Synthesis and X-Ray Crystallographic Characterisation of *o*-Phenylenediamidomagnesium·Tetrahydrofuran: The First Octahedral Mg_6 Cluster

William Clegg,[a] Michael Frank,†[b] Robert E. Mulvey*[b] and Paul A. O'Neil[a]

[a] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL*

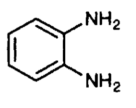
Crystals of *o*-phenylenediamidomagnesium·tetrahydrofuran, prepared at the interface of a *sec*-butyl-*n*-butyl magnesium in heptane–*o*-phenylenediamine in THF bilayered solution, have been shown by an X-ray diffraction study to consist of unprecedented, discrete octahedral Mg_6 clusters, held in place by six bridging, divalent, *N*-bonding ligands, and solvated by THF molecules to give the Mg atoms a five-coordinate, square-based pyramidal geometry overall.

Dominated as it is by four-coordinate, pseudotetrahedral metal environments in monomeric, dimeric or polymeric arrangements, solid-state organomagnesium chemistry appears rather banal and largely predictable against the seemingly unabating novelty found in organolithium structural chemistry.[1,2] A strong hint that organomagnesium structural chemistry has potentially much more variety to offer was recently provided by Bickelhaupt *et al.*[3,4] Determining the crystal structures of three cyclic bifunctional organomagnesium·THF complexes, naphthalene-1,8-diylmagnesium, *o*-phenylenemagnesium and *cis*-diphenylvinylenemagnesium, they established for the first time the existence of tetrameric clusters with C–Mg bonded cores. Common to them all is a distorted tetrahedron of four Mg atoms with one organic group occupying each of its faces. Prior to the establishment of this series of tetramers, organomagnesium cluster chemistry was limited to two miscellaneous structures, each containing two very different ligand types. The more straightforward of the two compounds, the mixed cyclopentadienylide-alcoholate, $(\eta^5\text{-}C_5H_5)MgOEt$,[5] is based on an $(O\text{–}Mg)_4$ heterocubane. On the other hand, the mixed amido–nitrido quasi-organometallic species, $[(Bu^tNH)_9(N)Mg_6]$,[6] exhibits a rather odd 16-vertex N–Mg bonded polyhedron with a near-perfect trigonal prismatic disposition of Mg atoms. Our interest in this cluster theme stems from a continuing synthetic and structural investigation of organoamidomagnesium compounds[7] which, as reported herein, has uncovered a new type of Mg cluster in the *o*-phenylenediamine **1** derivative, *o*-phenylenediamidomagnesium·tetrahydrofuran **2**. In contrast to the aforementioned tetrahedral Mg_4-based clusters, this one is built up of a (distorted) Mg_6 octahedron, interpenetrated with a (distorted) N_{12} cuboctahedron constructed from six divalent, bifunctional $o\text{-}C_6H_4[N(H)^-]_2$ bridges. Whilst unique in Mg organic or organoelement chemistry, in terms of the numbers of and positions of its anionic centres (N^-) and cations, this structure bears some resemblance to classical 18-vertex clusters like $Nb_6Cl_{12}{}^{2+}$ found in certain halides of lower-valent niobium and tantalum,[8] with the important distinction that it lacks metal–metal bonds.

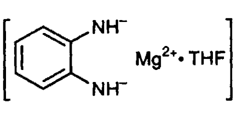
$$\mathrm{Bu^nBu^sMg} + \underset{\mathbf{1}}{o\text{-}\mathrm{C_6H_4(NH_2)_2}} \xrightarrow[-2\,\mathrm{BuH}]{\text{THF–heptane}} \underset{\mathbf{2}}{[o\text{-}\mathrm{C_6H_4(NH)_2}]\mathrm{Mg\cdot THF}} \qquad (1)$$

Double deprotonation of the parent diamine **1** by action of an equimolar amount of the base, *sec*-butyl-*n*-butyl magnesium [eqn. (1)], was relatively easy to achieve under stringently dry and oxygen-free conditions. However, growing X-ray quality crystals of the Mg product proved much more difficult. Simply mixing and stirring the reactants in a heptane–THF solution always gave an essentially insoluble microcrystalline precipitate.‡ A two-layer reaction performed without stirring proved more successful. Taking care to minimise agitation, this involved addition of a Bu^sBu^nMg–heptane solution (the top layer) to a diamine **1**–THF solution (the bottom layer), whereupon a narrow zone of intermixing of the two solutions occurred. Crystals formed at the interface of the two layers, growing in the direction of the bottom layer. After 18 h, the reaction was stopped, both layers were syringed off, and the crystals isolated. Studied initially by both IR and ^1H NMR spectroscopy,§ their identity as the new cluster **2** was only definitely established by a subsequent X-ray diffraction study.¶

Fig. 1 shows the full molecular structure of **2**, while Fig. 2 picks out its inorganic $Mg_6N_{12}O_6$ core. The octahedral Mg_6



1



2

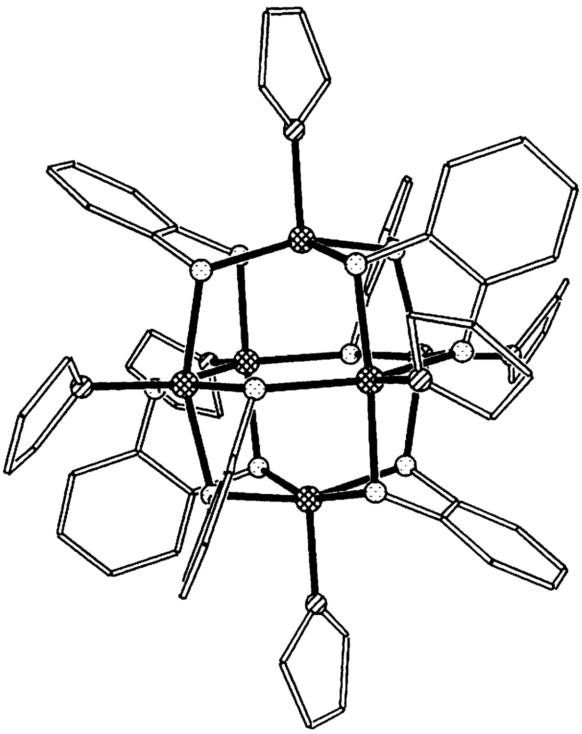


Fig. 1 Molecular structure of **2**, without hydrogen atoms. Key dimensions: (see Fig. 2 for numbering): Mg(1)–N(1) 2.138(7), Mg(1)–N(3) 2.165(7), Mg(1)–N(4) 2.146(7), Mg(1)–N(6′) 2.155(7), Mg(2)–N(2) 2.174(7), Mg(2)–N(4) 2.131(7), Mg(2)–N(5) 2.145(7), Mg(2)–N(6) 2.160(7), Mg(3)–N(1) 2.156(7), Mg(3)–N(2) 2.148(7), Mg(3)–N(3′) 2.165(7), Mg(3)–N(5′) 2.139(7) Å; N(1)–Mg(1)–N(3) 159.3(3), N(1)–Mg(1)–N(4) 93.8(3), N(1)–Mg(1)–N(6′) 92.3(3), N(3)–Mg(1)–N(4) 77.7(3), N(3)–Mg(1)–N(6′) 89.3(3), N(4)–Mg(1)–N(6′) 157.9(3), N(2)–Mg(2)–N(4) 92.4(3), N(2)–Mg(2)–N(5) 158.2(3), N(2)–Mg(2)–N(6) 89.8(3), N(4)–Mg(2)–N(5) 93.2(3), N(4)–Mg(2)–N(6) 158.3 (3), N(5)–Mg(2)–N(6) 77.5(3), N(1)–Mg(3)–N(2) 77.3(3), N(1)–Mg(3)–N(3′) 158.3(3), N(1)–Mg(3)–N(5′) 94.6(3), N(2)–Mg(3)–N(3′) 89.5(3), N(2)–Mg(3)–N(5′) 159.3(3), N(3′)–Mg(3)–N(5′) 91.9(3)°. Symmetry transformation to generate equivalent atoms (primed): $-x$, $-y+1$, $-z+1$.

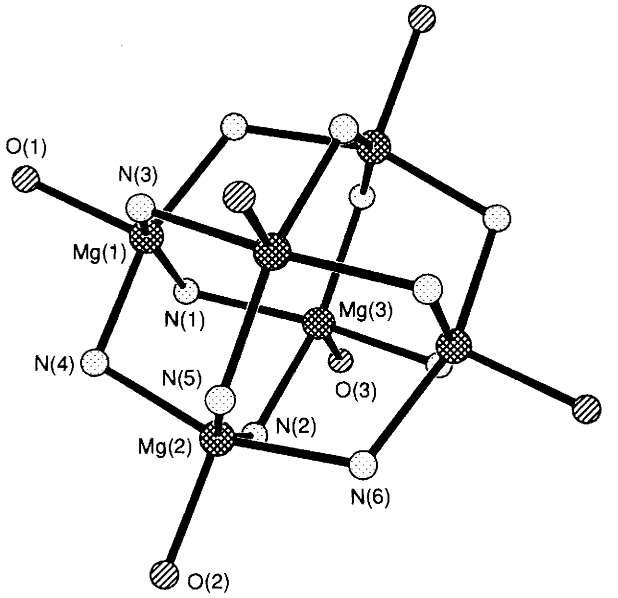


Fig. 2 View showing the inorganic $Mg_6N_{12}O_6$ central core and the atom-labelling scheme for the independent atoms

substructure, clearly visible in both, significantly deviates from an ideal octahedron as gauged by the $Mg\cdots Mg$ separation distances (each Mg forms two short and two long contacts, mean lengths 3.382 and 3.639 Å respectively, to its four nearest neighbours) and the MgMgMg angles in the eight triangular faces (range, 57.3–65.2°). Individually the Mg atoms occupy five-coordinate, (distorted) square-based pyramidal sites being surrounded by a N_4 basal plane and an apical O atom. The extent of the distortion can be judged by the fact that the Mg atom sits 0.37–0.38 Å out of the mean plane of its four bonded N atoms, which shows an rms deviation of 0.003–0.011 Å. Each diamido ligand acts simultaneously as a didentate source to one Mg atom [*e.g.* $\overline{\mathrm{N(1)}\,\mathrm{N(2)}}$ to Mg(3)] and as a monodentate source to two other Mg atoms [*e.g.* N(1) to Mg(1); N(2) to Mg(2)]. These three metal atoms lie well out of the *o*-$C_6H_4N_2$ plane, with the distinct chelated one being situated on the opposite side to the pair of Mg atoms. Including the additional bond to the remaining H atom, each sp^3-hybridised N atom displays a four-coordinate, (distorted) tetrahedral geometry. Only small variations are observed in the N–Mg interatomic distances [range, 2.131(7)–2.174(7) Å; mean, 2.152 Å]. Considerably shorter N–Mg bond lengths are found in the related, but silylated, *o*-phenylenediamidomagnesium–ether compound $[\{[o\text{-}(Me_3Si)NC_6H_4(SiMe_3)N]Mg\cdot(OEt_2)\}_2]$[9] [(sp^2)N–Mg, 1.997(7); (sp^3)N–Mg, 2.082(7) Å], owing to its lower Mg and dinitrogen ligand coordination numbers [Mg 4 (3 N, 1 O) and ligand 6 (2 C, 2 Mg, 2 Si), *cf.* in **2**: Mg 5 (4 N, 1 O) and ligand 7 (2 C, 2 H, 3 Mg)]. Replacement of a H atom by an Me_3Si branch at both N sites, and solvating with ether instead of THF, increases the steric bulk sufficiently to prevent cluster growth in this case and so association is limited to a dimeric, laterally-organised arrangement. Projecting radially from the octahedral cluster, THF ligands complete the square-based pyramidal coordinations of the Mg atoms in **2** (mean O–Mg bond length, 2.091 Å). In addition, the crystal structure of **2** contains two THF molecules of crystallisation per Mg_6 cluster.

Preference for this larger, more open hexameric cluster over the tetrameric alternative found in the previously discussed C–Mg compounds,[3,4] may be primarily linked to the number of atoms between the anionic centres of the dianionic ligands. In the $\overline{C^-\,C^-}$ examples, there are no atoms or only one atom between the C^- anions, whereas in **2**, two atoms separate the pair of N^- anions. Hence the $N^-\cdots N^-$ distances (mean, 2.696 Å) are substantially longer than the $C^-\cdots C^-$ ones (*e.g.* 1.418 Å in the *o*-phenylenemagnesium tetramer[4]) and so more space is required to accommodate the nitrogen ligand. The greater polarity of the N–Mg bonds with respect to the C–Mg counterparts may also influence the change to the higher aggregation state.

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Footnotes

† Participating in the ECTS-Pilot-Scheme of the EC-Erasmus-Programme. Resident university: Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

‡ Doubts remain as to whether this powder is compound **2** or another compound of a similar composition. From its IR spectrum it appears to be **2** but further investigations are underway in order to check this possibility.

§ The IR spectrum was taken as a Nujol mull. The bands of the symmetrical and antisymmetrical NH stretches of the amino groups of **1** (at 3383/3360 cm^{-1} and at 3292/3169 cm^{-1}, respectively) as well as their deformation band at 1629 cm^{-1} are missing in the spectrum of **2** but appear after exposure to air, as also does the band of $Mg(OH)_2$ (at 3697 cm^{-1}), which clearly establishes that metallation of **1** has occurred. In spite of the very poor solubility of **2**, we managed to do preliminary ^1H NMR studies (400 MHz, C_6D_6). The spectrum shows four multiplets between δ 6.75 and 6.10 with the typical coupling pattern of an unsymmetrically 1,2-substituted benzene system and this is consistent with the crystal structure of **2** which shows two distinct types of octahedral face, though this is not obvious from Fig. 1. The protons of the NH^- groups appear as two singlets at δ 2.54 and 2.04. The tetrahydrofuran ligands give strong signals at δ 3.58 and 1.41. Satisfactory analyses (C, H, Mg, N) were obtained.

¶ *Crystal Data* for **2**: $C_{60}H_{84}Mg_6N_{12}O_6\cdot 2C_4H_8O$, M = 1359.4, monoclinic, $P2_1/n$, $a = 12.469(4)$, $b = 21.292(8)$, $c = 13.580(4)$ Å; $\beta = 96.26(3)°$; $U = 3584(2)$ Å^3, $Z = 2$, $D_c = 1.258$ g cm^{-3}, $F(000) = 1452$; 4675 independent reflections were measured at 200 K on a Stoe-Siemens diffractometer using graphite-monochromated Mo-Kα radiation [$\lambda = 0.71073$ Å, μ(Mo-Kα) = 0.13 mm^{-1}], with ω–θ scans. Structure solution was by direct methods, refinement was by full-matrix least-squares analysis on F^2 for all independent reflections, with some restraints on disordered THF ligands. $wR2$ (all data) = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.2838$, conventional R [on F values for 2181 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0724. 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.

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