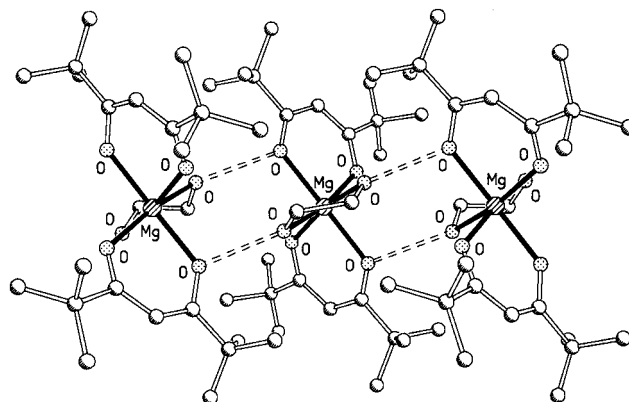

Figure 10. Partial packing diagram for complex **7** showing the weak Mg−N interaction in the *b*-axis direction. Other symmetry elements are omitted.

structure as shown in Figure 11. Complex **9** is a dimeric compound where one 1,3-propanediol molecule is bridging two Mg ions, and two thd ions and one ethanol molecule are coordinated to each of the Mg ions.

Conclusions

Mg(thd)$_2$ crystallizes as dimer from nonpolar solvents.[11] When multidenate amines or ethanol[10] are introduced, they coordinate to Mg and monomeric adducts with Mg coordination

Figure 11. Partial packing diagram for complex **8**. One chain formed through hydrogen bonding is shown.

number 6 are formed. When the neutral coordinating ligand is 1,2-ethanediol, a structure with hydrogen bonding is formed. Evidently, 1,3-propanediol is less capable than 1,2-ethanediol of replacing all EtOH in the coordination sphere of Mg(thd)$_2$-(EtOH)$_2$ because complex {[Mg(thd)$_2$(EtOH)]$_2$(1,3-propanediol)} was formed when the reaction conditions used in the preparation were the same as for Mg(thd)$_2$(1,2-ethanediol). Adducts of polyamines evaporate completely, while complexes with diols decompose upon heating. When complexes where the ancillary ligand is diamine are heated in normal pressure under nitrogen, dissociation of the complex occurs when a certain temperature level is exceeded. Below the dissociation temperature the diamine adducts seem to evaporate intact as whole adducted molecules.