

## Synthesis and Structural Characterisation of the Mixed Lithium–Magnesium Amide, $[\{\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{N}\}_4\text{Li}_2\text{Mg}]$ : a New Type of Magnesiate Complex Free of a Donor Solvent as Ligand

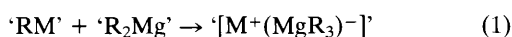
William Clegg,<sup>a</sup> Kenneth W. Henderson,<sup>b</sup> Robert E. Mulvey\*<sup>b</sup> and Paul A. O'Neil<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Newcastle, Newcastle Upon Tyne, UK NE1 7RU

<sup>b</sup> Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL

A mixture of the alkyl(amido)magnesium compound,  $[\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{NMgBu}^n]$ , the secondary amine,  $[\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{NH}]$ , and the alkyl lithium,  $(\text{Bu}^n\text{Li})$ , produces the lithium amidomagnesiate,  $[\{\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{N}\}_4\text{Li}_2\text{Mg}]$  which is shown by an X-ray diffraction study to have intramolecular (tertiary amine) N–Li coordinations in the solid state.

Considering that alkali metal magnesiate complexes have been known for over four decades<sup>1</sup> and that the reaction shown in eqn. (1) would (in theory) appear to be a general

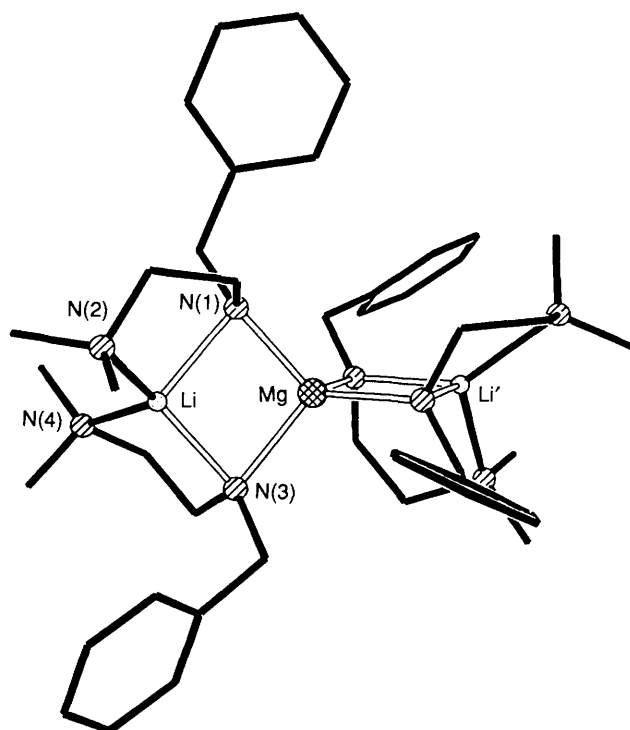


method for preparing them, a surprisingly limited number of well-characterised examples are known. Furthermore, crystallographic characterisation<sup>2</sup> is usually possible only when the ate is solvated by molecules of a donor solvent such as THF (tetrahydrofuran), TMEDA (tetramethylethylenediamine) or PMDETA (pentamethyldiethylenetriamine). Weiss and coworkers<sup>3–5</sup> have made a sterling contribution to this aspect of magnesiate chemistry. A search of the Cambridge Crystallographic Database<sup>6</sup> revealed only four categories of 'R' group (alkyl,<sup>4</sup> alkynyl,<sup>5</sup> aryl<sup>3,7</sup> and halo,<sup>8</sup> e.g. Me,  $\text{Bu}^t\text{C}\equiv\text{C}$ , Ph and Br, respectively) within the handful of reported crystal

structures. This paper describes an important extension to this series where 'R' = an amido group (derived from an amine). Mixed lithium–magnesium amide compositions could become a useful addition to the synthetic chemist's repertoire, given the importance and widespread use of (homometallic) lithium amide reagents and the enhanced reactivity reported for other magnesiate complexes.<sup>9</sup> The new compound,  $[\{\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{N}\}_4\text{Li}_2\text{Mg}]$  **1**, is also novel for another reason: though prepared in their presence, it is free of donor solvent (THF) molecules. Instead, complexation is achieved intramolecularly through the tertiary amine N centre of the chelating amido ligand.

Preparation and crystallisation of **1** were achieved by carrying out the following procedure under a protective argon atmosphere. To a chilled, stirred toluene solution of  $[\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{NMgBu}^n]$  (4 mmol), made as described previously,<sup>10</sup> was added, in order, the parent amine  $[\text{PhCH}_2(\text{Me}_2\text{NCH}_2\text{CH}_2)\text{NH}]$  (5 mmol) and  $\text{Bu}^n\text{Li}$  (5 mmol in hexane), effecting a yellow to deep-red colour change. No solid could be coaxed from this solution on standing it for two days at ca  $-20^\circ\text{C}$ . Subsequently, the solvents were removed under reduced pressure and the oily residue was then subjected to a series of different solvent systems including pentane, THF, hexane–toluene, and hexane–toluene–2,5-dimethyl-THF. A pentane–toluene mixture kept at  $50^\circ\text{C}$  for 16 h proved successful, depositing colourless, X-ray quality crystals of the title compound.<sup>†</sup>

An X-ray crystallographic study<sup>‡</sup> confirmed the 2Li:1Mg ratio indicated by microanalysis data. Fig. 1 shows the crystal structure. The centrally positioned Mg atom and both Li atoms occupy four-coordinate, distorted tetrahedral geometries. Having the greater charge, the  $\text{Mg}^{2+}$  cation attracts all four (amido) $\text{N}^-$  anions, while each  $\text{Li}^+$  cation binds to two (amido) $\text{N}^-$  anions and to two (tertiary amine) $\text{N}$  atoms. To facilitate the  $\text{MgNLi}$  heterometallic bridging, the  $\text{N}(1)\text{MgN}(3)$



**Fig. 1** Molecular structure of **1** without hydrogen atoms, and with important atoms labelled. Key dimensions: Mg–N(1) 2.067(2), Mg–N(3) 2.120(2), Li–N(1) 2.093(4), Li–N(3) 2.085(4), Li–N(2) 2.169(4), Li–N(4) 2.093(4) Å; N(1)–Mg–N(1') 115.16(9), N(1)–Mg–N(3') 115.92(6), N(1)–Mg–N(3) 97.55(6), N(3')–Mg–N(3) 115.97(8), N(3)–Li–N(4) 89.88(13), N(3)–Li–N(1) 97.85(14), N(4)–Li–N(1) 117.3(2), N(3)–Li–N(2) 142.3(2), N(4)–Li–N(2) 118.5(2), N(1)–Li–N(2) 90.71(14), Mg–N(1)–Li 82.84(10), Li–N(3)–Mg 81.77(10) $^\circ$ . Symmetry transformation to generate equivalent atoms (primed):  $-x, y, -z + \frac{1}{2}$ .

<sup>†</sup> The new amide is sensitive to moisture and to oxygen. Satisfactory analyses (C, H, Li, Mg, N) were obtained. M.p.  $180\text{--}182^\circ\text{C}$ . Yield (based on consumption of  $\text{Bu}^n\text{Li}$ ), 82%. From the reaction stoichiometry other products should exist. However, no solids other than **1** were isolated from the reaction mixture. The synthesis of **1** proved totally reproducible. A  $^1\text{H}$  NMR spectrum of **1** in  $[\text{D}_6]\text{benzene}$  solution at  $25^\circ\text{C}$  proved of little diagnostic value.

<sup>‡</sup> Crystal data for **1**:  $\text{C}_{44}\text{H}_{68}\text{Li}_2\text{MgN}_8$ ,  $M = 747.3$ , monoclinic, space group  $C2/c$ ,  $a = 14.124(2)$ ,  $b = 17.807(3)$ ,  $c = 18.096(3)$  Å;  $\beta = 93.90(2)^\circ$ ,  $U = 4540.7(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.093$  g cm<sup>-3</sup>; 3730 independent reflections were measured at 200 K on a Siemens AED2 diffractometer using graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å),  $\mu(\text{Cu-K}\alpha) = 0.62$  mm<sup>-1</sup>, with  $\omega/\theta$  scans,  $F(000) = 1624$ . Structure solution was by direct methods, refinement was by full-matrix least-squares analysis on  $F^2$  for all independent reflections.  $wR_2$  (all data) =  $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1447$ , conventional  $R$  [on  $F$  values for 2943 reflections with  $F_o^2 > 2\sigma(F_o^2)$ ] = 0.0485. The crystal was mounted under argon in a Lindemann glass capillary. Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

bond angle has to be narrow [97.55(6)° *cf.* the mean bond angle at Mg, 111.15°]. The other internal bond angles in the  $\overline{\text{MgNLiN}}$  ring are also small [at N 82.84(10)° and 81.77(10)°; at Li, 97.85(14)°, *cf.* mean at Li, 109.4°]. Two such dinuclear rings fuse through the magnesium atom. Terminal complexation of the Li atom occurs intramolecularly—a new bonding feature in alkali metal magnesiate chemistry, though it is well known in other types of lithium compound<sup>11,12</sup>—*via* the  $\text{CH}_2\text{CH}_2\text{NMe}_2$  sidearms. Steric factors affect the fit of these tertiary amine ligands as evidenced by the large disparity in the N(2)LiN(3) and N(4)LiN(1) bond angles [142.3(2) and 117.3(2)°, respectively], and in the N(2)–Li and N(4)–Li bond lengths [2.169(4) and 2.093(4) Å, respectively]. Mean (amido) N–M bond lengths, on the other hand, are very similar (2.089 Å for Li; 2.094 Å for Mg).

There is only one previous example of a crystallographically characterised lithium magnesiate having a 2Li:1Mg stoichiometry. The alkyl derivative in question,  $[\text{Me}_4\text{MgLi}_2\text{-(TMEDA)}_2]$ ,<sup>4</sup> displays similar gross structural features to **1** with the important exception that the N-donor atoms are not in-built within the anion, instead they belong to externally added TMEDA solvent molecules. Examining the structure of **1**, it is clear that the mixed metal stoichiometry is highly dependent on the chelating nature of the amido anion, for a 1Li:1Mg ratio, which was found in  $[\{(\text{Me}_3\text{Si})_3\text{C}\}(\text{THF})\text{-Mg}(\text{Br})_2\text{Li}(\text{THF})_2]$ ,<sup>8</sup> would leave one potential N-donor atom 'dangling' free.

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