Model Structural Types for rationalising Stoichiometries and Coordination Numbers in Lithium Amidomagnesiates: Syntheses and X-Ray Diffraction Studies of $[\{Mg(NR_2)_2\}_2]$, $[Li_2Mg(NR_2)_4]$ and $[LiMg(NR_2)_3{\cdot}py]$ (R = benzyl, py = pyridine)

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Factors governing the intermetallic ratios and coordination geometries in lithium amidomagnesiates are discussed with reference to three model crystal structures containing the same (dibenzylamido) ligand, which remarkably reveal that an unsolvated lithium can induce coordination expansion about a magnesium centre.

Mixed lithium magnesium amide chemistry is at an embryonic stage in its development with the first structure, $[Li_2Mg\{N(CH_2CH_2NMe_2)CH_2Ph\}_4]$, being reported as recently as 1993.[1] Other types of lithium magnesiate have been known since 1951,[2] though only a modest number have been well characterised in the intervening years. Interestingly, the Li : Mg stoichiometries in these compounds can vary *e.g.* 1 : 1 in $[LiMg(C_6H_2Pr^i{}_3\text{-}2,4,6)_3{\cdot}0.6THF{\cdot}0.4Et_2O]$,[3] 2 : 1 in $[Li_2MgMe_4{\cdot}2tmen]$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine),[4] 2 : 2 in $[Li_2Mg_2Ph_6{\cdot}2tmen]$,[5] and moreover, often these intermetallic ratios conflict with the stoichiometries of the reaction mixtures employed in their syntheses. Reported herein is a series of crystallographically characterised compounds, all containing the dibenzylamido $[\text{-}N(CH_2Ph)_2]$ ligand,[6] which serve as archetypal structures for explaining different stoichiometric preferences in lithium amidomagnesiates and in lithium magnesiates generally. Of perhaps even greater significance is the finding that the presence of Li can induce coordination expansion at a Mg centre. This comparison of isoleptic molecules shows that the Mg geometry changes from three-coordinate, (distorted) trigonal planar to four-coordinate, (distorted) tetrahedral under the influence of Li which, to effect this reorganisation, must be in its most active, sterically accessible, unsolvated state.

The new compounds were prepared by metallation of the secondary amine HNR_2 ($R{=}CH_2Ph$), in Schlenk tubes under protective argon blankets.† Magnesiation in each case was achieved *via* commercially available Bu^nBu^sMg (from Aldrich). The homoleptic magnesium bis(amide) $[\{Mg(NR_2)_2\}_2]$ **1**, was produced on performing the reaction in a donor-free medium. Equimolar mixtures of Bu_2Mg and Bu^nLi gave the intermetallic amide $[Li_2Mg(NR_2)_4]$ **2**; notable for having a Li : Mg ratio of 2 : 1 and not 1 : 1. However, addition of pyridine to the same equimolar mixture resulted in formation of the stoichiometry-correct (1Li : 1Mg) complex $[LiMg(NR_2)_3{\cdot}py]$ **3**.

All three amides were subjected to an X-ray diffraction study.‡ Homoleptic **1** was found to be a centrosymmetric dimer (Fig. 1). Its most salient feature is that the steric requirements of the dibenzylamido anions force Mg into a trigonal-planar coordination of 3N atoms, instead of its preferred four-coordinate, tetrahedral geometry. In common with other magnesium amides,[10] it has a planar, four-membered $\overline{\text{MgNMg}'\text{N}'}$ cyclic core. The next crystal structure determined, the lithium amidomagnesiate **2**, appears surprising in light of the previous structure, for its Mg centre attains the preferred higher coordination state even though it is in an isoleptic environment (Fig. 2). This structure can be viewed as two heterometallic $\overline{\text{MgNLiN}}$ rings fused through the tetrahedrally N_4-coordinated Mg centre giving a linear Li···Mg···Li arrangement. In this regard it is analogous to the aforementioned C–Mg 'ate $[Li_2MgMe_4{\cdot}2tmen]$,[4] but whereas its lithium centres are solvated and four-coordinate, those in **2** are solvent free and only two-coordinate (with respect to N§). Indeed, this is the first lithium magnesiate of any type to be totally devoid of complexant molecules, containing neither inter- nor intra-molecular donor atoms. This coordinative unsaturation accentuates the polarising power of Li^+, enabling it to draw the ligands tightly towards it, leading to a relaxation of the steric congestion that four dibenzylamido ligands would create around a single Mg^{2+} centre. This is one ligand greater than the sterically optimum number (three) as evidenced by the structure of **1**. Charge neutrality demands the participation of two Li^+ cations, and both pull together in concert to produce the 'drawn-out' $N_4(Mg)$ distorted tetrahedron. The final crystal structure (of **3** in Fig. 3) lends strong support to the view that Li^+ must be in an activated

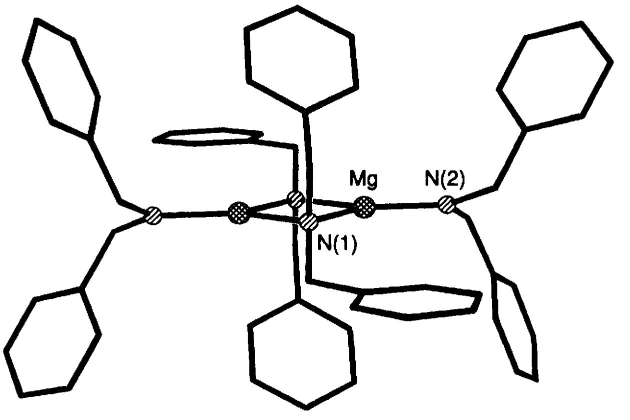

Fig. 1 Molecular structure of **1** without hydrogen atoms, and with important atoms labelled. Key dimensions (Å and °): Mg–N(1) 2.077(2), Mg–N(1′) 2.100(2), Mg–N(2) 1.935(2), N(1)–Mg–N(2) 135.51(6), N(1′)–Mg–N(2) 130.23(6), N(1)–Mg–N(1′) 94.22(5), Mg–N(1)–Mg′ 85.78(5). Primed atoms are related to their unprimed counterparts by inversion through the centre of the Mg_2N_2 ring

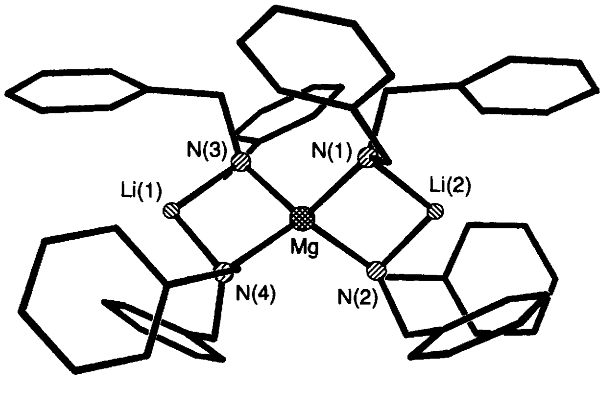

Fig. 2 Molecular structure of **2** without hydrogen atoms, and with important atoms labelled. Key dimensions (Å and °): Mg–N(1) 2.083(10), Mg–N(2) 2.119(8), Mg–N(3) 2.071(9), Mg–N(4) 2.117(9), Li(1)–N(3) 2.04(2), Li(1)–N(4) 1.92(2), Li(2)–N(1) 2.03(2), Li(2)–N(2) 1.98(2), N(1)–Mg–N(2) 95.9(4), N(1)–Mg–N(3) 108.5(3), N(1)–Mg–N(4) 119.6(4), N(2)–Mg–N(3) 119.8(4), N(2)–Mg–N(4) 118.3(3), N(3)–Mg–N(4) 96.0(4), N(3)–Li(1)–N(4) 103.7(10), N(1)–Li(2)–N(2) 102.2(10), Mg–N(1)–Li(2) 80.7(7), Mg–N(2)–Li(2) 81.1(6), Mg–N(3)–Li(1) 79.3(7), Mg–N(4)–Li(1) 80.8(6)

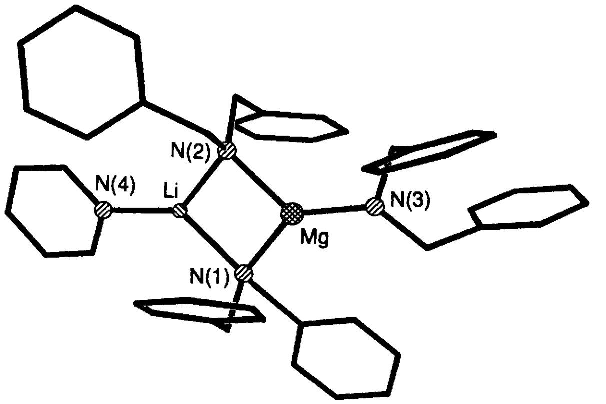

Fig. 3 Molecular structure of **3** without hydrogen atoms, and with important atoms labelled. Key dimensions (Å and °): Mg–N(1) 2.040(3), Mg–N(2) 2.050(3), Mg–N(3) 1.945(3), Li–N(1) 2.061(6), Li–N(2) 2.025(6), Li–N(4) 2.009(6), N(1)–Mg–N(2) 99.40(11), N(1)–Mg–N(3) 138.10(11), N(2)–Mg–N(3) 122.35(11), N(1)–Li–N(2) 99.6(2), N(1)–Li–N(4) 125.2(3), N(2)–Li–N(4) 134.4(3), Mg–N(1)–Li 80.2(2), Mg–N(2)–Li 80.8(2)

low-coordinate state to promote this coordination expansion. This follows since solvation by pyridine, thereby increasing the coordination of Li^+ (from two to three), reduces the acceptor capability of Li^+ so that its pull on the ligands is lessened—alternatively the increased steric bulk at Li^+ pushes the dibenzylamido ligands closer to Mg^{2+}. Either way, the phenyl rings adopt very different positions from that in **2** [*cf.*, for example, the N(1) unit in **3** with the N(4) unit in **2**], and four-coordination can no longer be sustained at the Mg^{2+} centre. Hence, the Mg geometry reverts to being (distorted) trigonal planar as in **1**. Stereochemically this dictates that one dibenzylamido ligand moves from a bridging to a terminal position which can only occur on displacement of another dibenzylamido anion and its Li^+ counter ion. Thus, the change in stoichiometry from 2Li : 1Mg to 1Li : 1Mg can be directly attributed to the solvation of the Li^+ by pyridine.

In conclusion, basing arguments on the structures of representative compounds, a rationale has been established for the stoichiometries and coordination patterns observed in certain lithium amidomagnesiates, and this should also apply to other categories of lithium magnesiates (*e.g.* with alkyl or aryl ligands[11]), provided that the steric requirements of the substituents are similar to that of the dibenzylamido group.

We thank ICI, their representative P. J. V. Jones, and the SERC for supporting this research.

Received, 14th December 1993; Com. 3/07383A

Footnotes

† The amides are sensitive to atmospheric oxygen and moisture. Satisfactory analyses (C, H, N, Mg, Li) were obtained. Mp 175–177 °C for **1**, 135–136 °C for **2** and 135–136 °C for **3**. Yields (based on consumption of the amine), 61% for **1**, 62% for **2** and 22% for **3**. The synthesis of the compounds proved totally reproducible with reactions depositing red crystals in all instances.

‡ *Crystal data* for **1**: $C_{56}H_{56}Mg_2N_4$, M = 833.76, monoclinic, space group $P2_1/c$, a = 9.943(2), b = 15.813(3), c = 14.559(2) Å, β = 97.57(2)°, U = 2269.1(7) Å^3, Z = 2, D_c = 1.220 g cm^{-3}, $F(000)$ = 888, μ(Mo-Kα) = 0.096 mm^{-1}, λ = 0.71073 Å. 3997 Independent reflections were measured by ω/θ scans and on-line profile fitting[7] at 200 K on a Stoe-Siemens diffractometer with a Cryostream cooler.[8] Structure solution was by direct methods, refinement by full-matrix least-squares on F^2 for all independent reflections.[9] wR (all data) = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$ = 0.1283, conventional R [on F values for 3180 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0390, goodness of fit S = 1.073 on F^2 values for 280 parameters. For **2**: $C_{56}H_{56}Li_2MgN_4$, M = 823.24, triclinic, space group $P\bar{1}$, a = 12.666(8), b = 14.516(11), c = 16.041(12) Å, α = 70.67(3), β = 73.93(3), γ = 67.32(3)°, U = 2330(3) Å^3, Z = 2, D_c = 1.173 g cm^{-3}, $F(000)$ = 876, μ(Mo-Kα) = 0.080 mm^{-1}. 6089 Independent reflections were measured at 160 K. wR (all data) = 0.4483, conventional R (2311 reflections) = 0.1005, S = 1.094, for 544 parameters. For **3**: $C_{47}H_{47}LiMgN_4$, M = 699.14, triclinic, space group $P\bar{1}$, a = 9.056(4), b = 12.186(6), c = 20.279(10) Å, α = 101.58(3), β = 96.11(3), γ = 110.69(2)°, U = 2012(2) Å^3, Z = 2, D_c = 1.154 g cm^{-3}, $F(000)$ = 744, μ(Mo-Kα) = 0.081 mm^{-1}. 7606 Reflections were measured at 160 K, to give 6837 independent data (R_{int} = 0.0529 on F^2). wR (all data) = 0.1999, conventional R (4668 reflections) = 0.0556, S = 1.112, for 478 parameters. Twofold disorder was refined for four of the benzyl groups in **2**, with geometrical and displacement parameter restraints. Constrained hydrogen atoms were included in all three structures, except for the disordered groups in **2**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Extensive disorder in the benzyl groups limit the precision of this structure and makes it difficult to assess the importance of the interaction of the Li centres with C–H bonds. Such interactions have been found previously for uncomplexed solid dibenzylamidolithium, and there are numerous Li···C distances between 2.36 and 2.77 Å in **2**.[12]

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