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Synthesis and crystal structure of the new heteroleptic magnesium bis(amide) [{Mg[μ-N(H)Ph][N(SiMe$_3$)$_2$]·THF}$_2$], and density functional MO calculations on model systems†

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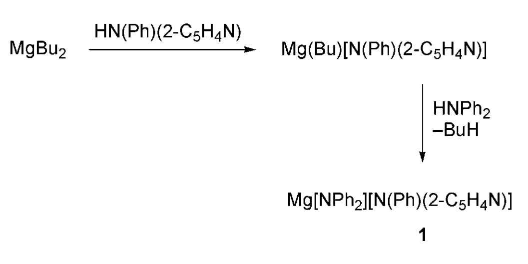
Reaction of Mg[N(SiMe$_3$)$_2$]$_2$ with one molar equivalent of the primary amine PhNH$_2$ in THF solution gave the transaminated THF-solvated heteroleptic bis(amide) [{Mg[μ-N(H)Ph][N(SiMe$_3$)$_2$]·THF}$_2$]. In the crystalline state the new amide is dimeric with a central, planar azamagnesacyclic (NMg)$_2$ ring. The resonance stabilised anilido units prefer to bridge to the magnesium centres whereas the bulkier secondary hexamethyldisilazanzide groups occupy terminal sites. Terminal solvation by THF completes the distorted tetrahedral environment about magnesium. Comparisons of this structure with other crystallographically characterised heteroleptic magnesium bis(amides) are made. The interesting, almost square geometry of this (NMg)$_2$ ring has also prompted a density functional MO study on magnesium systems and related molecules of Groups 1, 2 and 13, the results of which are also reported.

1 Introduction

In recent years magnesium homoleptic bis(amides) Mg(NR$_2$)$_2$ and their heterobimetallic derivatives have begun to receive increasing interest both synthetically[1] and structurally,[2] mainly through the development of the chemistries of magnesium bis[bis(trimethylsilyl)amide], Mg[N(SiMe$_3$)$_2$]$_2$ and magnesium bis(2,2,6,6-tetramethylpiperidinide), Mg-[NCMe$_2$CH$_2$CH$_2$CH$_2$CMe$_2$]$_2$. In contrast, relatively little information has been collected on heteroleptic magnesium bis(amide) compounds Mg(NR$_2$)(NR′$_2$), where R ≠ R′. In this regard we reported the first crystal structure of a magnesium heteroleptic bis(amide) in [{Mg[μ-N(Ph)$_2$][N(Ph)-(2-C$_5$H$_4$N)]}$_2$],[3] **1**. This was prepared by a stepwise double alkane elimination process as outlined in eqn. (1): 2-anilinopyridine was metallated by dibutylmagnesium to afford an alkylmagnesium mono(amide) intermediate (not isolated), which subsequently metallated the second amine, diphenylamine. The structure of **1** is noteworthy for displaying perfect right-angled endocyclic corners [90.0(2)°] within its four-membered azamagnesacyclic ring core. This unusual feature has prompted us to investigate the geometrical characteristics of a second magnesium heteroleptic bis(amide) dimer [{Mg-[μ-N(H)Ph][N(SiMe$_3$)$_2$]·THF}$_2$], **2**, the synthesis and crystal structure of which are reported herein. At the time of writing this represents only the third such complex in this class to be crystallographically characterised, following on from **1** and the novel solvent-free trinuclear species [Mg$_3${μ-N(H)(Dipp)}$_4${N(SiMe$_3$)$_2$}$_2$], **3** (Dipp = 2,6-Pr$^i_2$C$_6$H$_3$), reported by Power and co-workers,[4] which, in contrast to **1** and **2**, contains an unequal (2:1) stoichiometric ratio of its two distinct amide ligands. In addition, **2** represents the first crystal structure of a magnesium anilide species, providing a contrast with the aniline-based imides [(Et$_2$O·Mg)$_6$(NPh)$_4$(Br)$_4$][5] and [{Mg(N-Ph)·THF}$_6$],[6] also reported by Power and co-workers. Historically, the first magnesium anilide complex [Mg{N(H)Ph}$_2$] was prepared about 80 years ago[7] by the reaction of magnesium metal with aniline at high temperatures. Since then complexes of the type [Mg{N(H)Ph}X] (where X = Br or I) have been the subject of intermittent interest as novel reagents for carrying out organic transformations,[8,9] *e.g.* as nucleophiles for the synthesis of functionalised pyridyl compounds or the preparation of N,N-disubstituted amidines through reaction with nitriles.



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2 Results and discussion

2.1 Synthesis and characterisation

The new heteroleptic amide **2** was synthesized by a routine transamination approach involving re-dissolved crystalline Mg[N(SiMe$_3$)$_2$]$_2$ (prepared by heating to reflux a 1:2 stoichiometric mixture of *n,s*-Bu$_2$Mg:HN(SiMe$_3$)$_2$ in heptane solvent and cooling to ambient temperature) and aniline in a 1:1 molar ratio in toluene solution. Initially, a white, arene-insoluble, solid was produced, but this was dissolved on the addition of a fifteen molar excess of THF. The resulting solution afforded colourless crystals of the THF solvate **2**. Presumably the white solid produced at the intermediate stage is the (unknown) solvent-free analogue [{Mg[μ-N(H)Ph][μ-N(SiMe$_3$)$_2$]}$_n$]. This is likely to be a polymer ($n = \infty$) or high oligomer in which both amido anions bridge, before it deaggregates to a dimeric arrangement upon the addition of the Lewis base THF as shown in eqn. (2). Though terminally coordinated in **2** (see below), [(Me$_3$Si)$_2$N]$^-$ anions have been found previously in

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† Dedicated to the memory of Dr. Ron Snaith who was a loyal colleague, an inspirational co-worker and a treasured friend.

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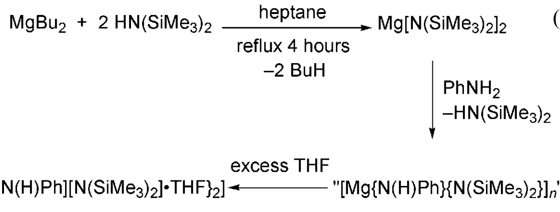
Table 1 Selected bond distances (Å) and angles (°) in compound **2**

N(1)–Mg	2.1404(11)	N(1A)–Mg	2.1020(10)	N(2)–Mg	2.0034(11)
O(1)–Mg	2.0255(9)	N(1)–C(1)	1.4144(15)	N(2)–Si(1)	1.7049(10)
N(2)–Si(2)	1.7022(10)				
N(1A)–Mg–N(1)	89.85(4)	N(1A)–Mg–N(2)	124.37(4)	O(1)–Mg–N(1A)	112.03(4)
N(1)–Mg–N(2)	120.88(4)	O(1)–Mg–N(1)	102.21(4)	Si(2)–N(2)–Mg	115.07(5)
N(2)–Mg–O(1)	105.39(4)	Si(2)–N(2)–Si(1)	124.08(6)	Mg(A)–N(1)–Mg	90.15(4)
C(1)–N(1)–Mg(A)	118.10(7)	C(1)–N(1)–Mg	115.60(7)	Si(1)–N(2)–Mg	120.83(6)

Symmetry transformation used to generate equivalent atoms: A $1 - x, 1 - y, 1 - z$.



(2)

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bridging modes in other magnesium structures such as the parent bis(amide) [{Mg[N(SiMe$_3$)$_2$]$_2$}$_2$][10] and the alkyl derivative [{Mg(Bu^s)[μ-N(SiMe$_3$)$_2$]}$_2$].[11] Although there are no other examples of X-ray characterised magnesium anilide species in the literature for comparison, anilide anions have been observed to adopt bridging positions in several lithiated derivatives including dinuclear [{PhN(H)Li·(2py)}$_2$],[12] [{PhN(H)Li·(2THF)}$_2$],[13] trinuclear [{PhN(H)Li}$_3$·2PMDETA] (PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine)[14] and tetranuclear [{PhN(H)Li}$_4$·6(4-Bu^t-py)].[12] The aforementioned solvent-free trinuclear species **3** was prepared by the same transamination approach. Its preference for an oligomeric structure over a polymeric alternative can be attributed to the increased steric hindrance caused by the incorporation of two isopropyl functions in the 2 and 6 positions on the anilide ring.

The ^{1}H NMR spectrum of compound **2** was recorded in d$_5$-pyridine solution at room temperature (298 K) and compared to a spectrum of pure aniline in the same solvent. Metallation of the NH$_2$ group was confirmed through the low frequency shift of the N–H signal from δ 5.39 for aniline to δ 3.62 for **2**. Similar, but not as pronounced, low frequency shifts are also observed in the aromatic resonances, *i.e.* by 0.13, 0.09 and 0.29 ppm for the *ortho*-, *meta*- and *para*-H resonances respectively. The methyl protons associated with the hexamethyldisilazanide ligand appear at δ 0.25. Furthermore, the metal bound THF molecules are clearly observed as two well defined multiplets at δ 3.68 and 1.65. Suitable ^{13}C NMR data were not obtained due to the poor solubility of **2** in both deuteriated arene and pyridine solvents.

Melting point studies of compound **2** revealed a much higher range (176–180 °C) than that found for the homoleptic bis(amide) [{Mg[N(SiMe$_3$)$_2$]$_2$}$_2$] (122–123 °C).

2.2 X-Ray crystallographic study

The molecular structure of compound **2** is that of a strictly centrosymmetric dimer (Fig. 1). Its salient feature is a central planar (NMg)$_2$ cyclic ring. The magnesium centres are four-coordinate occupying distorted tetrahedral geometries (range of bond angles, 89.85(4)–124.37(4)°; mean 109.1°). The N atoms within this ring belong exclusively to the anilide anion. These atoms are four-coordinate displaying a distorted tetrahedral geometry. The anilino hydrogen, which was detected by NMR spectroscopy, was clearly seen in a difference electron density map; it was refined with geometrical constraints, as were other hydrogen atoms in the structure. The phenyl rings are found to be disposed *trans* to one another across the central ring. A similar conformation has been observed in the thermally unstable terphenyl beryllium anilide, [ArBeN(H)Ph]$_2$, where Ar = C$_6$H$_3$Mes$_2$-2,6; Mes = 2,4,6-Me$_3$C$_6$H$_2$.[15] The terminally bound sp^2-N atoms in **2**, belonging to the hexamethyldisilazanide anion, have a three-coordinate distorted trigonal planar geometry [mean bond angle, 120°]. Furthermore it is noteworthy that the Si–N–Si bond angles in **2** [124.08(6)°] are significantly larger than those present within the terminal anions of [{Mg[N(SiMe$_3$)$_2$]$_2$}$_2$] [mean angle, 119.02°]. This discrimination is likely to be a consequence of steric factors as the hexamethyldisilazanide ligand in **2** shares a terminal site with a THF solvent molecule, whereas in [{Mg[N(SiMe$_3$)$_2$]$_2$}$_2$] no solvent molecules are present. Electronically, this makes little difference as gauged by the similarity in N–Si bond distances (mean distance, 1.704 Å for the former; 1.712 Å for the latter). The structural arrangement of anions in **2** is in accordance with that of **3**, where both structures can be rationalised in terms of the steric bulk of the amide units employed, with the larger silyl amide participating in a more favoured non-bridging role.

Table 2 Comparison of selected bond distances (Å) and angles (°) within heteroleptic magnesium bis(amide) complexes

Amide	N_{br}–Mg/Å	N_{br}–Mg–N_{br}/°	Mg–N_{br}–Mg/°	N_t–Mg/Å
1	2.080(5) 2.119(5)	90.0(2)	90.0(2)	2.025(5)^a
2	2.102(10) 2.140(11)	89.9(4)	90.1(4)	2.003(11)
3	2.095(6) 2.128(6)	89.5(2) 90.6(2)	90.3(2) 89.5(2)	1.966(6)

br = bridging; t = terminal. ^{a} = anionic N–Mg distance.

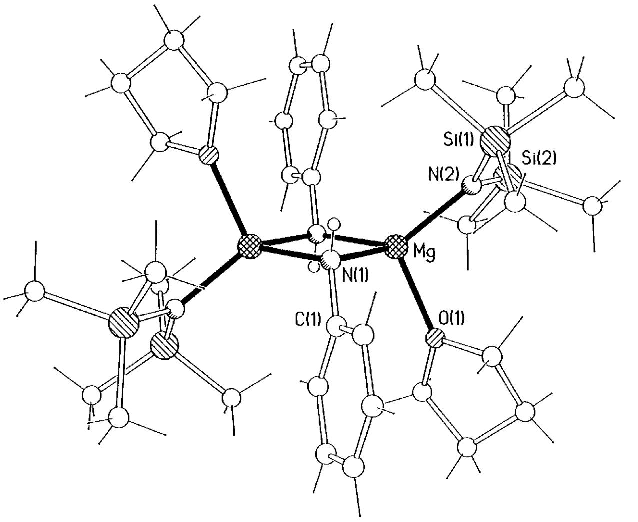

Fig. 1 Molecular structure of compound **2** with key atoms labelled; H atoms bonded to C are shown very small for clarity.

Table 1 gives individual bond distances and bond angles for compound **2**, while Table 2 compares selected dimensions of all three heteroleptic bis(amides). From the comparative data it is discernible that the N–Mg distances within the four-membered (NMg)$_2$ rings are in good agreement within experimental error (mean values for **1**, **2** and **3** are 2.099, 2.121, and 2.111 Å respectively). These distances are moderately shorter than those

Table 3 Calculated dimerisation energies and key dimensions of theoretical magnesium bis(amide) dimers

Groups (bridging, terminal)	Total energy/au	Dimerisation energy/kcal mol^{-1}	N–Mg/Å		Ring angles/° N–Mg–N, Mg–N–Mg
			Ring	Terminal	
NH_2, NH_2	−624.269319	−65.8	2.088	1.911	90.1, 89.9
NH_2, NHMe	−702.886677	−65.6	2.089, 2.089	1.919	90.2, 89.8
NHMe, NH_2	−702.879877	−61.4	2.094	1.913	91.2, 88.8
NH_2, NMe_2	−781.517088	−65.5	2.088	1.929	90.2, 89.8
NMe_2, NH_2	−781.502149	−56.1	2.100	1.912	92.1, 87.9
NHMe, NHMe	−781.496631	−61.0	2.093, 2.095	1.921	91.3, 88.7
NHMe, NMe_2	−860.126686	−61.0	2.093	1.930	91.4, 88.6
NMe_2, NHMe	−860.118235	−55.7	2.101, 2.100	1.920	92.2, 87.8
NMe_2, NMe_2	−938.747565	−55.5	2.100	1.929	92.3, 87.7

present in the unsolvated three-coordinate homoleptic amide $[\{Mg[N(SiMe_3)_2]_2\}_2]$ [mean, 2.15 Å]. The terminal N–Mg bond distance in **2** [2.003(11) Å] lies within the range of those present in both $[\{Mg[N(SiMe_3)_2]_2\}_2]$ [mean, 1.980 Å] and the bis THF-solvated monomer $[Mg\{N(SiMe_3)_2\}_2\cdot 2THF]$[16] [mean, 2.021 Å]. The O–Mg bond distance of 2.026(9) Å in **2** is similar to those found in the aforementioned imido complex $[\{Mg(NPh)\cdot THF\}_6]$ [mean, 2.040 Å]. Interestingly **2** can be regarded as a potential intermediate to this imide complex, through further elimination of $HN(SiMe_3)_2$: future studies will explore this possibility. There are several examples in the literature of dimeric amido magnesium complexes with terminal THF solvation including homoleptic $[Mg\{N(CH_2Ph)_2\}_2\cdot THF]_2$[17] [O–Mg, 2.070(2) Å], the alkylamido species $[MgBu^t\{N(H)Bu^t\}\cdot THF]_2$[4] [O–Mg, 2.085(4) Å] and the dianionic five-coordinate complex $[\{MgN(Ph)CH_2CH_2N(Ph)\cdot 2THF\}_2]$[18] [mean O–Mg, 2.125 Å]. Turning to bond angles, it is noteworthy that the central $(NMg)_2$ ring in **2** bears a close resemblance to that of **1** with almost perfect right angled corners at magnesium and nitrogen (see Table 1). The following *ab initio* study will consider this point in more detail and also explore how systematic substitution of the bridging and terminal hydrogens of $[Mg(NH_2)_2]$ by methyl groups affects the geometrical parameters of the dimer and the energy of dimerisation.

2.3 Theoretical calculations

Initially, *ab initio* geometry optimisation calculations[19] were performed on nine centrosymmetric dimers formed from the six monomers of the magnesium bis(amide) series $Mg[NH_x(CH_3)_{2-x}][NH_y(CH_3)_{2-y}]$ where x and y can be 0, 1, or 2. Although no symmetry constraints were present in the calculational process, the dimeric rings were constructed so that identical components occupied *trans* positions with respect to the ring. When the magnesium bis(amide) species was heteroleptic the two possible centrosymmetric dimers were examined. Each dimer and monomer were initially optimised at the Hartree–Fock level using the 6-31G* basis set[20] and subjected to a frequency analysis before being re-optimised using the Density Functional Theory Process (B3LYP)[21] and the 6-311G** basis set.[22] The results of the latter calculation are exclusively reported here.

The calculated dimerisation energy and the key structural features of the magnesium bis(amide) dimers are presented in Table 3. It can be seen that the dimerisation energies which range from −65.8 to −55.5 kcal mol^{-1} are principally a function of the nature of the bridging group while substitution of the terminal groups has a comparatively minor effect. The most stable bridging group is found to be the unsubstituted NH_2 functionality. Thus when each H on the bridging nitrogen is replaced, the dimerisation energy becomes less stable by ≈4.5 kcal mol^{-1} (on the first substitution) and by a further ≈5.4 kcal mol^{-1} (on the second replacement). The steric effects of a larger methyl group are more manifested at the four-coordinate bridging nitrogen atoms since the angular separations of the bridging groups are smaller than those at the three-coordinate terminal nitrogen atoms.

Table 4 Calculated ring angles of related theoretical dimers

Monomer	Ring angle of dimer at metal/°
$LiNH_2$	107.5
$NaNH_2$	102.4
$Be(NH_2)_2$	95.5
$Mg(NH_2)_2$	90.1
$Mg(OH)_2$	83.3
$Mg(PH_2)_2$	88.8
$Mg(CH_3)_2$	105.6
$B(NH_2)_3$	88.4
$Al(NH_2)_3$	86.7
MgF_2	81.6

The calculated ring N–Mg bond distances lie within a narrow range [2.088–2.101 Å] with the longer distances associated with greater substitution by methyl groups. They are in reasonable agreement with the experimental range reported herein [2.080–2.140 Å]. The shorter terminal N–Mg bond distances are also found within a small range [1.911–1.930 Å] with the upper end values corresponding to a greater participation of N–CH_3 bonds present. These values are much shorter than the N_t–Mg experimental distances reported [2.003 Å]; however this is reasonable as the magnesium atoms in the crystal structure have a higher (four) coordination due to the presence of a coordinated THF solvent molecule. The corresponding series of calculated N–Mg bond distances for the magnesium bis(amide) monomers exhibit values between 1.897 and 1.913 Å which as expected are marginally shorter than the N_t–Mg bond distances found for the dimers.

The calculated ring angles reveal that when the bridging group is NH_2 the ring angles approach those of a square *i.e.* 90°. Increased methyl substitution at the bridging nitrogen slightly increases the angle at magnesium (up to 92.3°) thus separating the amido groups further. These findings support the crystal structure data where azamagnesacyclic rings are found to exhibit approximately right-angled corners. Further calculations were performed on dimeric molecules related to $Mg(NH_2)_2$ *i.e.* $LiNH_2$, $NaNH_2$, $Be(NH_2)_2$, $B(NH_2)_3$, $Al(NH_2)_3$, $Mg(OH)_2$, $Mg(PH_2)_2$, $Mg(CH_3)_2$ and MgF_2. The ring angle at the metal for each of the dimers is presented in Table 4. It can be seen that it is a periodic property, which depends on the metal and the bonding group. For the species $[M(NH_2)_x]_2$ with a bridging NH_2 group, it can be seen from Table 4 that the ring angle at the metal decreases as M goes from Group 1 to 2 to 13 and from Period 2 to 3. In a similar way for the dimers of the type $[Mg(ZH_x)_y]_2$ the ring angle at Mg decreases as Z goes from Group 14 to 17. Analysis of the geometries of the $[M(NH_2)_x]_2$ dimers indicates that as M goes from Group 1 to 2 to 13 the metal–metal separation does not vary significantly. For the Period 2 metals, the range of distances is 2.24–2.36 Å ($\Delta = 0.12$

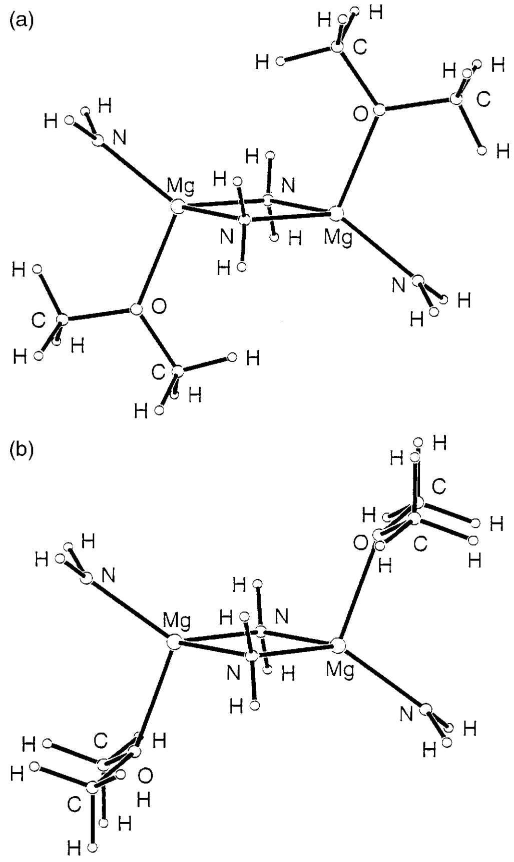

Fig. 2 The two initial conformations of the solvated magnesium bis(amide) dimers. The dimethyl ether either lies (a) perpendicular to or (b) parallel with the Mg···Mg axis.

Å), while for the larger Period 3 metals the corresponding range is 2.86–2.95 Å ($\Delta = 0.09$ Å). In contrast the nitrogen–nitrogen distances alter significantly as M changes giving the ranges 2.30–3.09 ($\Delta = 0.79$) and 2.71–3.55 Å ($\Delta = 0.84$ Å) respectively. For both series the highest value of the N···N distance occurs when M is a Group 1 metal. As M goes from Group 1 to 2 to 13 the reduction in this distance and thus the decrease in the bond angle at M can be correlated with a decrease in negative charge found on the bridging NH_2 groups (given by a Mulliken population analysis). A similar analysis of dimers of the type $[Mg(ZH_x)_y]_2$ reveals that the range of the Mg···Mg separations is relatively narrow [2.74–2.95 Å; $\Delta = 0.09$ Å] while the Z···Z distance variation is large [2.50–3.62 Å; $\Delta = 1.12$ Å]. As Z progresses from Group 14 to 17 the Z···Z distance decreases and hence the angle at M decreases; this can be linked with the corresponding decrease in the atomic radius of Z.

The next stage of the calculational investigation was to evaluate the effect of donor solvents on the energies and geometries of the magnesium bis(amide) dimers. Dimethyl ether was chosen as a model solvent to represent the oxygen donating solvent THF. For each of the solvated dimers, two initial structures were constructed by allowing the C–O–C backbone of dimethyl ether to lie (a) perpendicular to or (b) parallel with the Mg···Mg axis (Fig. 2).

The calculations found that the perpendicular orientation of the dimethyl ether was less favourable than the parallel alignment. Indeed for the triply substituted species either one or both of the perpendicularly placed Me_2O species moved during the optimisation procedure to lie approximately parallel with Mg···Mg axis. The energy difference between the two orientations ranged from 3.7 to 7.8 kcal mol^{-1}. Examination of the geometries where the Me_2O lies parallel to the Mg···Mg axis revealed that upon increased Me substitution at nitrogen the centrosymmetric structure of the dimer was being distorted through a long range interaction between a hydrogen of the dimethyl ether species and the nitrogen of a terminal amino group positioned directly across the four-membered ring. This results in a buckling of the four-membered ring as illustrated in Fig. 3. A measure of the ring distortion is given by the dihedral angle involving the ring atoms *i.e.* Mg–N–Mg–N which ranges from 0.0° for $[Mg(NH_2)_2{\cdot}Me_2O]_2$ to 18.4° for $[Mg\{N(CH_3)_2\}_2{\cdot}Me_2O]_2$. The energy involved in this distortion can be estimated by recalculating the complexes and imposing C_i symmetry. The largest energy stabilisation amounts to 2.3 kcal mol^{-1} and occurs when all the amido hydrogens have been substituted by methyl groups. It is interesting that to date this ring buckling has not been found experimentally. However the terminal and bridging groups present in these crystal structures are much larger than the methyl groups employed in the calculations. Therefore it is likely that ring distortion in these systems will be accompanied by unfavourable steric effects which will override the small energy stabilisation obtained by the ring buckling.

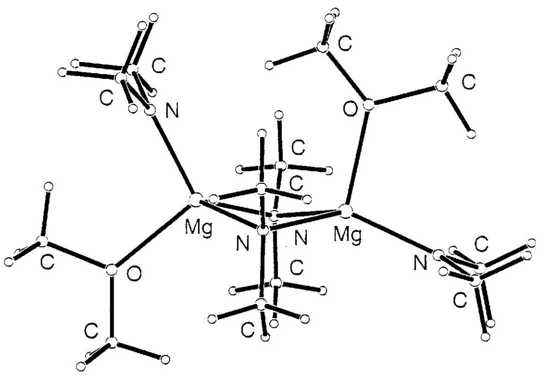

Fig. 3 Optimised geometry of $[Mg\{N(CH_3)_2\}_2{\cdot}Me_2O]_2$ illustrating the buckling of the $(NMg)_2$ ring.

The solvation energies of the dimers are calculated simply as the energy difference between the energy of the solvated dimers and the sum of the energies of the unsolvated dimer and the donor solvent. The resulting energies have a narrow range (−33.0 to −34.7 kcal mol^{-1}) and are not affected by the methyl substitution process. This parallels the solvation energy values of the monomeric magnesium bis(amides) which lie between −20.2 and −21.1 kcal mol^{-1}. The calculated dimerisation energies of the solvated monomers show the same trend as those of the unsolvated monomers. Thus for $[Mg(NH_2)_2{\cdot}Me_2O]$ the dimerisation energy is found to be −58.7 kcal mol^{-1} while for $[Mg\{N(CH_3)_2\}_2{\cdot}Me_2O]$ the value is calculated to be −48.2 kcal mol^{-1}.

Owing to the distortion of the four-membered dimeric rings it is only realistic to discuss the dimensions of the solvated dimers in general terms. The N–Mg ring bond distances are observed to lengthen slightly upon solvation, lying within the range 2.093–2.144 Å. In contrast the terminal N–Mg bond distances lengthen by ≈0.05 Å giving a spread of 1.964–1.990 Å within reasonable agreement with the experimental values reported herein. The O–Mg coordinate bond distances for all nine solvated dimers are found within the range 2.122–2.143 Å which are ≈0.05 Å longer than those reported previously and perhaps reflects the weaker coordination properties of Me_2O compared to those of THF. Finally, the endocyclic ring angles at magnesium, over the series, are marginally greater than 90° while the ring angles at nitrogen are much less than 90° as reported for the unsolvated species.

3 Experimental

3.1 Synthesis

The reaction to prepare compound **2** was carried out using conventional Schlenk apparatus under a protective blanket of oxygen-free argon gas. Solvents were distilled over a sodium–benzophenone mixture and degassed immediately prior to use. Amines were stored over KOH and distilled from CaH_2. All reagents were purchased from Aldrich Chemical Co.

Freshly prepared, crystalline $Mg[N(SiMe_3)_2]_2$ (2 mmol, 0.69 g) was dissolved in toluene (9 ml). To the resultant colourless solution an equimolar amount of aniline (2 mmol, 0.19 ml) was added, resulting in a vigorous reaction and the formation of a white precipitate. This solid dissolved on addition of the donor solvent THF (30 mmol, 2.5 ml). The Schlenk tube was then placed in a hot water bath and left to cool to ambient temperature, after which colourless crystals of compound **2** were produced. Yield of first batch: 0.50 g based on consumption of $Mg[N(SiMe_3)_2]_2$ (17.9%). mp 176–180 °C. Found: C, 55.0; H, 8.4; Mg, 6.8; N, 7.8. Calc. for $C_{16}H_{32}MgN_2OSi_2$: C, 55.1; H, 9.2; Mg, 7.0; N, 8.0%. ^1H NMR (400 MHz, pyridine-d_5, 298 K): δ 0.25 (s, Me), 1.65 (m, CH_2 of THF), 3.62 (s, N–H), 3.68 (m, OCH_2 of THF), 6.50 (m, *p*-H of Ph), 6.82 (m, *o*-H of Ph) and 7.16 (m, *m*-H of Ph).

Elemental analysis was carried out using a Perkin-Elmer 2400 elemental analyser and magnesium analysis was performed by atomic absorption using a PU9100 Philips spectrometer.

3.2 X-Ray crystallography

Data for compound **2** were measured on a Bruker AXS SMART CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 160 K. Crystal data: $C_{32}H_{64}Mg_2N_4O_2Si_4$, $M = 697.9$, monoclinic, space group $P2_1/n$, $a = 8.9338(4)$, $b = 21.3111(10)$, $c = 10.8059(5)$ Å, $\beta = 95.616(2)°$, $U = 2047.45(16)$ Å^3, $Z = 2$ (dimeric molecule on inversion centre), $\mu = 0.21$ mm^{-1}, 14245 measured data, 4728 unique ($R_{int} = 0.0171$); R (F, $F^2 > 2\sigma$) = 0.0299, wR (F^2, all data) = 0.0803, 205 refined parameters. Hydrogen atoms were constrained. Programs: Bruker SMART, SAINT and SHELXTL.

CCDC reference number 151831.

See http://www.rsc.org/suppdata/dt/b0/b008756o/ for crystallographic data in CIF or other electronic format.

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