The first magnesium amide trimer, magnesio-1,8-diaminonaphthalene·hexamethylphosphoramide: introducing an unprecedented cage assembly incorporating an Mg_3 unit within a N_6 trigonal prism

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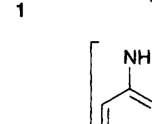
Doubly deprotonating 1,8-diaminonaphthalene with dibutylmagnesium in the presence of hmpa leads to the formation of the title compound, which establishes a new aggregation state and cage architecture within magnesium amide chemistry; the departure from classical, non-cage, organomagnesium structures can be attributed to the bifunctional and steric design of the involved 'dianion'.

Stimulated by the report of C–Mg bonded tetrameric organomagnesium cages by Bickelhaupt and coworkers,[1] we have been exploring ways of assembling N–Mg bonded cage architectures based on amide ligands (*i.e.* derived from organic amines). In general, conventional organomagnesium aggregates form ring or chain arrangements,[2] in preference to such cage structures, the like of which have long been a trademark of organolithium chemistry.[3] Recently, however, we prepared the first octahedral Mg_6 cage structure in hexameric *o*-phenylenediamidomagnesium tetrahydrofuran, **1**.[4] The controlling factor behind this cage construction is the molecular design of the anion. First, it is a bifunctional dianion. Second, the ligand backbone is entirely flat. Third, the steric requirements of its metal binding sites $[N(H)^-]$ are kept to a minimum by having small hydrogen atoms attached. Finally, its two linked anionic N centres are separated by two carbon atoms. Here, by deliberately keeping the first three of these features constant, but increasing (to three) the number of carbon atoms separating the N centres of the dianion in going from a monocyclic to a bicyclic ligand backbone, we show that a markedly different cage arrangement can be constructed. Originating from 1,8-diaminonaphthalene **2**,[5] the new complex **3**, to the best of our knowledge, represents the first *trimeric* magnesium amide. X-Ray crystallography has established its unprecedented N_6Mg_3 cage structure, the simplistic architectural design of which belies the fact that in order to achieve it Mg must surrender its usual four- coordinate, tetrahedral geometry for a five-coordinate alternative.

In a Schlenk tube filled with argon, complex **3** was synthesised from a 1 : 1 : 1 mixture of 1,8-diaminonaphthalene, dibutylmagnesium and hexamethylphosphoramide (hmpa), in tetrahydrofuran (thf) solution.† Crystallisation of **3** as its bis(thf) solvate proved straightforward, effected by simply surrounding the solution mixture with a Dewar flask containing moderately hot water, and letting it cool slowly to ambient temperature. Characteristic of magnesio or lithio aniline-type derivatives, these crystals are extremely surface sensitive (turning dark green from colourless), even when isolated in an argon-filled dry box: they completely degrade on exposure to the atmosphere.



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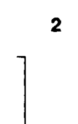

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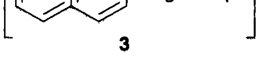

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An almost perfectly equilateral Mg_3 triangle (side lengths 2.903, 2.913, 2.916 Å; endocyclic angles, 59.7, 60.1 and 60.2°) encapsulated within, and staggered with respect to, the six N corners of a trigonal prism make up the open cage structure of **3** (Figs. 1 and 2).‡ Alternatively, the core could be viewed as a cyclical arrangement of three highly puckered four-membered $(NMg)_2$ fused rings with Mg spiro atoms. Either way, the architecture of this trimer contrasts vividly with that previously found in the trimeric *o*-xylidene species $[\{Mg(CH_2C_6H_4CH_2\text{-}o)(thf)_2\}_3]$,[6] which is based on a 15-membered metallocyclic ring (note that no magnesium amide trimer is available for

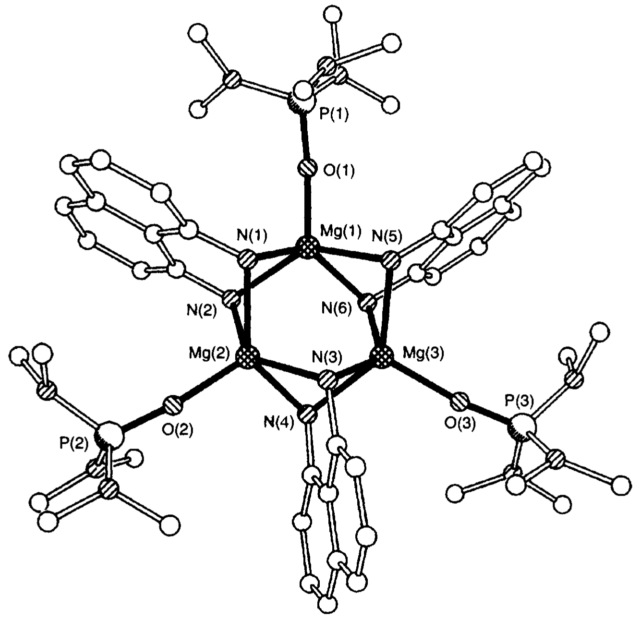

Fig. 1 Molecular structure of **3** without hydrogen atoms and thf molecules of crystallisation, showing numbering scheme for key atoms. Selected distances (Å) and angles (°): Mg(1)–O(1) 1.930(2), Mg(2)–O(2) 1.916(2), Mg(3)–O(3) 1.933(2), Mg(1)–N(1) 2.189(3), Mg(1)–N(2) 2.153(2), Mg(1)–N(5) 2.164(2), Mg(1)–N(6) 2.168(2), Mg(2)–N(1) 2.165(3), Mg(2)–N(2) 2.178(2), Mg(2)–N(3) 2.150(2), Mg(2)–N(4) 2.157(2), Mg(3)–N(3) 2.166(3), Mg(3)–N(4) 2.168(3), Mg(3)–N(5) 2.153(3), Mg(3)–N(6) 2.150(2), O(1)–P(1) 1.494(2), O(2)–P(2) 1.483(2), O(3)–P(3) 1.489(2); O–Mg–N 107.17(10)–115.56(10), N–Mg–N (same ligand) 73.54(9)–74.77(9), N–Mg–N (different ligands, *cis*) 88.31(9)–91.07(9), N–Mg–N (*trans*) 135.84(10)–137.61(10), Mg–N– Mg 83.62(9)–84.96(9), Mg(1)–O(1)–P(1) 151.2(2), Mg(2)–O(2)– P(2) 171.0(2), Mg(3)–O(3)–P(3) 167.5(2).

comparison, though the monomeric, trinuclear structure of $[MeSi\{Bu^tNMgN(SiMe_3)_2\}_3]$,[7] derived from a triaminosilane, exhibits a tricyclic SiN_3Mg_3 skeleton). Binding to an N_4 rectangular base made up of two short intra-ligand contacts (mean length, 2.61 Å) and two long inter-ligand contacts (mean length, 3.06 Å), and capped by an apical O atom, the Mg centres in **3** occupy a five-coordinate, (distorted) square-based pyramidal geometry. In this respect there is parity with the structure of **1**;[4] however, one feature setting the two structures apart is the bonding mode of the bifunctional ligands, as each intraligand N–N unit bridges two Mg centres in **3**, compared with three in **1**. Individually, the N atoms in **3** are four-coordinate (in a pseudo-tetrahedral geometry) bonding to two Mg atoms, one *ipso*-C atom and one H atom. Hmpa ligands complete the molecular structure, though there are also two thf molecules of crystallisation present (per trimer) in the extended lattice structure.

Covering a narrow range (2.150–2.189 Å), the N–Mg bond lengths in **3** have a mean value (2.163 Å) very close to that in **1** (2.152 Å) reflecting the coordinative equivalency of the like atoms involved. Significantly, the hmpa molecules in **3** approach the Mg centres more closely (mean O–Mg bond length, 1.926 Å) than the thf molecules in **1** (corresponding length, 2.091 Å); this, combined with the fact that hmpa is more sterically demanding because of its branched tail, could be a contributory factor in the reduced aggregation of **3** compared with **1**. This will also be strongly influenced by the greater size of the naphthalene ring compared with the phenyl ring. In this regard, the number of C centres separating the N centres is of less significance, as the N···N separation distances in **3** (mean, 2.61 Å) are shorter than those in **1** (mean, 2.71 Å), corresponding to the difference between 1,3 and 1,4 distances in a planar six-membered ring. Turning to bond angles, four distinct categories exist at the metal centre: most significantly, where the ligand chelates in a η^2-fashion, *e.g.* N(1)–Mg(1)–N(2), mean value, 74.2°; those made with edges within the trigonal faces of the N_6 prism, *e.g.* N(1)–Mg(1)–N(5), 90.1°; those made with diagonal pairs within rectangular faces of the N_6 prism, *e.g.* N(1)–Mg(2)–N(4), mean value, 136.8°; and those involving O atoms, *e.g.* N(1)–Mg(1)–O(1), mean value 111.6°. More dimensions are listed in the figure legend.

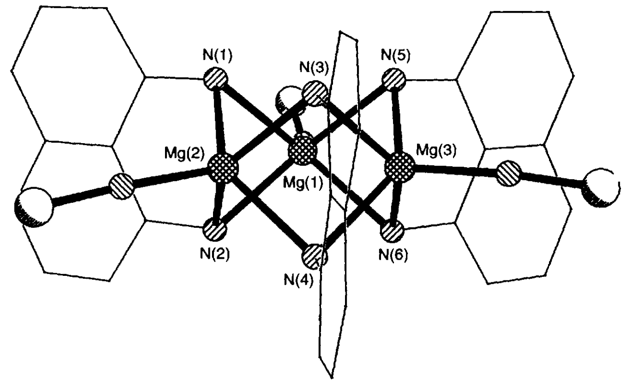

Fig. 2 Alternative view of the structure highlighting the N_6Mg_3 cage arrangement. For clarity, the hmpa NMe_2 groups have been omitted and the naphthalene ring C atoms have been reduced in size.

In conclusion, a new cage architecture has been developed in magnesium amide chemistry by metallating a diamine substrate with specific, in-built design features, the most important of which are the primary NH_2 functions and the planar, bicyclic backbone.

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Footnotes

† Yield (first batch, not optimised), 38%; mp > 300 °C. ^1H NMR spectrum (400 MHz, $[^2H_5]$pyridine) δ 1.64 (m, CH_2, thf), 2.05 (d, CH_3, hmpa), 3.67(m, CH_2O, thf), 6.29 (d, CH), 6.90 (d, CH), 7.03 (t, CH). Integrals match formula established by X-ray crystallographic study. Satisfactory analytical data were obtained.

‡ *Crystal data for* **3**·2thf: $C_{48}H_{78}Mg_3N_{15}O_3P_3\cdot 2C_4H_8O$, $M_r = 1223.3$, triclinic, space group $P\bar{1}$, $a = 14.4134(8)$, $b = 14.7158(8)$, $c = 15.7422(9)$ Å, $\alpha = 86.9910(10)$, $\beta = 87.7990(10)$, $\gamma = 78.2800(10)°$, $U = 3263.6(3)$ Å^3, $Z = 2$, $D_c = 1.245$ g cm^{-3}, $\mu = 0.18$mm^{-1} for Mo-Kα radiation ($\lambda = 0.71073$ Å), $F(000) = 1312$, $T = 160$K. 17328 reflections measured on a Siemens SMART CCD area detector diffractometer yielded 11374 unique data ($R_{int} = 0.038$) for structure solution (by direct methods) and refinement (full-matrix least squares on F^2 with statistical weights, anisotropic displacement parameters, riding isotropic H atoms, and restraints on geometry and displacement parameters of thf molecules); $R^1 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.165$ for all reflections, conventional $R = 0.057$ on F values of 9476 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.04 for all F^2 values, 757 parameters and 106 restraints. All features in a final difference synthesis were within ±0.8 e Å^{-3}. Programs: Siemens SMART, SAINT and SHELXTL and local programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/141.

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