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Synthesis, Structure, and Computational Studies of the Tetrameric Magnesium Imides $[2,4,6\text{-}Cl_3C_6H_2NMg\cdot S]_4$ (S = 1,4-Dioxane and Tetrahydrofuran)

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The magnesium imide complexes $[(ArNMg\cdot diox)_4\cdot 3(diox)]$ (**4**) and $[(ArNMg\cdot THF)_4\cdot tol]$ (**5**) (where Ar = 2,4,6-$Cl_3C_6H_2$, diox = 1,4-dioxane, and THF = tetrahydrofuran) were prepared by the equimolar reaction of Bu_2Mg with the primary amine in suitable solvent mixtures. The successful synthesis of the halide-substituted imides is notable because similar reactions with the less acidic organo-substituted anilines cease upon monodeprotonation. Both **4** and **5** form unusual Mg_4N_4 cubane aggregates in the solid state. Computational studies (HF/6-31G*) indicate that a combination of sterics and metal solvation determines the aggregation state adopted.

Metal imides are well-known to form a wide variety of aggregated structures in the solid state.[1] In comparison, only three homoleptic magnesium imides have been reported.[2] Power and co-workers prepared the complexes $[(PhNMg\cdot THF)_6]$ (**1**), $[\{(1\text{-naphthyl})NMg\cdot THF\}_6\cdot 2.25THF]$ (**2**), and $[\{(1\text{-naphthyl})NMg\cdot HMPA\}_6\cdot 2tol]$ (**3**) (where THF = tetrahydrofuran and tol = toluene) through the reaction of Bu_2Mg with either aniline or 1-naphthylamine in the appropriate donor solvent.[3−5] All three complexes adopt similar prismatic hexameric arrangements in the solid state. To date, attempts to extend this class of materials have been frustrating because of inhibition of the alkyl(amido), $R_2N(H)MgR'$, or bis(amido), $[R_2N(H)]_2Mg$, intermediates toward further deprotonation.[6] This has proved to be the case both for primary alkylamines and also for 2,6-organo-substituted anilines.[6]

Our interest in magnesium imides originated in their possible use as preassembled secondary building units to rationally construct extended frameworks.[7] Recently, we have demonstrated that divergent donor solvents may be used to link specific alkali-metal aryloxide aggregates to form coordination polymers.[8] Magnesium imides are attractive candidates for this purpose because their strong Mg−N bonding should minimize troublesome dynamic solution behavior between competing aggregation states.[9] Also, each metal in the known complexes **1**−**3** is singly solvated, allowing the possibility of replacement by a divergent base.

Initial efforts to prepare crystalline polymers using aniline or 1-naphthylamine with 1,4-dioxane as a linker produced insoluble powders or microcrystalline materials. We also reexplored the use of various alkyl-substituted anilines as substrates and confirmed that only primary amide derivatives were formed.[6,10] We then considered that it may be possible to drive imide formation through the use of more acidic anilines. In particular, 2,4,6-trichloroaniline was targeted because it is more acidic than alkyl-substituted anilines by ~5−6 pK_a units.[11]

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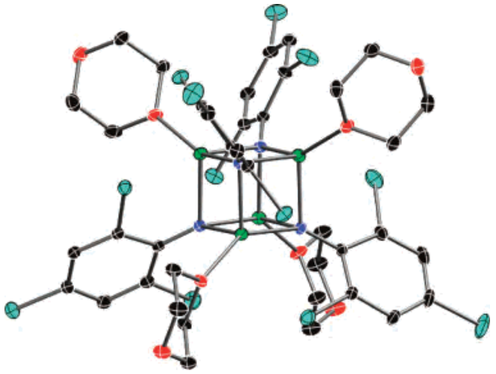
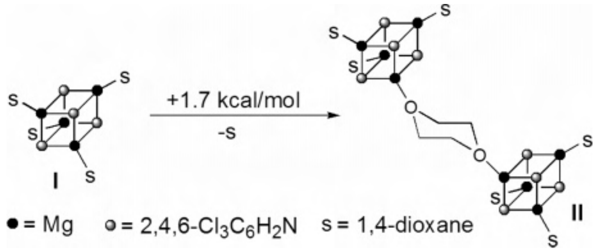


Figure 1. Molecular structure of tetrameric **4**, with H atoms and lattice solvent molecules omitted for clarity. Color code: Mg, green; C, black; N, blue; Cl, teal.

The reaction of Bu_2Mg with the primary amine in 1,4-dioxane resulted in precipitation of a white solid after the mixture was maintained at reflux for 1 h.[12] The solid was completely dissolved upon dilution by 1,4-dioxane, and slow cooling afforded high-quality crystals. NMR analyses in pyridine-d_5 indicated the presence of the aromatic unit and the absence of the amide, N(H), signal, suggestive of successful imide formation. In turn, single-crystal X-ray diffraction analyses (Figure 1) revealed the magnesium imide complex [$(ArNMg{\cdot}diox)_4{\cdot}3(diox)$] (**4**; where Ar = 2,4,6-$Cl_3C_6H_2$).[13] Subsequently, the isostructural solvate [$(ArNMg{\cdot}THF)_4{\cdot}tol$] (**5**) was prepared by a similar reaction carried out at ambient temperature, followed by replacement of the solvent in vacuo with tol and THF (Figure S1 in the Supporting Information).[14,15] Hence, imide formation is a facile process using the halide-substituted aniline.

Scheme 1. Relative Energies (HF/6-31G*) of Terminally Solvated and Singly Bridged Cubanes



Both complexes adopt unusual Mg_4N_4 cubane aggregates, with each metal being singly solvated by either diox or THF. Indeed, the Mg_4N_4 cubane arrangement is extremely rare in general, with the only other reported example being the phosphoraneiminato complex [$Me_3PNMgBr]_4$.[16,17] The average Mg−N distances of 2.085(2) Å for **4** [range 2.032(2)−2.131(2) Å] and 2.094(2) Å for **5** [range 2.048(2)−2.158(2) Å] are marginally longer than those of hexamers **1**−**3**, at 2.061, 2.064, and 2.079 Å, respectively (ranges 2.000−2.113, 2.023−2.106, and 2.057−2.115 Å). Also, the average Mg−O distances of 2.061(2) and 2.057(2) Å within **4** and **5**, respectively, are also noticeably longer than those of 2.028, 2.019, and 1.963 Å found in **1**−**3**, respectively. The internal N−Mg−N and Mg−N−Mg bond angles in **4** and **5** deviate only slightly from an ideal cubane, lying within the narrow ranges of 87.50(9)−92.49(1)° for **4** and 86.41(9)−93.15(9)° for **5** (with the more acute angles being associated with the N centers). The mean N−C distance in aniline is 1.392 Å, compared with those in **1**−**5** at 1.386, 1.368, 1.383, 1.332, and 1.335 Å, respectively.[18] The short distances found in **4** and **5** indicate that there is substantial back-donation of the charge into the aromatic systems of these molecules.

The formation of a molecular complex for the 1,4-dioxane solvate **4** contrasts with that of the closely related polymeric alkali-metal aryloxide systems.[8] We have previously shown through computation studies that bridging $Li_4(OPh)_4$ cubanes by 1,4-dioxane is thermoneutral and that polymerization is likely driven by entropic effects.[8a] However, an analogous study (HF/6-31G*) on the magnesium imide systems **I** and **II** indicates that bridging two cubanes by 1,4-dioxane is disfavored by ~1.7 kcal/mol (Scheme 1).[19] This is presumably a consequence of interaggregate repulsions, and the

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[12] Synthesis of **4**: 2,4,6-trichloroaniline (0.39g, 2 mmol) was dissolved in a solution of 1,4-dioxane (7 mL). Bu_2Mg (2 mmol of a 1.0 M solution in heptane) was added dropwise to the mixture. The reaction was heated to reflux for 1 h until a white precipitate appeared, which was subsequently solubilized upon further addition of 1,4-dioxane. The hot solution was allowed to slowly cool in a hot water bath to afford a batch of clear, colorless, crystals of **4**. Yield: 0.4284 g, 65%. Elemental analysis proved problematic due to decomposition and loss of solvent. ^1H NMR (300 MHz, pyridine-d_5): δ 7.15 (s, 2H, Ar−H), 3.64 (s, 26H, OCH_2, 1,4-dioxane). ^{13}C NMR (300 MHz, pyridine-d_5): δ 157.48 (*i*-ArC−N), 127.36 (*p*-ArC−Cl), 126.33 (*m*-ArC−H), 108.50 (*o*-ArC−Cl), 67.20 (O−CH_2, 1,4-dioxane).

[13] Crystal data for **4**: $C_{52}H_{64}Cl_{12}Mg_4N_4O_{14}$, a colorless plate of approximate dimensions 0.39 × 0.23 × 0.22 mm crystallized in the triclinic space group $P\bar{1}$, $a = 13.922(3)$ Å, $b = 15.111(3)$ Å, $c = 17.506(4)$ Å, $\alpha = 67.57(3)°$, $\beta = 81.47(3)°$, $\gamma = 73.71(3)°$, $V = 3264.0(11)$ Å^3, $Z = 2$, $T = 100$ K, $\rho_{calc} = 1.513$ Mg/m^3, λ(Mo Ka) = 0.710 73 Å. The structure was solved and refined on F^2 to convergence using *SHELXTL*. R1 = 0.0482 and wR2 = 0.1418. Highest residual electron density 1.741 e/Å^3, located 0.16 Å from C7s, which represents possible unmodeled disorder of the solvent. H atoms were placed in their calculated positions and allowed to ride the position of the parent atom.

[14] Synthesis of **5**: 2,4,6-Trichloroaniline (0.39 g, 2 mmol) was dissolved in 1,4-dioxane (5 mL). Bu_2Mg (2 mmol of a 1.0 M solution in heptane) was added dropwise to the mixture. The reaction was allowed to stir at ambient temperature for a period of 2 h, after which the solvent was removed in vacuo to leave a white precipitate. The precipitate was solubilized in a mixture of hot toluene/THF (~3:1) and allowed to slowly cool in a hot water bath. This method afforded high-quality, colorless, crystals of **5**. Yield: 0.323 g, 52%. ^1H NMR (300 MHz, pyridine-d_5): δ 7.2−7.4 (br, Ar−H, toluene), 7.15 (s, 2H, Ar−H), 3.65 (m, 5.6H, OCH_2, THF), 2.23 (s, 3H, CH_3, toluene), 1.62 (m, 5.6H, CH_2, THF). ^{13}C NMR (300 MHz, pyridine-d_5): δ 157.48 (*i*-ArC−N), 127.36 (*p*-ArC−Cl), 126.33 (*m*-ArC−H), 108.50 (*o*-ArC−Cl), 67.92 (O−CH_2, THF), 25.89 (CH_2, THF).

[15] Crystal data for **5**: $C_{47}H_{48}Cl_{12}Mg_4N_4O_4$; a colorless block of approximate dimensions 0.27 × 0.25 × 0.24 mm crystallized in the monoclinic space group $P2_1/n$, $a = 16.3454(2)$ Å, $b = 12.8441(2)$ Å, $c = 25.5481(4)$ Å, $\beta = 94.438(1)°$, $V = 5347.47(13)$ Å^3, $Z = 4$, $T = 100$ K, $\rho_{calc} = 1.560$ Mg/m^3, λ(Cu Ka) = 1.541 78 Å. The structure was solved and refined on F^2 to convergence using the *SHELXTL* package. R1 = 0.0357 and wR2 = 0.0862. Highest residual electron density 1.171 e/Å^3 located 1.2 Å from H40b, which represents possible unmodeled disorder of C39. H atoms were placed in their calculated positions and allowed to ride the position of the parent atom.

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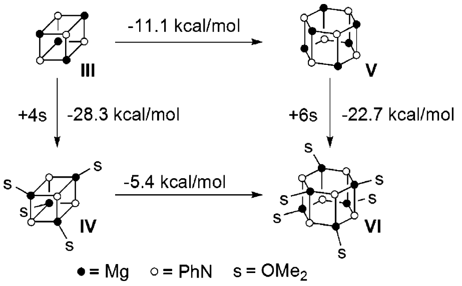
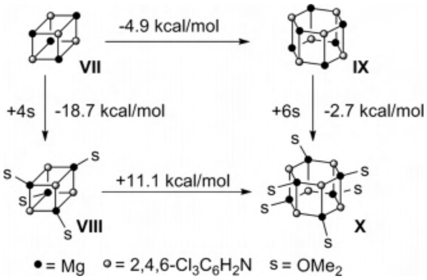
Scheme 2. Relative Energies (HF/6-31G*) of Geometry-Optimized PhNMg Cubic Tetramers and Prismatic Hexamers[a]



[a] Values are normalized to a per monomer basis.

Scheme 3. Relative Energies (HF/6-31G*) of Geometry-Optimized 2,4,6-$Cl_3C_6H_2$NMg Cubic Tetramers and Prismatic Hexamers[a]



[a] Values are normalized to a per monomer basis.

cumulative energetic penalty of multiple bridging may inhibit polymer formation.

A computational study proved helpful in evaluating the influences of ligand substitution and Lewis base solvation on the relative stabilities of the tetrameric and hexameric aggregates.

A summary of the results for the unsubstituted anilides **III**−**VI** is shown in Scheme 2. Hexameric aggregation is strongly favored (−11.1 kcal/mol) over the tetrameric alternative for the unsolvated complexes **III** and **V**. Similarly, the hexamer is again favored upon solvation of the metal centers by dimethoxy ether but to a lesser degree (−5.4 kcal/mol). The preference for the increased aggregation is due to a more isotropic distribution of the electron density around the metals.[20] Also, the difference of 5.6 kcal/mol between the solvation energies of the tetramer and hexamer may be explained by the increased steric hindrance within the larger aggregate. In any event, the fully solvated hexamer **VI** is clearly the most stable structure, in agreement with the experimentally observed formation of **1**.

Analogous calculations on the 2,4,6-$Cl_3C_6H_2$NMg systems **VII**−**X** showed distinctly different behavior (Scheme 3). The unsolvated hexamer **IX** is again preferred over the tetramer **VII** but now by only −4.9 kcal/mol. This reduction in the aggregation energy is a result of the increased steric encumbrance of the substituted anilide. Solvation of the tetramer is strongly favored (−18.7 kcal/mol), whereas the energy gain from solvation of the hexamer is dramatically reduced (−2.7 kcal/mol). The large difference in the solvation energies is caused by the increased steric crowding around the metal centers of the larger aggregate. The solvated tetramer **VIII** is now the most stable structure, as was found experimentally for **4** and **5**. Therefore, solvation is a critical element in determining the aggregation state adopted for the magnesium imides.

A final set of calculations were completed for the methyl-substituted systems 2,4,6-$Me_3C_6H_2$NMg **XI**−**XIV**. The trends in the relative stabilities mirror those found for the chloro-substituted derivatives, with the solvated tetramer being stabilized by 5.8 kcal/mol over the solvated hexamer. These calculations indicate that sterics rather than electronics are the dominate factor in the preference for tetrameric aggregation.[21]

Analysis of the metrical parameters within the calculated structures supports the above views. In particular, the average Mg−N and Mg−O distances are instructive. For the unsolvated and solvated PhNMg complexes **III**−**VI**, the average Mg−N distances are similar at 2.058, 2.060, 2.081, and 2.084 Å, respectively. The Mg−O distances increase slightly from 2.073 to 2.121 Å from tetramer **IV** to hexamer **VI**. In this case, the aggregation energy offsets the weaker solvation. The average Mg−N distances in the four 2,4,6-$Cl_3C_6H_2$NMg systems **VII**−**X** are noticeably different at 2.073, 2.076, 2.111, and 2.158 Å, respectively. Also, the average Mg−O distances are 2.130 and 2.217 Å for tetramer **VIII** and hexamer **X**. From these values, it can be seen that both the Mg−N and Mg−O bonding is significantly weakened in the solvated hexamer **X**, leading to the thermodynamic preference for tetramer **VIII**. In addition, the combination of chloro substitution and solvation leads to the lengthening of the Mg−N distances. These data parallel the experimentally derived comparisons of bond lengths in **4** and **5** with those in **1**−**3**.

In conclusion, our studies suggest that a wide range of magnesium imides may be accessible through the judicious choice use of appropriately acidic primary amine substrates. It is likely that further investigations will reveal a rich coordination chemistry for magnesium and also potentially for other alkaline-earth metal imides.

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Supporting Information Available: Crystallographic data for **4** and **5** in CIF format, details of the calculations, and the complete list of authors for ref 20. This material is available free of charge via the Internet at http:/pubs.acs.org.

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