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Synthesis and Crystal Structure of UiO-16: An Organically Templated Layered Magnesium Phosphate

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The first organically templated layered magnesium phosphate, $[Mg_6(H_2O)_2(PO_4)_2(HPO_4)_3H_2PO_4]^-[N_2C_4H_{11}]^+H_2O$, has been synthesized under hydrothermal conditions and characterized by powder and single-crystal X-ray diffraction, solid-state ^{31}P MAS and CP-MAS NMR spectroscopy, and thermogravimetric analysis. The compound is isostructural with an iron phosphate, $[Fe_3(HPO_4)_2(PO_4)(H_2O)][C_4H_{11}N_2]_{0.5}$, and it crystallizes in the monoclinic space group $C2/c$ with $a = 31.076(6)$ Å, $b = 6.3198(13)$ Å, $c = 12.470(3)$ Å, $\beta = 103.90(3)°$, $V = 2377.4(8)$ Å^3, and $Z = 4$. The structure consists of macroanionic sheets of magnesium phosphate separated by piperazinium ions and water molecules. The basic building unit of the inorganic layers is a hexamer of edge-sharing Mg polyhedra. Proton disorder leading to disordered P−OH and P═O functionality in one phosphate tetrahedra was indicated from the X-ray single-crystal solution and confirmed by solid-state NMR spectroscopy.

Introduction

The application of zeolites in ion exchange and catalysis has stimulated great interest in synthesis of novel materials with layered and open framework structures. The most developed class of such materials contains structures built by linked SiO_4 and AlO_4 tetrahedra, but microporous materials containing other elements have been synthesized in great numbers in recent years. Most of these materials are metal phosphates. The first step in this evolution was the synthesis of open framework structures denoted $AlPO_4$-*n*,[1] which was soon followed by synthesis of similar gallium,[2] beryllium, and zinc phosphates.[3] Open framework and layered transition metal phosphates have furthermore been synthesized with iron,[4−6] cobalt,[7,8] molybdenum,[9] vanadium,[10−12] titanium,[13−16] and zirconium.[17,18] Similar structures also exists for phosphates with indium,[19,20] tin,[21,22] and uranium.[23] Most of these materials have been synthesized hydrothermally in the presence of cationic organic templates. By such means a large variety of metastable 2D- and 3D-framework structures have been stabilized. A complex hydrogen-bonding situation between protonated amine templates and framework oxygens strongly influences the crystallization process. In many cases there is a subtle relationship between the charge, shape, and volume of the cationic template and the nature of the anionic framework.

The present paper concerns the crystal structure and properties of the novel magnesium phosphate, UiO-16, which has been obtained by hydrothermal synthesis in the presence of an organic template. A number of magnesium phosphates are well-known, and they are, e.g., important ingredients in castable refractories and rapid-setting cement, in agriculture, and some may form under physiological conditions as calculi in the human body. Structurally they exhibit a large diversity. For instance, struvite,[24] $NH_4MgPO_4 \cdot 6H_2O$, is an orthophosphate with unconnected PO_4 tetrahedra where hydrogen bonding plays an important role in linking the anions and cations. In schertelite,[25] $(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$,

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finite anionic magnesium phosphate clusters are linked together by hydrogen bonding from the ammonium cations, whereas collinsite,[26] $CaMg(PO_4)_2{\cdot}2H_2O$, contains infinite magnesium phosphate chains. There are several examples of 2D layered magnesium phosphates showing large diversity with respect to main structural units. In newberyite,[27] $MgHPO_4{\cdot}3H_2O$, and bobierrite,[28] $Mg_3(PO_4)_2{\cdot}8H_2O$, the 2D magnesium phosphate layers are neutral, and the sheets are held together by direct hydrogen bonding. Interstitial cations provide interlayer bonding in dittmarite,[29] $NH_4MgPO_4{\cdot}H_2O$, hannayite,[30] $(NH_4)_2Mg_3(HPO_4)_4{\cdot}8H_2O$, and brianite,[31] $Na_2CaMgPO_4$. Magnesium phosphates also exists as framework structures with different degree of openness. Examples of dense phases are farringtonite,[32] $Mg_3(PO_4)_2$, and holthedalite,[33] Mg_2PO_4OH. The framework of panasqueraite,[34] $CaMgPO_4OH$, is however more open with cavities filled with Ca cations. The octahedral−tetrahedral framework in kovdorskite,[35] $Mg_2PO_4(OH){\cdot}3H_2O$, can be classified as a open-framework structure with a 1D 10-ring channel system. The present paper extends the number of variants of magnesium phosphates and reports the first example of a organically templated layered magnesium phosphate.

Experimental Section

Synthesis. The UiO-16 magnesium phosphate was synthesized hydrothermally from a mixture of magnesium acetate tetrahydrate (99%, Aldrich), phosphoric acid (85%, Fluka), piperazine hexahydrate (99%, Fluka), and water. The molar composition of the starting gel was 2.0 MgO:1.0 P_2O_5:1.5 piperazine:50 H_2O and the initial pH was 5.1. The crystallization took place in a Teflon-lined steel autoclave, filled to 80% of the maximum volume, at 180 °C for 4 days. The final pH after the crystallization was 4.95. The resulting crystalline product was recovered by filtration, washed with water, and dried in air at 80 °C overnight. The yield based on Mg was 46%.

Powder X-ray diffraction. Powder diffraction patterns were collected on a Siemens D5000 diffractometer equipped with a Ge primary monochromator, giving Cu $K\alpha_1$ radiation, and a Braun position sensitive detector. Diffraction data were collected in transmission geometry using a 0.5-mm rotating borosilicate capillary for the 2θ interval 5−90°.

Thermogravimetric Analysis (TGA). TGA data were obtained using a Scientific Rheometric STA 1500. The sample was heated to 800 °C in a flow of nitrogen gas at a heating rate of 5 K min^{-1}.

X-ray Single-Crystal Structure Determination. A platelet of the transparent UiO-16 sample, ∼0.3 × 0.15 × 0.04 mm, was mounted on a thin glass fiber. Diffraction data were collected on a Siemens SMART CCD diffractometer at 150 K using monochromatized Mo Kα radiation. The collected data covered one hemisphere of the reciprocal space. Data reduction and absorption correction was carried out with the programs SAINT[36] and SADABS,[37] respectively. Experimental conditions are summarized in Table 1.

Table 1. Crystal Data and Structure Refinement for UiO-16

empirical formula	$Mg_6P_6O_{27}N_2C_4H_{22}$
formula weight	861.92
temperature	150 K
wavelength	0.71073 Å
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
unit cell dimensions	
a, Å	31.076(6)
b, Å	6.3198(13)
c, Å	12.470(3)
β, deg	103.90(3)
V, $Å^3$	2377.4(8)
Z	4
density (calculated), d cm^{-3}	2.408
absorption coefficient, mm^{-1}	0.745
F(000)	1752
crystal size, mm^3	0.30 × 0.15 × 0.04
θ range for data collection, deg	2.70 to 23.31
Miller index ranges	$-34 \leq h \leq 34$ $-7 \leq k \leq 7$ $-13 \leq l \leq 13$
reflections collected	8768
independent reflections	1708 [*R*(int) = 0.0375]
reflections observed (> $2\sigma(I)$)	1545
refinement method	full-matrix least squares on F^2
data/restraints/parameters	1708/0/207
goodness-of-fit on F^2	1.235
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0398 wR2 = 0.1195
R indices (all data)	R1 = 0.0458 wR2 = 0.1252
largest diff. peak and hole, e $Å^{-3}$	1.074 and −0.669

The SHELXTL program package[38] was used for structure solution and refinement. The structure was solved in a monoclinic cell: $a = 31.076(6)$ Å, $b = 6.3198(13)$ Å, $c = 12.470(3)$ Å, and $\beta = 103.90(3)°$. The systematic absences indicated the space group *C*2/*c* (no. 15). The direct method solution gave positions of the Mg and P atoms, whereas the O, C, and N atoms were found from subsequent difference Fourier maps. No hydrogen atoms could be located, but were placed geometrically and refined in the riding mode for the carbon atoms of piperazine [C(1) and C(2)] and for two OH groups [O(5) and O(10)]. The least-squares refinements, including atomic positions and anisotropic displacement factors for all atoms, except for the hydrogen atoms with riding constraints which were refined with isotropic displacement factors, converged to residual factors R1 = 0.0398 and wR2 = 0.1195 for 1545 reflections [$I > 2\sigma(I)$]. The (002) at $d = 15.08$ Å could not be observed with the actual diffractometer, and was omitted from the refinement.

^{31}P Solid-State NMR Spectroscopy. The ^{31}P high-power ^1H decoupled solid-state MAS NMR spectra were recorded at 81 MHz using a Bruker DMX-200 spectrometer at a spinning frequency of 8.0 kHz. The exitation pulse was 3 μs (π/2), and the repetition times were 4 and 300 s, with and without cross-polarization (CP), respectively. The contact time in the CP experiment was 1 ms. The ^{31}P chemical shifts were defined relative to a 85% H_3PO_4 standard. The spectra were deconvoluted assuming Lorentzian peak shape.

Results and Discussion

Characterization. The powder diffraction pattern of UiO-16 did not correspond to any known Mg compound.

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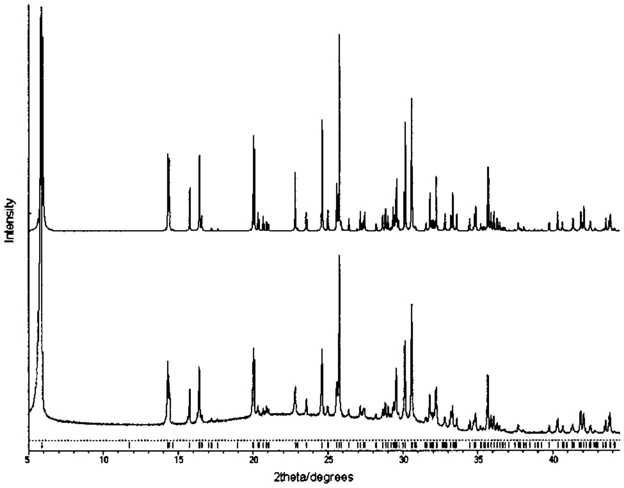

Figure 1. Powder X-ray diffraction patterns for UiO-16. Simulated from single-crystal solution (top), experimental (bottom), $\lambda = 1.540\ 598$ Å

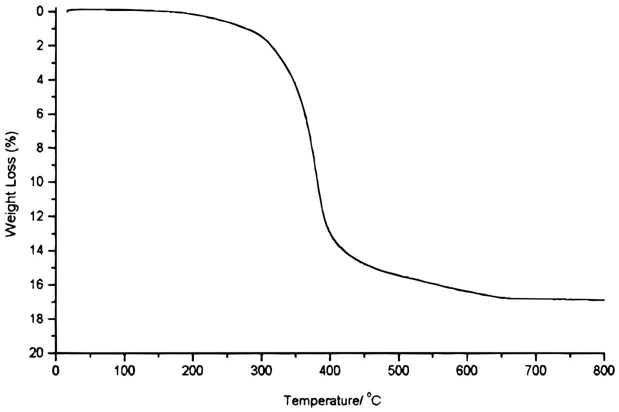

Figure 2. TGA data for UiO-16 on heating to 800 °C in nitrogen at a rate of 5 K min^{-1}.

The crystal structure was solved on the basis of a small single crystal. The powder pattern simulated from the single-crystal structure solution by means of the PowderCell program[39] showed close correspondence to that determined experimentally (Figure 1). This clearly proves the individual crystal specimen picked for single-crystal analysis of the UiO-16 material is representative of the bulk phase.

The TGA data for UiO-16 (Figure 2) show a total weight loss of 16.83% above 150 °C. This is consistent with the loss of three water molecules and one piperazine molecule (calculated loss 16.50%) and is in agreement with the chemical formula $[Mg_6(H_2O)_2(PO_4)_2(HPO_4)_3H_2PO_4]^-[N_2C_4H_{11}]^+H_2O$ which was suggested by the single-crystal analysis and the NMR data. UiO-16 transforms into an amorphous material on heating above 400 °C.

Crystal Structure. Crystallographic data are given in Table 1. The atomic coordinates and displacement parameters are given in Table 2 with selected bond distances and bond angles in Table 3. The crystal structure of UiO-16 is of layered nature with macroanionic sheets of magnesium phosphate stacked along [001] separated by piperazinium ions and water molecules (Figure 3). The basic building unit of the inorganic sheets is a hexamer of edge-sharing Mg polyhedra (Figure 4). The connection of these hexamers into the 2D sheets is quite complex and as illustrated in Figure 5, it involves two orientations of the hexamers and linkage between Mg polyhedra. The phosphate tetrahedra is also involved in the cross-linking of the hexamers, but is not included in Figure 5.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for UiO-16 in Space Group *C*2/*c*

atom	*x*	*y*	*z*	*U*(eq)[a]
P(1)	2541(1)	−1013(2)	11551(1)	8(1)
P(2)	1569(1)	1739(2)	9785(1)	9(1)
P(3)	4176(1)	−2300(2)	11989(1)	19(1)
Mg(1)	2489(1)	−5871(2)	10847(1)	9(1)
Mg(2)	3313(1)	−4457(2)	12598(1)	13(1)
Mg(3)	1626(1)	−3051(2)	10361(1)	13(1)
O(1)	3027(1)	−1614(5)	12028(2)	13(1)
O(2)	2312(1)	−585(5)	12491(2)	11(1)
O(3)	2284(1)	−2826(5)	10844(2)	9(1)
O(4)	2516(1)	950(5)	10815(2)	10(1)
O(5)	1076(1)	2254(5)	9150(3)	18(1)
O(6)	1802(1)	704(5)	8973(2)	12(1)
O(7)	1780(1)	3803(5)	10279(2)	12(1)
O(8)	1532(1)	160(5)	10692(2)	13(1)
O(9)	4612(1)	−3329(7)	11904(3)	34(1)
O(10)	4275(2)	−91(7)	12554(4)	50(1)
O(11)	3946(1)	−3610(6)	12698(3)	23(1)
O(12)	3906(1)	−1919(6)	10835(3)	30(1)
OW1	3528(1)	−8439(5)	13113(2)	17(1)
OW2	5000	1760(30)	2500	313(15)
N	4524(1)	−4799(8)	14769(4)	37(1)
C(1)	4733(2)	−6501(10)	14264(5)	36(1)
C(2)	5182(2)	−7101(9)	14990(5)	31(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Calculated standard deviations in parentheses.

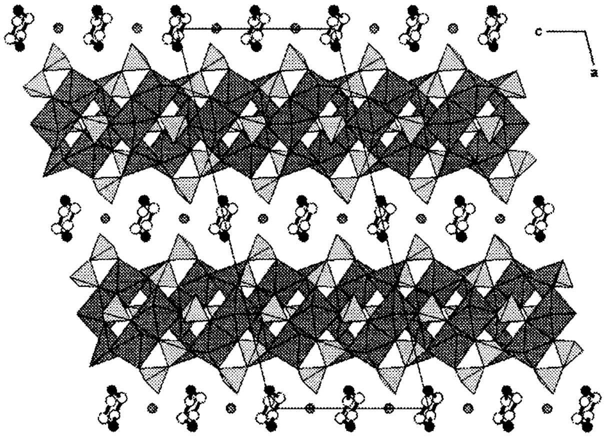

Figure 3. Polyhedral representation of UiO-16 along [010]. Mg polyhedra are depicted with darker shading; PO_4 tetrahedra, with lighter shading; C atoms, with open circles; water oxygen, with shaded circles, and N atoms, with filled circles.

The hexamer is built up by three nonequivalent Mg polyhedra, two with six-coordinated Mg's and one with a five-coordinated Mg, see Table 3. For the distorted Mg(1)O_6 octahedron, all oxygen atoms participate in edge sharing, and they are trigonally coordinated to two magnesium atoms and one phosphorus atom. The Mg−O bond distances between 2.012 and 2.165 Å are in the same range as in other magnesium phosphates.[27,33] The Mg(2)O_5(H_2O) octahedron share one edge with Mg(1)O_6, and has five normal Mg−O bond distances in the range 2.016−2.086 Å. The six coordination is fulfilled with a long separation, 2.645 Å, to a

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Table 3. Bond Lengths (Å) and Bond Angles (deg) for UiO-16[a]

P(1)−O(1)	1.532(3)	O(1)−P(1)−O(4)	109.65(17)
P(1)−O(4)	1.534(3)	O(1)−P(1)−O(2)	110.00(17)
P(1)−O(2)	1.535(3)	O(4)−P(1)−O(2)	110.41(17)
P(1)−O(3)	1.546(3)	O(1)−P(1)−O(3)	111.35(17)
		O(4)−P(1)−O(3)	108.24(16)
		O(2)−P(1)−O(3)	107.15(16)
P(2)−O(7)	1.522(3)	O(7)−P(2)−O(6)	114.17(17)
P(2)−O(6)	1.527(3)	O(7)−P(2)−O(8)	111.16(17)
P(2)−O(8)	1.533(3)	O(6)−P(2)−O(8)	110.01(17)
P(2)−O(5)	1.582(3)	O(7)−P(2)−O(5)	107.29(18)
		O(6)−P(2)−O(5)	108.20(17)
		O(8)−P(2)−O(5)	105.56(17)
P(3)−O(12)	1.500(4)	O(12)−P(3)−O(11)	114.7(2)
P(3)−O(11)	1.509(4)	O(12)−P(3)−O(9)	107.5(2)
P(3)−O(9)	1.531(4)	O(11)−P(3)−O(9)	111.0(2)
P(3)−O(10)	1.561(4)	O(12)−P(3)−O(10)	107.1(3)
		O(11)−P(3)−O(10)	107.3(2)
		O(9)−P(3)−O(10)	109.1(2)
Mg(1)−O(4)	2.012(3)	O(4) −Mg(1)−O(2)	96.05(13)
Mg(1)−O(2)	2.024(3)	O(4)−Mg(1)−O(3)	164.41(14)
Mg(1)−O(3)	2.026(3)	O(2)−Mg(1)−O(3)	86.32(12)
Mg(1)−O(4)	2.069(3)	O(4)−Mg(1)−O(4)	86.91(13)
Mg(1)−O(7)	2.156(3)	O(2)−Mg(1)−O(4)	162.65(13)
Mg(1)−O(6)	2.165(3)	O(3)−Mg(1)−O(4)	95.42(13)
		O(4)−Mg(1)−O(7)	86.74(12)
		O(2)−Mg(1)−O(7)	112.46(13)
		O(3)−Mg(1)−O(7)	78.15(12)
		O(4)−Mg(1)−O(7)	84.73(12)
		O(4)−Mg(1)−O(6)	90.19(12)
		O(2)−Mg(1)−O(6)	80.53(12)
		O(3)−Mg(1)−O(6)	105.40(13)
		O(4)−Mg(1)−O(6)	82.37(12)
		O(7)−Mg(1)−O(6)	166.88(13)
Mg(2)−O(11)	2.015(4)	O(11)−Mg(2)−O(2)	175.00(16)
Mg(2)−O(2)	2.046(3)	O(11)−Mg(2)−O(1)	97.11(14)
Mg(2)−O(1)	2.054(3)	O(2)−Mg(2)−O(1)	87.73(13)
Mg(2)−O(6)	2.061(3)	O(11)−Mg(2)−O(6)	95.94(14)
Mg(2)−O(8)	2.085(3)	O(2)−Mg(2)−O(6)	82.56(13)
Mg(2)−OW1	2.643(4)	O(1)−Mg(2)−O(6)	92.54(13)
		O(11)−Mg(2)−O(8)	89.14(13)
		O(2)−Mg(2)−O(8)	89.90(13)
		O(1)−Mg(2)−O(8)	115.47(13)
		O(6)−Mg(2)−O(8)	150.73(15)
		O(11)−Mg(2)−OW1	92.97(13)
		O(2)−Mg(2)−OW1	82.09(12)
		O(1)−Mg(2)−OW1	168.53(13)
		O(6)−Mg(2)−OW1	80.96(12)
		O(8)−Mg(2)−OW1	69.98(11)
Mg(3)−O(12)	1.943(4)	O(12)−Mg(3)−O(3)	148.85(15)
Mg(3)−O(3)	1.992(3)	O(12)−Mg(3)−O(7)	96.76(16)
Mg(3)−O(7)	2.052(3)	O(3)−Mg(3)−O(7)	81.42(13)
Mg(3)−OW1	2.085(3)	O(12)−Mg(3)−OW1	111.04(15)
Mg(3)−O(8)	2.105(3)	O(3)−Mg(3)−OW1	100.12(13)
		O(7)−Mg(3)−OW1	92.18(13)
		O(12)−Mg(3)−O(8)	91.53(16)
		O(3)−Mg(3)−O(8)	93.02(13)
		O(7)−Mg(3)−O(8)	171.18(14)
		OW1−Mg(3)−O(8)	82.01(13)
N−C(1)	1.475(8)	C(1)−N−C(2)	111.1(4)
N−C(2)	1.495(7)	N−C(1)−C(2)	111.4(5)
C(1)−C(2)	1.518(8)	N−C(2)−C(1)	110.5(5)

[a] Calculated standard deviations are in parentheses

water molecule, OW(1), leading to a (5 + 1) octahedral arrangement. The Mg(2) octahedron is very distorted as seen by the long Mg(2)−OW(1) bond and the bond angle $\angle$[O(6)−Mg(2)−O(8)] = 150.66° deviating strongly from the ideal value of 180°. The $Mg(3)O_4(H_2O)$ polyhedron for the five-coordinated Mg(3) share one edge with $Mg(1)O_6$, see Figure 4, and can be described as a distorted tetragonal pyramid where the basal plane contains O3, O7, O8, and O12, whereas OW1 is in apical position. The Mg−O bond distances range between 1.945 and 2.104 Å are comparable to those found for similar polyhedra in $Na_3Mg_3(PO_4)_3$[40] and $Na_2Mg_5(PO_4)_4$.[41]

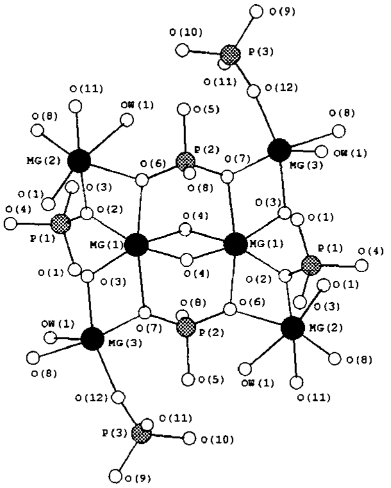

Figure 4. Coordination environment for Mg and P in UiO-16, showing hexameric Mg units.

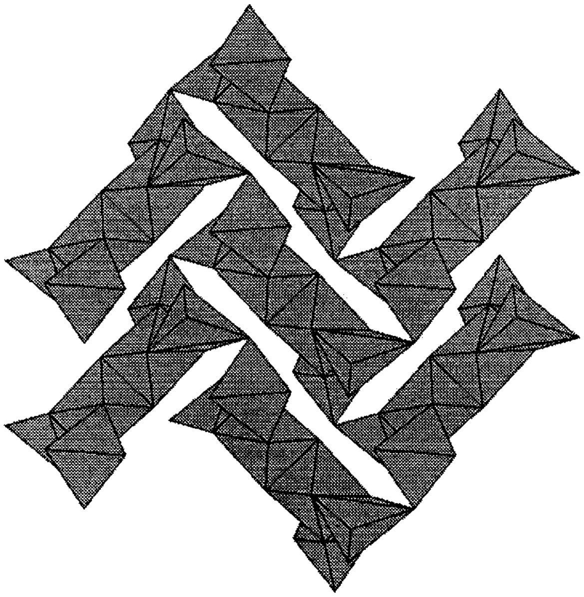

Figure 5. Connection of hexameric Mg units into 2D sheets.

There are three crystallographically distinct phosphorus sites in the UiO-16 structure. The $P(1)O_4$ tetrahedra share all four vertexes with Mg polyhedra. Three of the oxygen atoms, O(2), O(3), and O(4), are trigonally coordinated to P(1) and two magnesium atoms. The bond distances between 1.531 and 1.549 Å are within the expected range. For the $P(2)O_4$ tetrahedra, three of the four vertexes are shared with Mg polyhedra. These oxygen atoms, O(6), O(7), and O(8), are again trigonally coordinated and the P−O bond distances range is between 1.521 and 1.532 Å. The elongated P−O bond distance to the terminal oxygen, *d*[P(2)−O(5)] = 1.586 Å, indicates the presence of a P−OH group. The $P(3)O_4$ tetrahedra share two vertexes with neighboring Mg polyhedra, and the involved oxygen atoms, O(11) and O(12), are two-coordinated. The P−O and Mg−O bond distances are rather short for

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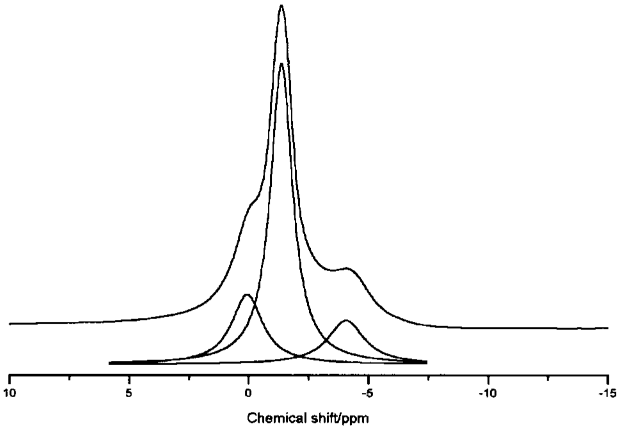

Figure 6. ^{31}P MAS NMR spectrum of UiO-16.

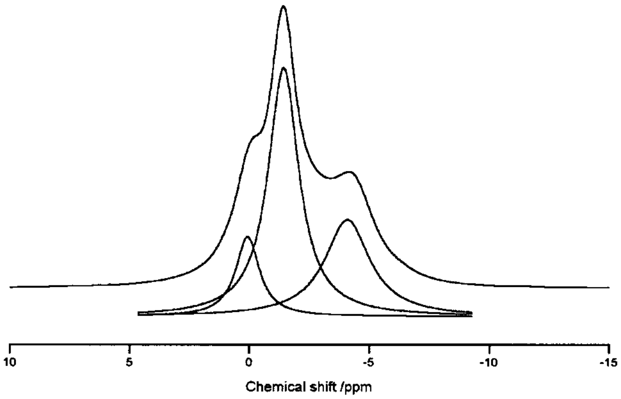

Figure 7. ^{31}P CP MAS NMR spectrum of UiO-16.

these bridging oxygen atoms, which is consistent with their two-coordination compared with three-coordination for the remaining O atoms. The rather long distance d[P(3)−O(10)] = 1.567 Å indicates a P−OH group. On the other hand, the d[P(3)−O(9)] = 1.533 Å distance for the terminal O(9) is between that expected for a terminal P−OH (around 1.57 Å) and a terminal P═O (around 1.50 Å). This may indicate disorder between terminal P−OH and P═O functionalities for the O(9) position since a proton is in hydrogen-bonding contact with nitrogen of the piperazinium ion.

^{31}P MAS and CP MAS NMR measurements were undertaken to possibly verify the presence of H disorder. The ^{31}P MAS NMR spectrum (Figure 6) exhibit signals at −4.1, −1.4, and 0.1 ppm in an intensity ratio of around 15:64:21. This clearly does not correspond to three peaks in a 1:1:1 ratio which would be expected on the basis of the crystallographic data. The two peaks at −4.1 and 0.1 ppm have in sum around $^1/_3$ of the intensity and could tentatively be assigned to $H_2P(3)O_4$ and $HO_3P(3){=}O$. The protonation of phosphates generally leads to more negative chemical shift values.[42] Thus, $H_2P(3)O_4$ is assigned to the peak at −4.1 ppm. This assignment is furthermore supported by the ^{31}P CP MAS NMR spectrum (Figure 7), where the enhancement of the −4.1 ppm signal is greater than the enhancement in the 0.1 ppm signal, which indicates a larger amount of protons being involved for the −4.1 ppm signal.[43]

A consequence of these assignments is that the signal at −1.4 ppm results from overlap between signals from the unprotonated $P(1)O_4$ group and the protonated $HP(2)O_4$ group. This is surprising, since the general trend of shifts toward lower frequency at higher hydrogen levels have few exceptions. The chemical shift value of −1.4 ppm corresponds to what is observed for PO_4 groups in magnesium phosphates such as holtedahlite, phosphoellenbergerite,[44] and farringtonite.[45] The structures of holtedahlite and phosphoellenbergerite also contain HPO_4 groups, and their chemical shift values are around −8.0 ppm. The same is the case for the HPO_4 group in newberyite where a chemical shift value of −7.2 ppm is reported.[46] The reason the HPO_4 group in UiO-16 is not shifted to a more negative chemical shift value remains open, but could possibly be related to the hydrogen-bonding scheme, where water molecules and piperazinium ion are involved.

Table 4. Bond Valences for UiO-16

	P(1)	P(2)	P(3)	Mg(1)	Mg(2)	Mg(3)	Σ
O(1)	1.258				0.377		1.635
O(2)	1.248			0.409	0.385		2.042
O(3)	1.212			0.407		0.446	2.064
O(4)	1.251			0.422			2.036
				0.362			
O(5)		1.099					1.099
O(6)		1.275		0.279	0.370		1.924
O(7)		1.293		0.286		0.379	1.958
O(8)		1.255			0.347	0.328	1.930
O(9)			1.262				1.262
O(10)			1.163				1.163
O(11)			1.339		0.419		1.758
O(12)			1.372			0.509	1.881
OW1					0.077	0.347	0.423
Σ	4.969	4.922	5.136	2.165	1.974	2.009	

The hydrogen-bonding scheme in UiO-16 is quite complex, and involves the water molecule which coordinates magnesium, OW(1), the interlammellar water molecule OW(2) and the piperazinium ion. OW(1) participates in intralayer hydrogen bonds to O(1) [d(O···O) = 2.69 Å] and O(10) [d(O···O) = 2.75 Å], whereas OW2 participates in interlayer hydrogen bonds to O(10) [2 × d([O···O) = 2.58 Å] and contributes thereby to bonding the inorganic layers along [001]. Also the piperazinium ion participates in interlayer bonding since its two nitrogen atoms are anchored by hydrogen bonding to subsequent layers. The relevant hydrogen bonding contact is d[O(9)···N] = 2.86 Å, d[O(5)···N] = 2.85 Å, and d[O(11)···N] = 2.87 Å.

A bond-valence analysis[47] of UiO-16 (Table 4) gives calculated valences close to the expected values of 2 and 5 for magnesium and phosphorus, respectively. The oxygens, except for O(1), O(5), O(9), O(10), and O(11), have calculated valences close to the expected value of 2. O(1) and O(11) fulfill their valences by being involved in hydrogen-bonding interactions (see above). O(5) and O(10) are as stated above OH groups, while the valence of the disordered O(9) is fulfilled by both being a OH group and by being an acceptor of a hydrogen bond from the piperazinium ion. The piperazinium ion is partly

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protonated as a consequence of the disordered proton. Judged from the intensities in the NMR spectra (Figure 6), the occupation factor for the protonation of N is about 0.6. This means that the piperazinium ion in sum is monoprotonated, and the formula for UiO-16 will then be $[Mg_6(H_2O)_2(PO_4)_2(HPO_4)_3H_2PO_4]^-[N_2C_4H_{11}]^+H_2O$.

Compared with other layered magnesium phosphates the structure of UiO-16 is quite complex. Quite typically, the earlier known layered structures are almost all formed by vertex-sharing Mg and P coordination polyhedra. In dittmarite,[29] Mg octahedra form infinite vertex-sharing chains which are cross-linked by phosphate tetrahedra; in newberyite,[27] P tetrahedra and Mg octahedra are linked with vertex-sharing to form a 6_3 net. An exception in that respect is the structure of bobierrite[28] where edge-sharing $Mg_2O_6(H_2O)_4$ dimers are present. Clusters of edge-sharing Mg polyhedra are on the other hand more common in framework magnesium phosphates. Kovdorskite[35] is for example formed by tetramers of edge-sharing Mg octahedra which further are cross-linked by phosphate tetrahedra.

An iron phosphate[48] is isostructural to UiO-16. A number of organically templated iron phosphates have been synthesized recently, and they are also providing open framework structures.[4−6,49−51] On the basis of the successful synthesis of UiO-16, it is likely that open-framework magnesium phosphates can be synthesized. Further support for this view is the existence of a open structure for the mineral kovdorskite.

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Supporting Information Available: Crystallographic data and structure factors for UiO-16. This material is available free of charge via the Internet at http://pubs.acs.org.

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