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New Polymorphs of Magnesium-Based Metal–Organic Frameworks $Mg_3(ndc)_3$ (ndc = 2,6-Naphthalenedicarboxylate)

Irena Senkovska,[a] Julia Fritsch,[a] and Stefan Kaskel*[a]

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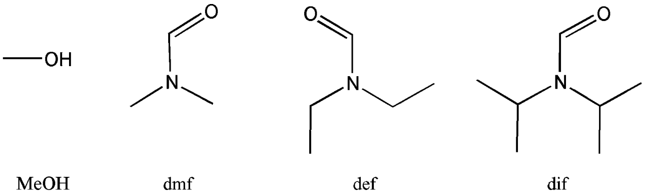
Two new magnesium 2,6-naphthalenedicarboxylate (ndc) metal–organic frameworks, $[Mg_3(ndc)_3(dif)_4]$ (**1**) (dif = *N*,*N*-diisopropylformamide) and $[Mg_3(ndc)_3(dmf)_2(CH_3OH)(H_2O)](dmf)$ (**2** = TUDMOF-3) (dmf = *N*,*N*-dimethylformamide), have been synthesised under solvothermal conditions from $Mg(NO_3)_2{\cdot}6H_2O$ and pure 2,6-naphthalenedicarboxylic acid. According to single-crystal X-ray crystallographic studies, complex **1** crystallises in the space group $P2_1/n$ [a = 14.769(3) Å, b = 13.325(3) Å, c = 17.998(4) Å, β = 108.67(2)°] and complex **2** in the space group $P\bar{1}$ [a = 11.1116(11) Å, b = 12.6229(13) Å, c = 17.800(2) Å, α = 88.568(14)°, β = 83.833(13)°, γ = 70.167(11)°]. The structures of compounds **1** and **2** consist of trinuclear magnesium clusters connected to six dicarboxylate ligands; for **2**, the clusters act as distorted octahedral nodes to give a 3D network. In contrast, the trinuclear clusters in **1** act as pseudo-planar-hexagonal nodes to give a 2D network assembly. According to nitrogen and hydrogen physisorption measurements at 77 K for compounds **1** and **2**, TUDMOF-3 has a permanent porosity with a Langmuir surface area of 632 $m^2 g^{-1}$, a specific pore volume of 0.21 $cm^3 g^{-1}$ and a hydrogen storage capacity of 1.23 wt.-% at 77 K and 1 bar, whereas compound **1** is not porous.

Introduction

Metal–organic frameworks (MOFs) are compounds in which organic multifunctional molecules act as linkers to interconnect metal ion or multinuclear complex (cluster) nodes into a 3D network of predefined topology.[1–6] MOFs are a relatively new class of microporous materials that show promise for diverse applications because of their high porosity, tunable pore size and functionality.[7–10]

2,6-Naphthalenedicarboxylate (ndc) is an adequate molecular linker for the construction of coordination polymers because of its rigidity and stability. Recently, several interesting examples of MOF structures containing ndc were discovered: $[Al(OH)(ndc)(H_2O)]$ (MIL-69),[11] $[M(ndc)(H_2O)]$ (M = Mn, Zn or Cd),[12,13] $[Yb_2(ndc)_3(H_2O)_3]$,[14] $[M_2(OH)_2(ndc)]$ (M = Zn or Co),[15,16] $[M_2(ndc)_3(dmf)_4](H_2O)_m$ (M = Eu, Tb or Ce),[17] $[M(ndc)(H_2O)_m]$ (M = Ni or Co),[13,16] $Zn_6(ndc)_5(OH)_2(dmf)_6$ (MOF-48)[18] and $Zn_4O(ndc)_3$ (IRMOF-8).[10] The MOFs based on light metals such as Li, Mg and Al have recently received more attention. Constructing light-metal-based MOFs should allow the formation of lightweight materials that can be useful in gas storage applications.[19]

In a previous paper, we have reported a Mg-ndc-based MOF, $[Mg_3(ndc)_3(dmf)_4]$ (TUDMOF-2), and have shown that the pore size of the $Mg_3(ndc)_3$ networks can be adjusted by using different solvents (dmf, def).[20] In fact, TUDMOF-2 has the same network topology as $[Mg_3(ndc)_3(def)_4]$,[21] but the smaller solvent molecules induce the widening of pores, which leads to a larger specific surface area (SSA). In order to verify this concept, we have studied other solvents with smaller and larger diameters (Scheme 1).



Scheme 1. The solvents used for pore size adjustment in $Mg_3(ndc)_3$.

In the following, we describe the structure of two new magnesium carboxylates, $[Mg_3(ndc)_3(dif)_4]$ (**1**) and $[Mg_3(ndc)_3(dmf)_2(CH_3OH)(H_2O)](dmf)$ (**2** = TUDMOF-3) (*Technical University Dresden Metal–Organic Framework No. 3*), which are also constructed from Mg clusters and 2,6-naphthalenedicarboxylate linkers.

Results and Discussion

Synthesis and Structural Characterisation of 1 and 2

The solvothermal reaction of $Mg(NO_3)_2{\cdot}6H_2O$ and H_2ndc in dif at 383 K results in the formation of yellow

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[a] Department of Inorganic Chemistry, Dresden University of Technology
Mommsenstr. 6, 01069 Dresden, Germany
Fax: +49-351-46337287
E-mail: Stefan.Kaskel@chemie.tu-dresden.de

crystals of **1**. For the same reaction carried out in dmf/CH_3OH (1:1) solution, colourless crystals of **2** were obtained.

Complex **1** crystallises in the monoclinic space group $P2_1/n$ and contains two crystallographically independent magnesium atoms (Mg1 and Mg2). Mg1 and one of the two independent ndc^{2-} anions are located at a general position. Mg2 and the middle of the central C–C bond in the naphthalene system in the second anion are positioned on crystallographic centres of inversion. The three magnesium atoms in **1** form a perfectly linear $[Mg_3(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4]$ unit with C_1 symmetry (Figure 1a).

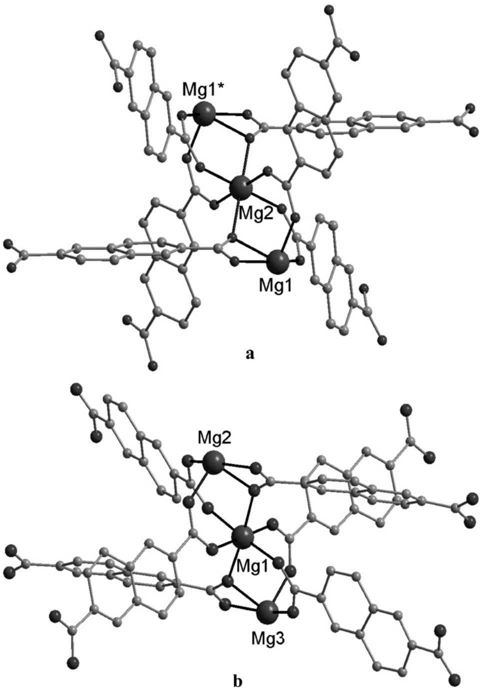

Figure 1. Trinuclear Mg carboxylate clusters and representation of the inorganic six-coordinate SBUs in **1** (a) and in **2** (b). Symmetry operation (*): $-x$, $-y$, $-z$.

The $[Mg_3(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4]$ unit can be regarded as a secondary building unit (SBU). This trinuclear unit is a successful SBU, through which many interesting structures have been constructed in the past decade.[14,22–25] It should be noted that the trinuclear SBU is the most important Mg cluster, because the same structural motif was found in all Mg MOFs with a rigid 3D framework and permanent porosity reported so far.[20,21,25–29] Obviously, this SBU plays a key role in the formation of 3D networks in magnesium coordination polymers and a study of the multinuclear magnesium complexes assumes considerable importance.

The trinuclear magnesium clusters in **1** are connected by rigid organic linkers (ndc). The ndc ligands in compound **1** adopt two coordination modes that connect two Mg atoms: a bidentate bridging mode and an asymmetric chelating bridging mode. Consequently, a 2D layered MOF with triangular meshes and a 3^6 topology is formed (Figure 2b). The Mg–O(carboxylate) distances for the terminal Mg1 atoms are in the range 1.997(3)–2.180(3) Å, whereas the Mg–O(carboxylate) distances for the central Mg2 atom are between 2.046(3) and 2.123(3) Å.

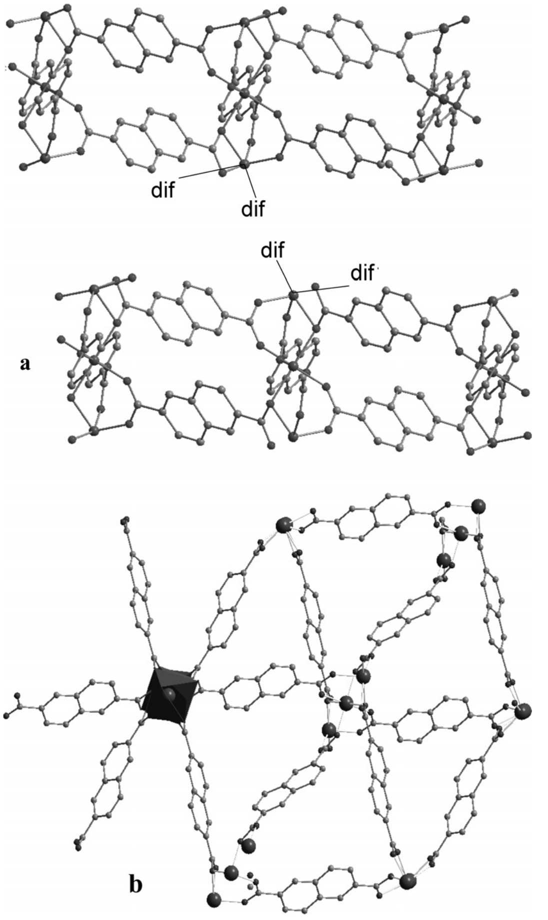

Figure 2. (a) The layer structure of **1** viewed along the crystallographic *b* axis (the dif molecules are presented schematically); (b) the 3^6 2D layer network of **1** (coordinated dif molecules are not shown).

The thickness of the layer, given by the Mg–Mg distance between the terminal Mg atoms in the same SBU, is 7.15(1) Å, and the distance between two adjacent layers, given by the Mg–Mg distance between the terminal Mg atoms in neighbouring SBUs, is 9.48(1) Å (Figure 2a).

Two of the four dif molecules coordinated to a trinuclear cluster protrude into the triangular cavities, whereas the other two dif molecules fill the space between the layers, thereby separating two adjacent layers; therefore, the existence of the 2D network can be explained by the dif-induced steric hindrance that prevents the formation of coordinative bonds between adjacent SBUs and in this way prevents the formation of the 3D network too.

Single-crystal X-ray diffraction analysis reveals that compound **2** has essentially the same SBU (Figure 1b); the difference is that all three Mg atoms are located at a general position, and the SBU has no higher symmetry. Consequently, the cluster loses the perfect linearity and the Mg2–Mg1–Mg3 angle in this case is 176.75(1)°. The Mg2–O(carboxylate) distances range from 2.022(3) to 2.205(3) Å, the Mg3–O(carboxylate) distances are between 1.967(3) and 2.188(3) Å, and the central Mg1–O(carboxylate) distances are between 2.038(4) and 2.118(4) Å.

The eight six-coordinate SBUs in **2** are interlinked through the ndc^{2-} anions to form a highly distorted cubic network (Figure 3). One methanol and one dmf molecule are bound to Mg3 and one water and one dmf molecule are bound to Mg2 to give six-coordinate magnesium atoms. The solvent molecules in **2** can be removed to give a porous network having open magnesium sites. A summary of crystal data and structure refinement is provided in Table 2.

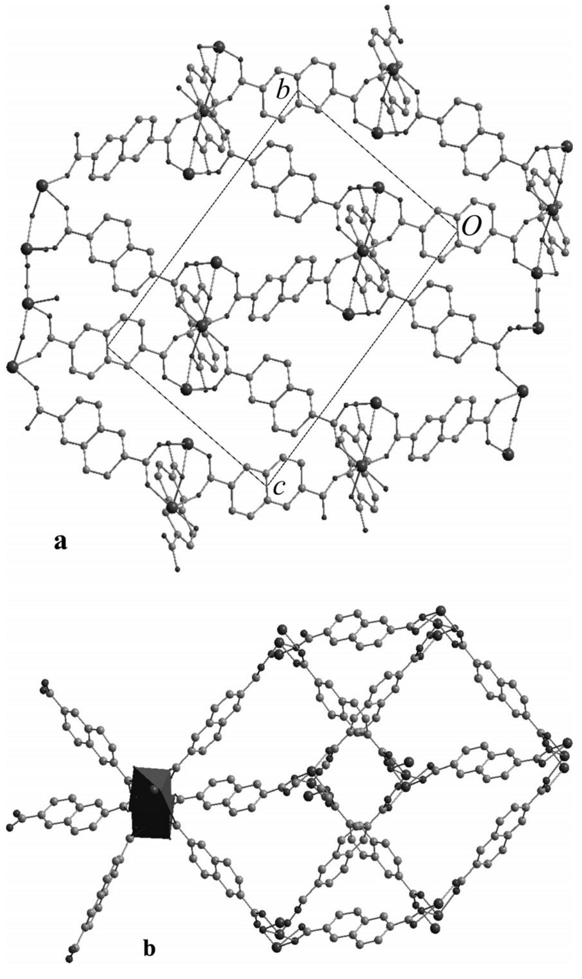

Figure 3. Extended structure of **2**: (a) viewed along the crystallographic *a* axis; (b) the 3D distorted cubic network cell of **2** (solvent molecules are omitted in both cases).

Thermogravimetric Analysis

The thermogravimetric analysis (TGA) of **1** shows continuous weight loss in the temperature range from 330 to 790 K. The weight loss of 42.1% observed from 330 to 680 K can be attributed to the loss of four coordinated dif molecules (expected weight loss: 41.94%). The linker starts to decompose at 680 K.

A weight loss for **2** occurs between 398 and 693 K corresponding to the loss of dmf, CH_3OH and H_2O solvent molecules (observed: 28.0%, calculated: 27.35%), followed by the decomposition of the ligand in the temperature range 758–918 K. The weight loss is consistent with the elemental analysis and the empirical formula deduced from the single-crystal X-ray crystallographic analysis.

Evacuated Frameworks and Sorption Properties

All materials were evacuated under vacuum and heated to 423 K. The desolvated $Mg_3(ndc)_3$ framework of $[Mg_3(ndc)_3(dmf)_2(CH_3OH)(H_2O)](dmf)$ is hereafter denoted as **2a**. The powder XRD pattern of **2** changes after removal of the guest molecules relative to that of the as-synthesised product (Figure 4a). A similar behaviour of the framework was observed for TUDMOF-2. But in the case of TUDMOF-3 the original framework of **2** could not be regenerated through a treatment of **2a** with dmf or a dmf/CH_3OH mixture. According to XRD analysis (Figure 4b), a new unknown structure can by identified as a result of the resolvation. This compound has no porosity.

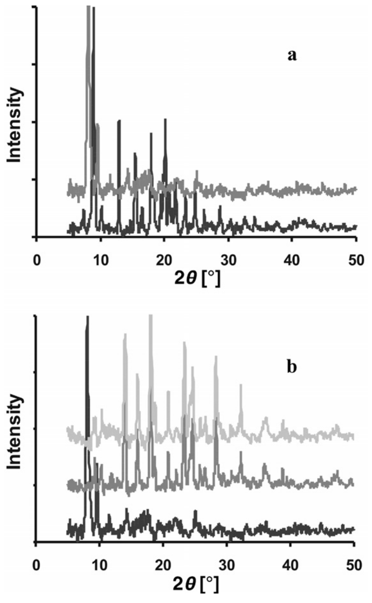

Figure 4. X-ray powder diffraction patterns (a) for **2** as synthesised (black) and **2** desolvated (grey); (b) for **2** desolvated (black), **2** resolvated with dmf (dark grey) and **2** resolvated with dmf/CH_3OH (1:1) (light grey).

Gas-sorption properties of **1** and **2** were examined by measuring N_2 and H_2 adsorption isotherms at 77 K. Significant differences between **1** and **2** were observed in the gas-adsorption properties. The N_2 isotherms for **2** display typical type-I adsorption characteristics (Figure 5a).

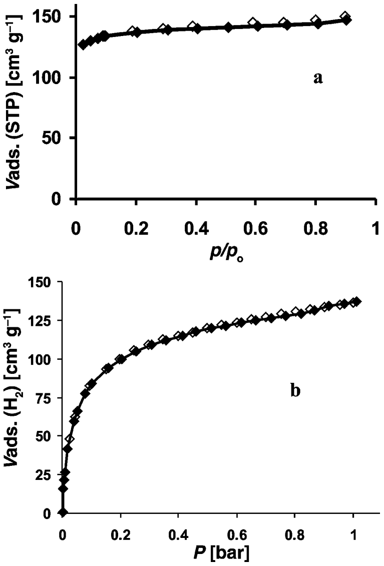

Figure 5. (a) The N_2 adsorption (solid symbols) and desorption (empty symbols) isotherms of **2** at 77 K; (b) H_2 adsorption (solid symbols) and desorption (empty symbols) isotherms of **2** at 77 K.

The Brunauer–Emmett–Teller (BET) surface areas of the solvent-free frameworks of **2** were estimated to be 418 $m^2 g^{-1}$ at 0.3 p/p_0. The sorption isotherm was also fitted to a Langmuir equation; the resulting specific surface area is 623 $m^2 g^{-1}$. The micropore volume obtained from nitrogen adsorption at 77 K and 0.2 p/p_0 is 0.21 $cm^3 g^{-1}$. The hydrogen adsorption isotherm for **2** measured at 77 K is given in Figure 5b. The maximum H_2 uptake of **2** is 1.23 wt.-% at 1 bar. Compound **1** is essentially nonporous; it has only a low N_2 adsorption capacity and a type-II adsorption isotherm.

The Role of Solvent

It was shown that the use of def, dmf or dmf/CH_3OH mixtures as solvents in the solvothermal reaction of $Mg(NO_3)_2·6H_2O$ and H_2ndc leads to the formation of three different porous compounds, $Mg_3(ndc)_3(def)_4$, $Mg_3(ndc)_3(dmf)_4$ (TUDMOF-2) or $[Mg_3(ndc)_3(dmf)_2(CH_3OH)(H_2O)](dmf)$ (TUDMOF-3), respectively. The networks formed have identical topology, but the minor structural differences (lattice constants) influence the sorption properties of the materials. Several reactions were carried out to elucidate the influence of the solvent mixture composition on the formation of the different compounds. $Mg(NO_3)_2$ and H_2ndc were treated at 110 °C for 24 h with varying proportions of def (or dmf) and CH_3OH (or C_2H_5OH) (Table 1). The products were identified by powder X-ray diffraction analysis.

Table 1. The role of solvent in defining the product from the solvothermal reaction of $Mg(NO_3)_2$ and H_2ndc at 383 K.

Solvent	Solvent ratio [%]	Product
def	100	$Mg_3(ndc)_3(def)_4$
dmf	100	$Mg_3(ndc)_3(dmf)_4$
dmf + C_2H_5OH	50:50	$Mg_3(ndc)_3(dmf)_4$
def + C_2H_5OH	50:50	$Mg_3(ndc)_3(def)_4$
dmf + CH_3OH	50:50	$[Mg_3(ndc)_3(dmf)_2(CH_3OH)(H_2O)](dmf)$
dmf + def	25:75	$Mg_3(ndc)_3(def)_4$
dmf + def	50:50	$Mg_3(ndc)_3(dmf)_4$
dmf + def	75:25	$Mg_3(ndc)_3(dmf)_4$

In the case of solvent mixtures containing def and dmf, the resulting product is a compound incorporating only one type of solvent. In the case of mixed-solvent solutions containing dmf and methanol, TUDMOF-3 was obtained as the main product. If dmf or def is mixed with ethanol (1:1), then the compound containing only formamide is obtained.

Furthermore, the hydrothermal treatment of TUDMOF-2 or $Mg_3(ndc)_3(def)_4$ in def or dmf, respectively, did not convert one into the other; thus, a given network retains its structure irrespective of the postsynthetic solvothermal treatment.

Conclusion

In summary, TUDMOF-3 has the same network topology as TUDMOF-2, but the occlusion of smaller solvent molecules induces significant structural changes resulting in a different space group and higher specific surface area. On the other hand, the larger solvent molecule in **1**, dif, hinders the formation of a 3D network, resulting in a 2D double-layered structure. The solvent plays a key role in the construction of the networks and predetermines the formation of a certain product. The selection of the solvent or solvent mixture demonstrates the potential for pore size adjustment in metal–organic frameworks.

Experimental Section

General Remarks: All reagents and solvents (reagent-grade) were used as received. Elemental analyses (C, H, N) were performed by the Elemental Analysis Service, Institute of Organic Chemistry, Dresden University of Technology. Powder X-ray diffraction (PXRD) data were collected by using a Stoe STADI P powder diffractometer with Cu-$K_{\alpha1}$ radiation. Thermogravimetric analyses (TGA) were carried out by using a Netzsch STA 409 thermal analyser with heating in air at 10 K min⁻¹ to 1273 K. Physisorption isotherms were measured at 77 K with a Quantachrome Autosorb1C apparatus. High-purity gases were used (nitrogen: 99.999 %, hydrogen: 99.999 %). Prior to the measurement, the samples were evacuated for 16 h at 423 K. The specific surface areas and porosity parameters were derived from the N_2 adsorption data.

X-ray Crystallography: Single-crystal X-ray diffraction data for complexes **1** and **2** were recorded with a STOE IPDS I image plate diffractometer by using Mo-K_α radiation. The structures were solved by direct methods with the help of SHELXS-86[30] and refined by full-matrix least-squares techniques with SHELXL-97.[31] Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of the CH_3 groups and aromatic hydrogen atoms were positioned geometrically and refined by using a riding model; the remaining hydrogen atoms were located from the difference Fourier maps. Further details of the structural analysis are summarised in Table 2. CCDC-650990 (for **1**) and -650991 (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 2. Crystallographic data for compounds **1** and **2**.

Compound	1	2
Chemical formula	$C_{64}H_{78}Mg_3N_4O_{16}$	$C_{46}H_{45}Mg_3N_3O_{17}$
Mol. mass	1232.23	984.78
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	14.769(3)	11.1116(11)
b [Å]	13.325(3)	12.6229(13)
c [Å]	17.998(4)	17.800(2)
α [°]	90	88.568(14)
β [°]	108.67(2)	83.833(13)
γ [°]	90	70.167(11)
V [Å^3]	3355.3(12)	2334.8(4)
Z	2	2
Reflns. collected/independent	14802/4255	12566/5605
Reflns. observed [$I > 2\sigma(I)$]	2308	3026
GoF on F^2	1.005	0.944
R, wR [$I > 2\sigma(I)$]	0.0659, 0.1115	0.0535, 0.1207
Max., min. peaks [e Å^{-3}]	0.221, –0.221	0.076, –0.066

Preparation and Characterisation

[$Mg_3(ndc)_3(dif)_4$] (1): 2,6-Naphthalenedicarboxylic acid (0.16 g, 0.75 mmol) was dissolved in dif (10 mL). $Mg(NO_3)_2 \cdot 6H_2O$ (0.26 g, 1.0 mmol) was added to this solution. The mixture was filled into a 40-mL Teflon liner and was heated in an autoclave at 383 K for 20 h. It was then cooled to room temperature at a rate of 0.05 K min^{-1} to produce large crystals of **1**, which were suited for X-ray analysis. Yield: 0.10 g (32.5%). $Mg_3C_{64}H_{78}N_4O_{16}$ (1232.23): calcd. C 62.38, H 6.38, N 4.55; found C 62.10, H 6.37, N 4.52.

[$Mg_3(ndc)_3(dmf)_2(CH_3OH)(H_2O)$](dmf) (2): A mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (0.52 g, 2.0 mmol) and 2,6-naphthalenedicarboxylic acid (0.32 g, 1.4 mmol) in dmf (20 mL) and CH_3OH (20 mL) was filled into a 250-mL Teflon liner. The mixture was heated in an autoclave at 383 K for 24 h, then cooled to room temperature at a rate of 0.05 K min^{-1}. The resulting colourless crystals were collected, washed with methanol and dried under argon to give **2**. Yield: 0.36 g (73.5%). $Mg_3C_{46}H_{45}N_3O_{17}$ (984.78): calcd. C 56.10, H 4.61, N 4.27; found C 55.46, H 4.62, N 4.22.

Acknowledgments

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