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Synthesis, Structures, and Adsorption Properties of Two New La^{III}–Mg^{II} Heterometallic Polymers

Yun Xu,[a] Yun-Xia Che,[a] Fang-Yi Cheng,[b] and Ji-Min Zheng*[a]

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Two new La^{III}–Mg^{II} heterometallic polymers, $\{[La_2(oda)_6Mg_2][Mg(H_2O)_6]\cdot 6H_2O\}_n$ (**1**) and $\{[La_2(pda)_6Mg_3(H_2O)_6]\cdot 11H_2O\}_n$ (**2**) (H_2oda = oxydiacetic acid, H_2pda = pyridine-2,6-dicarboxylic acid), have been synthesized under solvothermal conditions. Structural analysis reveals that **1** contains two types of 3D cavities, one of which is occupied by $[Mg(H_2O)_6]^{2+}$ units, and the other is occupied by free water molecules. The metal-only structure of **2** is a hexagonal network, in which the cavities are occupied by free water molecules. The adsorption properties of **1** and **2** have been investigated. The hydrogen adsorption and desorption curves of the two polymers show an unusual, pronounced hysteresis behavior.

Introduction

Crystal engineering based on metal–organic frameworks (MOFs) has received considerable attention because of their intriguing, aesthetic structures and topological features as well as their applications in areas such as catalysis, sorption, ion exchange, luminescence, magnetism, and nonlinear optics.[1–6] However, most of the work has so far centered on the assembly of 3d or 3d–4f metal–organic open frameworks.[7] Alkaline-earth metals, especially Mg^{II} with its large polarizing power, are predicted to have strong binding affinities for hydrogen and can be used to reduce the framework density in porous materials.[8] Mg-based MOFs have been reported previously; Long et al. reported the first $Mg_3(ndc)_3$ framework (H_2ndc = 2,6-naphthalenedicarboxylic acid), and Kaskel et al. reported the solvent-induced pore-size adjustment of an $Mg_3(ndc)_3(DMF)_4$ network (DMF = *N*,*N*-dimethylformamide).[8d,9] Palomino et al. studied the H_2 adsorption enthalpy of Mg-exchanged zeolites and proposed that Mg-containing materials are ideally suited to H_2 storage applications.[8b] Goddard et al. studied Mg-based MOFs to improve their hydrogen storage capabilities, and Davies et al. synthesized a series of Mg-based MOFs. Cheetham et al., Bu et al., and Henderson et al. prepared Mg-based chiral materials.[8c,10] Maji et al. reported temperature-and stoichiometry-controlled dimensionality in a magnesium–4,5-imidazoledicarboxylate system.[11] Zhou et al. reported the role of open metal sites in MOFs, Thomton et al. reported Mg-decorated fullerenes in MOFs for methane and hydrogen storage, and Zhang et al. reported Mg-based MOFs that exhibited hydrogen sorption hystereses.[12] Compared to the many reported 3d- and 4f-metal-based MOFs, it is clear that reports on Mg-based MOFs are scarce.[13] To the best of our knowledge, the application of Ln^{III}–Mg^{II} heterometallic frameworks on the adsorption of hydrogen has not been reported.

Multidentate carboxylic acids, such as oxydiacetic acid (H_2oda) and pyridine-2,6-dicarboxylic acid (H_2pda), have proved to be ideal ligands for forming coordination polymers with special properties.[14,15] In our investigations on heterometallic MOFs with these ligands, we found that the polymers bear a high concentration of unsaturated metal centers, which can potentially adsorb H_2 on removal of the coordinated water molecules.

Inspired by these results, we set out to prepare two new heterometallic polymers using La^{III} and Mg^{II} with H_2oba and H_2pda. We describe the preparation, structures, and adsorption properties of the two new La^{III}–Mg^{II} heterometallic polymers $\{[La_2(oda)_6Mg_2]\ [Mg(H_2O)_6]\cdot 6H_2O\}_n$ (**1**) and $\{[La_2(pda)_6Mg_3(H_2O)_6]\cdot 11H_2O\}_n$ (**2**).

Results and Discussion

Crystal Structure of 1

X-ray structure analysis reveals that **1** crystallizes in the cubic crystal system, space group $Fd\bar{3}c$. Most of the reported Ln^{3+}–M^{2+} (M = Co, Mn, Cu, etc.) polymers based on H2oda crystallize in hexagonal crystal systems,[14d–14i] and those that crystallize in cubic crystal systems are relatively rare.[14a,14j,14k] The asymmetric unit of **1** consists of one independent La^{3+} ion, two independent Mg^{2+} ions

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[a] Department of Chemistry, Nankai University,
Tianjin 300071, P. R. China
Fax: +86-22-23508056
E-mail: jmzheng@nankai.edu.cn
[b] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University,
Tianjin 300071, P. R. China

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($Mg1^{2+}$ and $Mg2^{2+}$), one independent oda^{2-} anion, one independent coordinated water molecule, and one independent free water molecule. The coordination environments of La1, Mg1, and Mg2 are presented in Figure 1. La^{3+} is nine-coordinate with a distorted tricapped trigonal-prismatic geometry, which is composed of six carboxylate oxygen atoms (O2) and three alkoxo oxygen atoms (O3) from three oda^{2-} anions to form an $[La(oda)_3]^{3-}$ unit [La1–O2 2.505(4), La1–O3 2.540(5) Å]. $Mg1^{2+}$ is six coordinate with a regular octahedral geometry, which is composed of six carboxylate oxygen O1 atoms from six neighboring $[La(oda)_3]^{3-}$ units [Mg1–O1 2.057(4) Å]. $Mg2^{2+}$ is also six-coordinate with an octahedral geometry, which is composed of six O4 atoms from six water molecules to form an $[Mg2(H_2O)_6]^{2+}$ unit [Mg2–O4 2.095(6), La1···Mg2 5.656(3), Mg1–Mg2 5.656(3) Å]. Each oda^{2-} anion acts as a pentadentate ligand, which bridges one La^{3+} and two $Mg1^{2+}$ ions in a μ_3:η^1,η^1,η^1,η^1,η^1 coordination mode. Each $[La(oda)_3]^{3-}$ unit is surrounded by six $Mg1^{2+}$ ions, which creates a cubic lattice with 3D cavities in the structure [La1–Mg1 6.531(4), Mg1–Mg1 9.236(8) Å]. As shown in Figure 2, there are two types of cavities that are arrayed alternatively along three directions, in which the larger cavities are occupied by $[Mg2(H_2O)_6]^{2+}$ units, which is the thermodynamically stable species required to neutralize the charge of the MOF, whereas the smaller cavities are occupied by free water molecules. In view of the topology, the metal-only matrix of La^{III} and $Mg1^{II}$ ions can be described as an NaCl network (Figure S1). Further analysis of the crystal packing reveals that this structure contains extensive hydrogen bonding between the coordinated (O4) and free (O5) water molecules. The most significant of these are O4···O5 [3.216(1) Å] and O5···O5 [2.440(4) Å], which afford an $(H_2O)_4$ hydrogen-bonding chain to link adjacent $[Mg2(H_2O)_6]^{2+}$ units and form an interesting twofold 3D supramolecular network. The twofold 3D supramolecular networks interpenetrate with the metal-only NaCl network and form a threefold interpenetrated topology (Figure 3). Additionally, the carboxylate O2 atoms are involved in hydrogen-bonding interactions with water molecules (O4) from the $[Mg2(H_2O)_6]^{2+}$ units [O2 ···O4 3.594(3) Å], which play an important role in stabilizing the network structure. The total volume accessible for potential water molecules determined by PLATON calculations is about 14.0% of void per unit volume (potential solvent area volume 2501.3 Å^3, per unit-cell volume of 17831.0 Å^3).[16]

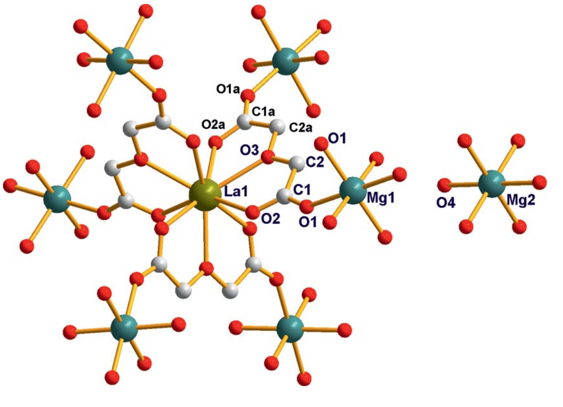

Figure 1. Coordination environments of the La^{3+} and Mg^{2+} ions in **1**. All H atoms and uncoordinated H_2O molecules are omitted for clarity.

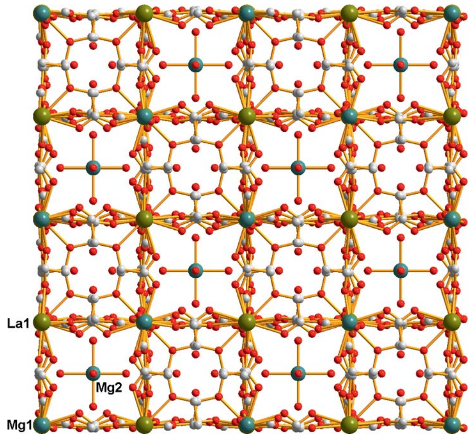

Figure 2. View of the packing diagram of **1** along the *c* axis, which shows the two types of cavities. H atoms are omitted for clarity.

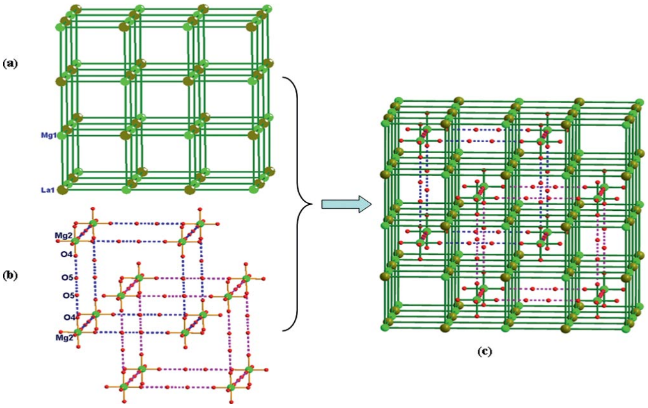

Figure 3. (a) Topological NaCl network of **1**; (b) twofold interpenetrating 3D supramolecular network; (c) threefold interpenetrated topology. Dotted lines depict hydrogen-bond interactions. C and H atoms are omitted for clarity.

Crystal Structure of 2

X-ray structure analysis reveals that **2** crystallizes in the hexagonal crystal system, space group *P6/mcc*. The asymmetric unit of **2** consists of one independent La^{3+} ion, one independent Mg^{2+} ion, one independent pda^{2-} anion, one independent coordinated water molecule, and three independent free water molecules. La^{3+} is nine-coordinate, and its coordination is completed by six carboxylate O2 atoms and three N1 atoms from three pda^{2-} ligands to form an $[La(pda)_3]^{3-}$ unit [La1–O2 2.518(1), La1–N1 2.629(2) Å]

(Figure 4). $Mg1^{2+}$ is six-coordinate in a slightly distorted octahedral geometry with four oxygen (O1) atoms from $[La(pda)_3]^{3-}$ in the equatorial plane and two oxygen (O3) atoms from two free water molecules at the apical sites [Mg1–O1 2.085(3), Mg1–N1 2.107(4) Å]. Each pda^{2-} anion acts as a pentadentate ligand, which bridges one La^{3+} and two Mg^{2+} ions in a μ_3:η^1,η^1,η^1,η^1,η^1 coordination mode. Each $[La(pda)_3]^{2-}$ unit links six adjacent $Mg1^{2+}$ ions through the carboxylate groups to generate a new 3D hexagonal network structure with 1D cavities along the *c* axis. The metal-only lattice in the packing diagram can be described as a 4,6-connected hexagonal topology (Figure S2). Further analysis of the crystal packing reveals that this structure also contains extensive hydrogen-bonding interactions between the coordinated O3 and free O4, O5, and O6 water molecules [O4···O6 2.724(3)/2.810(2), O4···O3 2.884(1)/3.029(4) Å] where each free water oxygen atom position was refined disordered equally between OA and OB with equivalent thermal parameters. The H_2O3, H_2O4, and H_2O6 molecules form a coplanar water cluster with a hexagonal gear-wheel geometry by O4···O6 and O4···O3 hydrogen-bonding interactions. The average O···O distance is ca. 2.86 Å, which is slightly longer than the corresponding value of 2.759 Å in ice.[17] In addition, two O5 atoms lie on the center of the plane of the water cluster with an O5A···O6A interaction [2.701(6) Å], which links neighboring water clusters into a unique 1D chain (Figure S3). These free water molecules abound in the cavities of the structure (Figure 5). The total volume accessible for potential water molecules determined by PLATON calculations is about 22.6% of void per unit volume (potential solvent area volume 727.6 $Å^3$, per unit-cell volume of 3213.9 $Å^3$).[16]

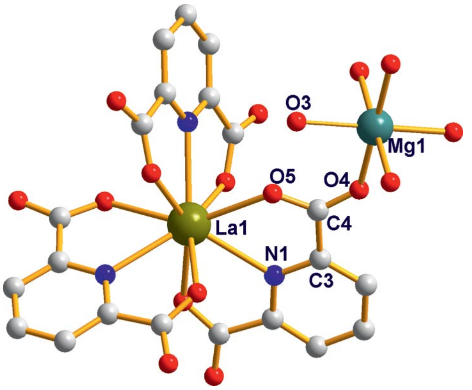

Figure 4. Coordination environments of La^{3+} and Mg^{2+} ions in **2**. All H atoms and uncoordinated H_2O are omitted for clarity.

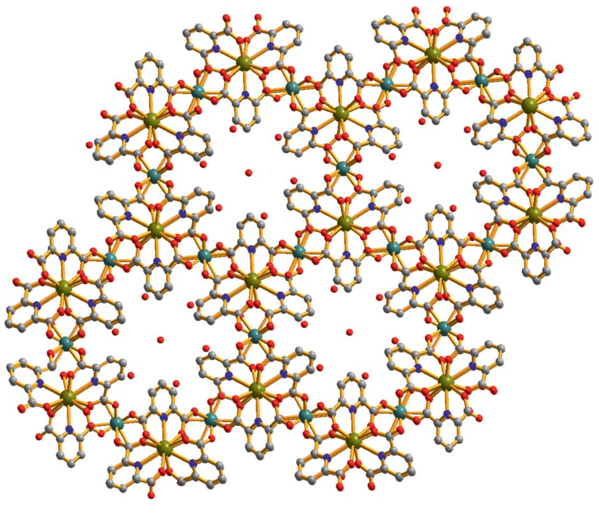

Figure 5. View of the packing diagram of **2** along the *c* axis, which shows the cavities. H atoms are omitted for clarity.

Adsorption Properties of 1 and 2

The dehydration of **1** and **2** will leave many cavities and unsaturated metal ions, which can potentially adsorb H_2 molecules; therefore, the adsorption properties of **1** and **2** were studied. The solid–gas adsorption properties of **1** and **2** were evaluated towards H_2 (77 and 305 K) and N_2 (77 K). At 305 K, they exhibited a low hydrogen uptake, and the maximum hydrogen adsorption capacity under 5000 mbar for **1** and **2** was 0.05 and 0.20%, respectively. At 77 K, the maximum hydrogen adsorption capacity reached 0.27 and 0.73% under approximately 5000 mbar for **1** and **2**, respectively (Figure 6). Under low pressure, the two polymers showed pronounced hysteresis in their adsorption and de-

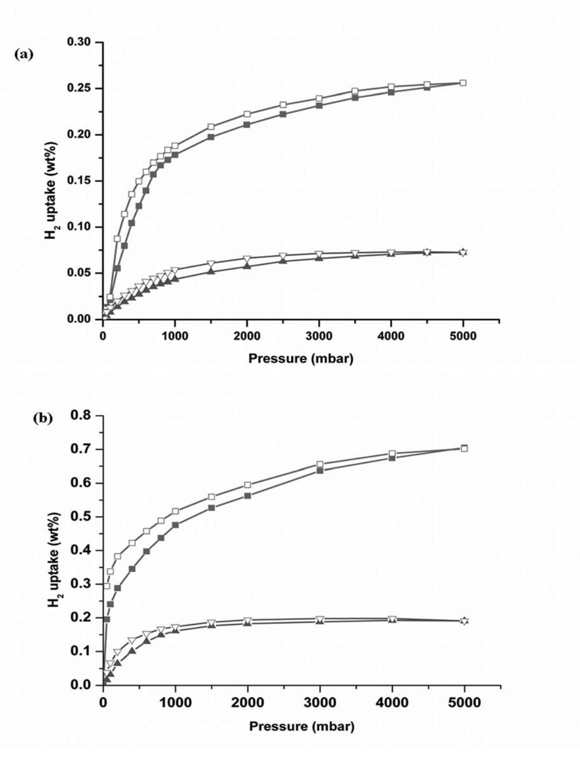

Figure 6. Hydrogen adsorption and desorption isotherms for (a) **1** and (b) **2** (triangles: H_2 adsorption and desorption at 305 K; squares: H_2 adsorption and desorption at 77 K; closed symbols: adsorption; open symbols: desorption).

sorption H_2 isotherms, which may be ascribed to the dehydrated Mg^{II} sites and the indented narrow channels of the two structures.[18] To date, only a few MOFs have shown such a pronounced hysteresis adsorption behavior.[18b,19] Conversely, **1** and **2** only adsorb a negligible amount of N_2 (Figure S4). Desolvated **1** and **2** show Brunauer–Emmett–Teller (BET) surface areas of 6.39 and 8.57 $m^2 g^{-1}$, respectively (measured by using nitrogen). Compared to some reported polymers with large hydrogen adsorptions,[20] the amounts of adsorbed hydrogen in **1** and **2** are smaller; however, these compounds will enrich the exploration of hydrogen storage in heterometallic frameworks.

Thermal Properties and PXRD

The thermogravimetric analysis (TGA) curves show that free and coordinated water molecules are removed in the range 25–300 and 25–220 °C for **1** and **2**, respectively. Polymers **1** and **2** showed 15.78 and 18.16% weight loss of the guest and coordinated water molecules, which is in agreement with the calculated values of 15.89 and 18.57%, respectively. The decomposition of **1** occurred at 370 °C, and the framework of **2** was stable up to ca. 450 °C (Figure S5). The simulated and experimental powder X-ray diffraction (PXRD) patterns of **1** and **2** at room temperature are in good agreement, which proves the phase purity of the as-synthesized product. The thermal stability of **1** and **2** was also demonstrated by variable-temperature PXRD from 20–370 °C for **1** and 20–450 °C for **2** (Figure 7). Above 95 °C for **1** and 180 °C for **2**, variations in the diffraction intensities were observed in the PXRD patterns, which may be ascribed to small structural rearrangements that occur with the departure of the water molecules.[21] Above 370 °C for **1** and 450 °C for **2**, the order disappears, and amorphous phases are observed.

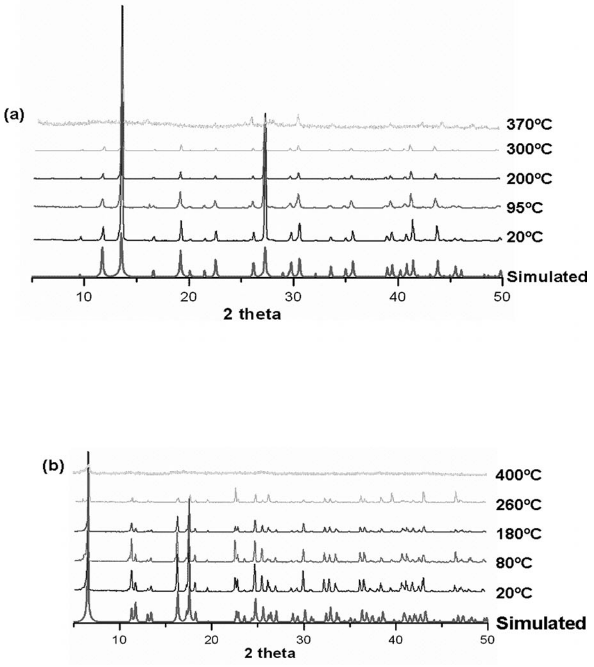

Figure 7. Simulated and experimental PXRD patterns of (a) **1** from 20–370 °C and (b) **2** from 20–450 °C in air.

Photoluminescent Properties

Photoluminescence experiments were performed at room temperature on **1** and **2** in the solid state. A blue emission with a maximum at 395 nm was detected when **1** was irradiated at 255 nm (Figure S6). This emission was very weak, because there are too many water molecules in **1** and no π–π* transition of the oda^{2-} ligand. Polymer **2** exhibits an intense blue emission peak at 413 nm (λ_{ex} = 310 nm), which can be assigned to the π–π* transition of pda^{2-}.[22]

Conclusions

Two new 3D La^{III}–Mg^{II} heterometallic frameworks were successfully obtained under solvothermal conditions. Polymer **1** is an unusual, anionic, porous MOF, which contains interesting twofold interpenetrating 3D hydrogen-bonded supramolecular networks. Polymer **2** is a porous MOF whose cavities are occupied by 1D water molecules. The two polymers are the first examples of La^{III}–Mg^{II} heterometallic frameworks used to investigate hydrogen adsorption. The two polymers show pronounced hysteresis in their H_2 adsorption and desorption isotherms. Although the amounts of adsorbed hydrogen in **1** and **2** are small, they are helpful examples for the exploration of hydrogen gas storage properties of heterometallic frameworks. It is believed that more Ln^{III}–Mg^{II} heterometallic polymers with interesting structures as well as excellent physical properties will be synthesized.

Experimental Section

Materials and General Procedures: All reagents were commercially available and used as received without purification. Elemental analyses for C, H, and N were carried out with a Perkin–Elmer analyzer. TGA experiments were performed with a NETZSCH TG 209 instrument with a heating rate of 5 °C min^{-1}. PXRD measurements were recorded with a D/Max-2500 X-ray diffractometer by using Cu-K_α radiation at room temperature. The pressure–composition–temperature curves for hydrogen adsorption were carried out with a computer-controlled "gas reaction controller" apparatus, which was manufactured by the Advanced Materials Corp. and Hiden Isochema (IGA 001, Hiden Analytical Ltd.),[23] and ultra-high-purity hydrogen (99.999%) was used. For the measurements, approximately 500 mg of sample was taken in a stainless-steel sample holder outgassed at 300 °C for **1** and 250 °C for **2** under 10^{-1} Pa vacuum for about 8 h. The volume in the hydrogen adsorption process was carefully calibrated before the measurement. The hydrogen adsorption was carried out at 77 and 298 K. The hydrogen adsorption amount was defined as the ratio of the mass gain and the mass of the starting polymers plus adsorbed hydrogen. The surface area and micropore volume of **1** and **2** were measured with an ASAP 2020 V3.00 H apparatus by using nitrogen gas.

Synthesis of $\{[La_2(oda)_6Mg_2][Mg(H_2O)_6]\cdot 6H_2O\}_n$ (1): A mixture of La_2O_3 (0.5 mmol, 0.16 g), MgO (1.5 mmol, 0.06 g), and H_2oda

(3 mmol, 0.40 g) was dissolved in distilled water (8 mL) and ethanol (2 mL). The pH was adjusted to 4 with triethylamine. The resulting solution was transferred to a 25 mL Teflon-lined stainless steel vessel, which was sealed and heated at 140 °C for 72 h. After the reactor had been cooled to room temperature at a rate of 5 °C/h, colorless cubic crystals were collected by filtration, washed with distilled water, and dried in air. Yield: 52% based on La. $C_{24}H_{48}La_2Mg_3O_{42}$ (1359.33): C 21.21, H 3.56; found C 21.24, H 3.53.

Synthesis of {[La$_2$(pda)$_6$Mg$_3$(H$_2$O)$_6$]·11H$_2$O}$_n$ (2): A mixture of La_2O_3 (0.5 mmol, 0.16 g), MgO (1.5 mmol, 0.06 g), and H_2pda (3 mmol, 0.49 g) was dissolved in distilled water (6 mL) and ethanol (3 mL). The pH was adjusted to 5 with triethylamine. The resulting solution was transferred to a 25 mL Teflon-lined stainless steel vessel, which was sealed and heated at 160 °C for 72 h. After the reactor had been cooled to room temperature at a rate of 5 °C/h, colorless crystals were collected by filtration, washed with distilled water, and dried in air. Yield: 63% based on La. $C_{42}H_{52}La_2Mg_3N_6O_{41}$ (1647.65): C 30.62, H 3.18, N 5.10; found C 30.65, H 3.15, N 5.12.

X-ray Crystallographic Determinations: Single-crystal analyses were performed with a Bruker SMART 1000 CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) by the ω-2θ scan technique. The structures were solved by direct methods using SHELXS-97 followed by structure refinement on F^2 with SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically. Aromatic and aliphatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters. The hydrogen atoms bonded to oxygen atoms of coordinated water molecules were located from difference maps and refined subject to O–H distance restraints. The hydrogen atoms of free water could not be located due to the disorder of the free water molecules in **2**; the final formula of this polymer was determined from elemental analysis and TGA. Crystal data and experimental details are summarized in Table 1. Selected bond lengths and angles are listed in Table S1. CCDC-757810 (for **1**) and -757811 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement information for **1** and **2**.

	1	**2**
Empirical formula	$C_{24}H_{48}La_2Mg_3O_{42}$	$C_{42}H_{52}La_2Mg_3N_6O_{41}$
F$_w$	1359.33	1647.65
T [K]	294(2)	298(2)
Crystal system	cubic	hexagonal
Cpace group	$Fd\bar{3}c$	$P6/mcc$
a [Å]	26.125(3)	15.677(2)
b [Å]	26.125(3)	15.677(2)
c [Å]	26.125(3)	15.100(3)
γ [°]	90	120
V [Å^3]	17832(4)	3213.9(9)
Z	16	2
F(000)	10848	1648
d [g cm^{-3}]	1.989	1.703
μ [mm^{-1}]	2.059	1.447
θ range [°]	3.12–27.43	3.00–27.48
R_1,[a] wR_2 [$I > 2\sigma(I)$]	0.0454, 0.1210	0.0189, 0.0527

[a] $R_1 = \Sigma(\|F_o - F_c\|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Supporting Information (see footnote on the first page of this article): NaCl network of **1**, metal-only lattice of **2**, 1D chain of water clusters in **2**, nitrogen adsorption and desorption isotherms for **1** and **2**, TGA curves for **1** and **2**, photoluminescent emission of **2**.

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