

# Encapsulation of a Magnesium Hydroxide Cubane by a Bowl-Shaped Polypyrrolic Schiff Base Macrocycle

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**S** Supporting Information

**ABSTRACT:** Hydrolysis of a Pacman-shaped binuclear magnesium complex of a polypyrrolic Schiff base macrocycle results in the formation of a new magnesium hydroxide cubane that is encapsulated by the macrocyclic framework through both coordinative and hydrogen-bonding interactions.

Molecular capsules present unique microenvironments for guest molecules and can be formed through spontaneous assembly processes.<sup>1</sup> For example, naturally curved building blocks such as glycourils, resorcinarenes, and cyclotrimeratrylenes that incorporate complementary recognition groups engender capsule formation through supramolecular interactions.<sup>2</sup> Alternatively, metallocenes allied with organic ligand spacers allow the construction, through metal–ligand bond formation, of well-defined nanoscale cavities based on Platonic and Archimedean polyhedra.<sup>3</sup> These enzyme-like environments facilitate a myriad of unusual chemical transformations and catalysis<sup>4</sup> and, significantly, can be used to pacify normally reactive materials such as white phosphorus or stabilize reactive intermediates and unstable species through cavity confinement.<sup>5</sup> Thus, the design of new frameworks that promote the formation of encapsulating environments is a burgeoning area of research.

We have extensively described the metalation chemistry of the Schiff base polypyrrolic macrocycle H<sub>4</sub>L.<sup>6,7</sup> In most cases, wedged-shaped complexes with “Pacman”-like structures are formed (Chart 1), providing unique molecular cleft environments for chemical reactions such as oxygen-reduction catalysis and uranyl reduction.<sup>8</sup> However, if the pyrrole nitrogens remain protonated, a different class of bowl-shaped binuclear complex is formed in which the pyrrole hydrogens participate in hydrogen bonding to the ancillary ligands.<sup>9,10</sup> In this work, we describe a Pacman-to-bowl geometry transformation due to hydrolysis that results in the formation of a new magnesium hydroxide cubane that is encapsulated by two bowl-shaped macrocyclic ligands through both supramolecular interactions and metal–ligand bond formation.

The reaction between Bu<sub>2</sub>Mg and H<sub>4</sub>L in THF resulted in the clean formation of the binuclear THF-solvated magnesium complex [Mg<sub>2</sub>(THF)<sub>2</sub>(L)] (**1**·THF) in excellent yield. The electron impact (EI) mass spectrum of **1**·THF displayed a peak at *m/z* 760 for the molecular ion, and the <sup>1</sup>H NMR spectrum (Figure S1 in the Supporting Information) showed the disappearance of the NH resonance of H<sub>4</sub>L and a shift of the imine resonance from 8.30 ppm in H<sub>4</sub>L to 7.71 ppm in **1**·THF. Two sets of resonances at 2.15/2.06 and 1.13/1.05 ppm for

the CH<sub>2</sub> and CH<sub>3</sub> protons, respectively, of the *meso*-ethyl substituents were seen, showing that a wedged, Pacman structure with dissimilar *endo*- and *exo*-ethyl substituents was present in solution. A similar reaction between Bu<sub>2</sub>Mg and H<sub>4</sub>L carried out in Et<sub>2</sub>O resulted in the formation of the Et<sub>2</sub>O-solvated complex [Mg<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>(L)] (**1**·OEt<sub>2</sub>), while dissolution of this material in pyridine formed the pyridine-solvated complex **1**·py quantitatively.

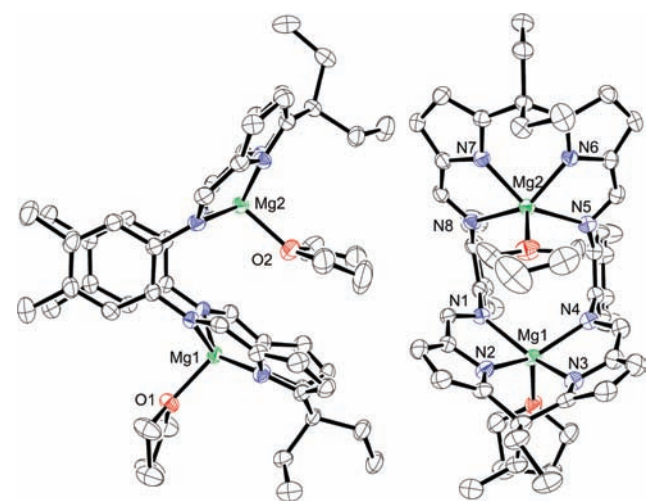
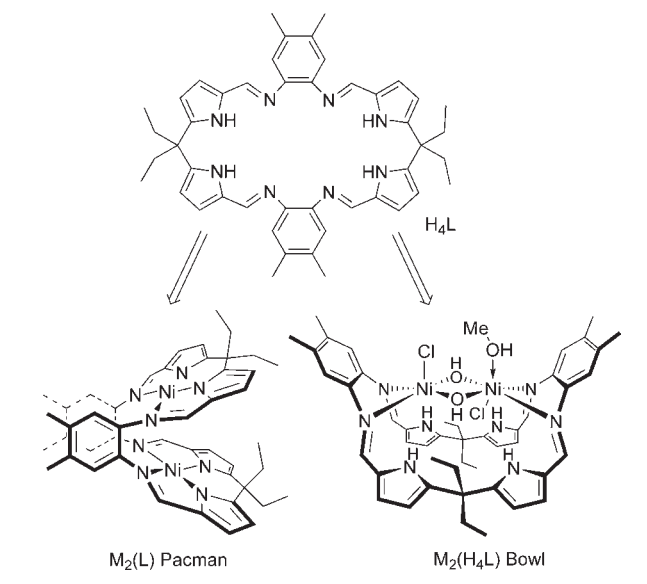
The X-ray crystal structure of **1**·THF determined using crystals grown from a toluene/hexane mixture confirmed the overall wedged-shaped structure (Figure 1). The two Mg cations adopt square-based pyramidal geometries in which the iminopyrrolide N<sub>4</sub>-donor sets occupy the basal planes (with Mg1/Mg2 located 0.56 Å out of the N<sub>4</sub> plane) and a molecule of THF is located at each apical site. Interestingly, one molecule of THF is found within the cleft while the other is outside. This causes the two metalated compartments to diverge significantly in order to accommodate the guest molecule, resulting in a Mg–Mg bite angle of 70.0° (which can be compared to the more usual 53–62° range seen for bimetallic complexes of L) and a small lateral twist angle of 7.0° [cf. 11–29° in M<sub>2</sub>(L) complexes with no endogenous ligand].<sup>7</sup> Similar geometric features were seen by us in the structurally-related complex [Cu<sub>2</sub>(*exo*-py)(*endo*-py)(L)].<sup>10</sup>

While **1**·THF appeared to be stable indefinitely under anhydrous conditions, an alternative attempt to crystallize **1** from a benzene/hexane mixture resulted in the formation of the new cluster complex [{Mg<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(OH)<sub>4</sub>}(H<sub>2</sub>L)<sub>2</sub>] (**2**), presumably through hydrolysis by adventitious water; **2** was also characterized by X-ray crystallography (Figure 2). The solid-state structure of **2** comprises a new magnesium hydroxide cubane, Mg<sub>4</sub>(μ-OH)<sub>4</sub>(OH)<sub>4</sub>, that is encapsulated by two orthogonally oriented H<sub>4</sub>L macrocycles through both coordinative and hydrogen-bonding interactions. In the asymmetric unit, the bonding of Mg1 is representative of each magnesium cation and is bound to the macrocycle through two imine nitrogens of H<sub>4</sub>L (N1 and N8), two bridging hydroxides (O1 and O2), and a terminal hydroxide (O4). This results in a binuclear arrangement of the metals in the asymmetric unit, with the bowl-shape arising from the hinging of the two H<sub>2</sub>N<sub>4</sub> compartments at the *meso*-carbons in a manner similar to that seen in Ni and Cd complexes of H<sub>4</sub>L.<sup>9,10</sup> This bimetallic structure is stabilized through a variety of reinforcing hydrogen-bonding interactions between the pyrrole hydrogens and both the bridging and terminal hydroxides [N···O, 2.734(3)–3.270(3) Å] and an internal hydrogen bond between the two

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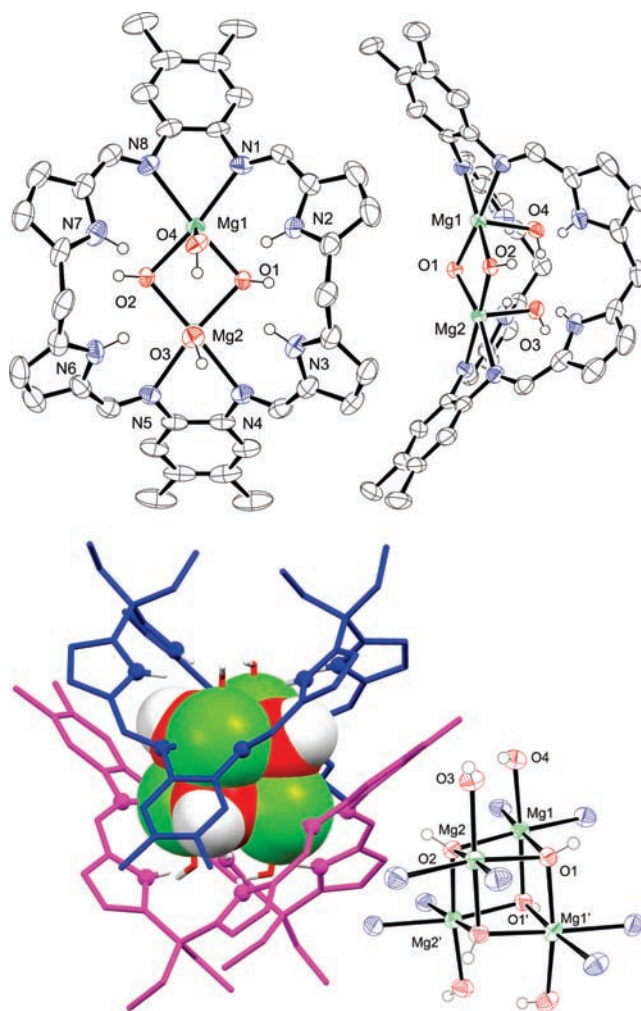
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**Chart 1.** Metallation (e.g., by Ni) of the Schiff Base Polypyrrolic Macrocycle  $H_4L$  Leading to Either Pacman or Bowl-Shaped Bimetallic Complexes



**Figure 1.** Side and face-on views of the solid-state structure of  $[Mg_2(THF)_2(L)] \cdot PhMe$  (**1**·THF). For clarity, the toluene molecule of crystallization, a disorder component in the *endo*-THF molecule, and all of the hydrogen atoms have been omitted. Displacement ellipsoids have been drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Mg1–N1, 2.165(2); Mg1–N2, 2.039(2); Mg1–N3, 2.067(2); Mg1–N4, 2.131(2); Mg1–O1, 2.043(2); Mg $\cdots$ Mg, 4.6504(9);  $\Sigma$ (Mg1 angles), 343.1; bite angle, 70.0; twist angle, 7.0.

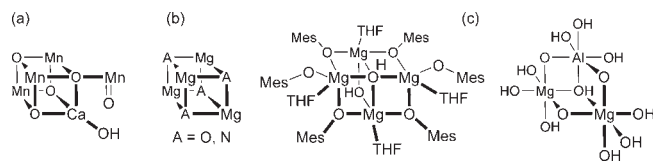
terminal hydroxides [O3 $\cdots$ O4, 2.605(3) Å]; all of these hydrogens were located in the difference Fourier map and refined with appropriate restraints. The octahedral coordination sphere of Mg1 is completed by a symmetry-related oxygen donor from a  $\mu_3$ -OH group, thus forming the Mg cubane through the orthogonal assembly of two binuclear  $Mg_2(OH)_4(H_4L)$  structural motifs. The encapsulation of the Mg hydroxide core by the organic framework results in an overall “tennis-ball” topology similar to those seen by Rebek and co-workers in spontaneously assembled C-shaped glycouril capsules,<sup>11</sup> although the cavity prescribed by



**Figure 2.** X-ray crystal structure of  $[Mg_4(\mu_3-OH)_4(OH)_4](H_2L)_2 \cdot (C_6H_6)_2$  (**2**). For clarity, the benzene solvent of crystallization, the ethyl substituents of the *meso*-carbons, and hydrogen atoms not involved in hydrogen-bonding have been omitted. Where shown, displacement ellipsoids have been drawn at 50% probability. (top) Back and side views of the asymmetric unit highlighting the hydrogen-bonding interactions and curvature of the ligand framework. (bottom left) Encapsulation of the cubane core by the organic framework. (bottom right) Mg cubane core showing all of the donor atoms. Selected bond lengths (Å) and angles (deg): Mg1–O1, 2.091(2); Mg1–O1', 2.049(2); Mg1–O2, 2.059(2); Mg1–O4, 2.065(2); Mg1–N1, 2.195(2); Mg1–N8, 2.240(3); Mg2–O3, 2.020(2); Mg2–O2', 2.058(2); Mg2–N4, 2.264(3); Mg2–N5, 2.216(3); Mg1 $\cdots$ Mg2, 3.040(1); Mg1–O1–Mg2, 94.00(8); Mg1–O2–Mg2, 94.06(8); O1–Mg1–O4, 170.06(9); O2–Mg2–O3, 170.25(9); O1–Mg1–O2, 84.60(8); O1–Mg2–O2, 84.34(8).

the framework in **2** is clearly much smaller as a consequence of encapsulation.

The tennis-ball structure of **2** seen in the solid state appears to be retained in solution. The  $^1H$  NMR spectrum of **2** (Figure S2) displays a broad resonance at 10.6 ppm that is attributable to hydrogen-bonded NH/OH protons; this feature is absent in the  $^1H$  NMR spectrum of **1**·THF. Furthermore, the imine resonance at 7.98 ppm in **2** has shifted from 7.71 ppm in **1**·THF. Significantly, two environments are seen for the *meso*-ethyl groups at 2.40 and 2.18 ppm ( $CH_2$ ) and 1.03 and 0.56 ppm ( $CH_3$ ), which are reflected in the  $^{13}C$  NMR spectrum with



**Figure 3.** Representative examples of metal cubanes: (a) oxygen-evolving center of Photosystem II; (b) Mg alkoxide or amide cubane; (c) theoretical models for brucite and layered double hydroxide minerals.

resonances at 26.36 and 25.38 ppm ( $\text{CH}_2$ ) and 8.49 and 7.92 ppm ( $\text{CH}_3$ ). This dissimilarity of the ethyl groups implies that a rigid, bowl-shaped structure is adopted in which the ethyl groups are oriented endo and exo to the encapsulated cubane. Significantly, the nuclear Overhauser effect spectroscopy (NOESY) spectrum of **2** displays NOEs between the pyrrole protons (6.58 and 6.08 ppm) and the aryl methyl protons (2.08 ppm) (Figure S3). Both of these interactions indicate that the macrocyclic environment in solution is similar to that in the solid state. The IR spectrum also supports the presence of OH and NH groups, with absorptions seen at 3440 and 3280  $\text{cm}^{-1}$ , and the electrospray ionization (ESI) mass spectrum displays a molecular ion at  $m/z$  1665 (9%).

The bulk formation of **2** by intentional hydrolysis of **1**·THF was also investigated. Addition of 4.7 equiv of water to **1**·THF in benzene resulted in the precipitation of pure **2** as a bright-yellow solid in 45% yield. Furthermore, the  $^1\text{H}$  NMR spectrum of the filtrate showed the presence of only **2** and the free macrocycle  $\text{H}_4\text{L}$  in a 1.0:1.5 ratio, which indicates that upon hydrolysis **1**·THF undergoes predominantly sole conversion to **2**. Upon standing in solution under aerobic conditions, **2** decomposed slowly to  $\text{H}_4\text{L}$  (25% after 48 h, Figure S4) but was stable indefinitely in the solid state.

Cubanes are an important class of cluster compound, with  $\text{Fe}_4\text{S}_4$  cubanes playing central electron transport and storage roles in biology and forming the basis of many FeS enzymes such as nitrogenases.<sup>12</sup> Furthermore, transition-metal and mixed-metal cubanes are current synthetic targets because of the identification of a Ca–Mn oxo cubane core at the oxygen-evolving center of Photosystem II (Figure 3)<sup>13</sup> and are also of interest as single-molecule magnets.<sup>14</sup> Magnesium cubanes usually comprise four magnesium centers occupying opposing corners of a cube that are bridged by  $\mu_3$ -N-imido or  $\mu_3$ -O-alkoxy substituents (Figure 3); the magnesium cations are octahedral or tetrahedral depending on the ligands used.<sup>15</sup> Of the 16 known structures of discrete  $\text{Mg}_4\text{O}_4$  cubanes,<sup>16</sup> none employ nitrogen donor ligands to complete the coordination sphere of the metal in the  $[\text{M}_4\text{O}_4]$  cubane core ( $\text{M}$  = group 2), in contrast to that seen in transition-metal analogues. The composition of the cubane core in **2** is also unique in that it contains only bridging and terminal OH groups [ $\text{Mg}-\text{O}$ , 2.020(2)–2.065(2) Å]. To our knowledge, structurally characterized cubanes in which the vertices are solely hydroxides are unknown, as are those with terminal hydroxides.<sup>16</sup> Furthermore, only a single structure incorporating a  $\text{Mg}-\mu\text{-OH}-\text{Mg}$  motif has been reported, wherein this motif is part of a face-shared methoxy–magnesium double cubane.<sup>17</sup> The  $\text{Mg}-\mu\text{-OH}$  bond distances in **2** [2.049(2)–2.095(2) Å] are within the ranges reported for  $\mu_3\text{-OH}$  [2.0030(16)–2.1208(15) Å] and  $\mu_2\text{-OH}$  [1.951(6)–2.093(2) Å] bond distances such as those found in closely related magnesium alkoxy cubanes.

The  $\text{Mg}(\text{OH})$  cubane in **2** has potential relevance to the mineralization of  $\text{Mg}(\text{OH})_2$  to form materials such as brucite, which

contains infinite  $[\text{Mg}(\text{OH})_4]$  sheets, or layered double hydroxides (LDHs) such as hydrotalcite,  $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4(\text{H}_2\text{O})$ . Furthermore, metal oxide nanoparticles, LDHs, and thin metal oxide films have potential as functional and optical materials and in catalysis and can be synthesized using a “bottom-up” approach by the controlled hydrolysis of Mg alkyls or alkoxide clusters.<sup>18</sup> The formation and stability of various Mg hydroxide clusters related to Al–Mg LDHs and brucite minerals were evaluated using density functional theory and compared to experimental findings (Figure 3c); these clusters contain structural motifs similar to those in **2**.<sup>19</sup> Thus, the formation of the cubane in **2** represents a possible structural motif on the pathway to magnesium hydroxide materials that has been stabilized through encapsulation by the macrocyclic framework.

We have shown that hydrolysis of the bimetallic magnesium Pacman complex **1**·THF results in the formation of a new magnesium hydroxide cubane **2** in which two orthogonally oriented macrocycles encapsulate the unusual core in a tennis-ball motif. It is hoped that the macrocycle and its variants have the potential to envelop and stabilize other metal clusters through a combination of dative and hydrogen-bonding interactions and that this may lead to the generation of new encapsulated materials and reagents.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Full experimental details and crystallographic data for **1**·THF and **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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