

# Synthesis and *ab-initio* structure determination of organically templated magnesium phosphates from powder diffraction data†

Kjell Ove Kongshaug, Helmer Fjellvåg\* and Karl Petter Lillerud

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, Oslo, Norway  
N-0315. E-mail: helmer.fjellvag@kjemi.uio.no

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$\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$  (dittmarite),  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_2\text{NH}_3]^{2+} [\text{MgPO}_4 \cdot \text{H}_2\text{O}]^-$  (UiO-24-EN) and  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{MgPO}_4 \cdot \text{H}_2\text{O}]^- \cdot \text{H}_2\text{O}$  (UiO-24-DAB) were prepared by hydrothermal methods, and their structures were determined *ab-initio* from powder diffraction data. The three compounds are composed of inorganic magnesium phosphate layers separated by charge compensating ammonium or organic cations and water molecules. Corner sharing magnesium octahedra crosslinked by phosphate tetrahedra form the inorganic layers in dittmarite. This atomic arrangement is identical in the UiO-24 type of compounds, and these structures can be viewed as dittmarite being intercalated by diamines and water molecules. The compounds have been characterized by thermogravimetric analysis, solid-state  $^{31}\text{P}$  MAS NMR spectroscopy and ion exchange experiments.

## Introduction

Metal phosphates offer a variety of crystal structures where the combination of chemical properties and structural topology can give rise to practical applications such as ionic exchange, ionic conductivity and catalysis. Some phosphates form 2D layered structures and are hence attractive for intercalation. Extensive intercalation studies have been carried out on *e.g.* layered vanadyl phosphates<sup>1</sup> and  $\alpha$ -zirconium phosphates.<sup>2</sup> The insertion of organic molecules into layered hosts has been of particular interest because such hybrid organic–inorganic materials might have enhanced properties relative to that achievable with either the guest or the host alone. The common method for intercalating organic molecules into a layered host is a direct heterogeneous reaction of the guest with the host lattice. This results in products which usually are not very crystalline and definite structural information about the arrangement of the organic molecules in the interlamellar space cannot be obtained. Recently, hydrothermal methods have opened up synthesis routes towards highly crystalline hybrid organic–inorganic materials.<sup>3–5</sup>

Ammonium phosphates with the general formula  $\text{NH}_4\text{M}^{\text{II}}\text{PO}_4 \cdot \text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Fe, Ni, Co}$ ) are well known.<sup>6</sup> The crystal structures of the transition metal variants have been refined from neutron powder diffraction data and their magnetic properties have been studied.<sup>7</sup> All these compounds are isostructural and crystallize in the space group  $Pmn2_1$ . They are composed of inorganic metal phosphate layers separated by ammonium cations. The magnesium variant  $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$  is found in nature as the mineral dittmarite.<sup>8</sup> Its structure has not yet been refined, however, it is assumed to be isostructural with the transition metal analogues.<sup>9</sup>

The present paper describes the synthesis and structure determination of dittmarite and two new organically templated layered magnesium phosphates denoted UiO-24. The UiO-24 type of compounds have an identical atomic arrangement in the inorganic layers as dittmarite and can be viewed as dittmarite being intercalated with diamines like ethylenediamine (UiO-24-EN) and 1,4-diaminobutane (UiO-24-DAB). Together with the recently reported UiO-16,<sup>10</sup> the UiO-24 type

of compounds are the only examples of organically templated magnesium phosphates.

## Experimental

### Syntheses

The materials were synthesized by the reaction between  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$  (85%), diamine and  $\text{H}_2\text{O}$ . The use of ethylenediamine as a template and a molar reactant ratio of 1 : 1.5 : 3 : 50 gave UiO-24-EN as product, whereas the use of 1,4-diaminobutane and molar reactant ratios of 1 : 2 : 3 : 50 and 0.67 : 2 : 3 : 50 resulted in UiO-24-DAB and dittmarite, respectively. The reactions were carried out under hydrothermal conditions at 150 °C (UiO-24-EN and UiO-24-DAB) and at 180 °C (dittmarite) for 24 h in Teflon-lined steel autoclaves followed by quenching in water, filtration and drying in air. All products were white powders with crystallites too small for conventional single-crystal X-ray analysis.

### Powder X-ray diffraction data collection

X-Ray powder diffraction patterns for the compounds were collected on a Siemens D5000 diffractometer equipped with an incident beam germanium monochromator ( $\text{CuK}\alpha_1$  radiation) and a Braun position sensitive detector. The patterns were collected at 25 °C in transmission mode with the samples in rotating 0.5 mm diameter borosilicate capillaries. The counting time was 15 s/step and data were typically collected between  $2\theta = 5$  and  $90^\circ$ , see Table 1.

### Thermal analysis

Thermogravimetric analysis (TGA) was performed on a Scientific Rheometric STA 1500. Samples with weights  $\approx 20$  mg were heated to 800 °C in a nitrogen gas flow at a rate of  $5^\circ\text{C min}^{-1}$ .

### Solid-state NMR spectroscopy

$^{31}\text{P}$  High-power  $^1\text{H}$  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 spectra were

†Electronic supplementary information (ESI) available: powder diffraction data. See <http://www.rsc.org/suppdata/jm/b0/b001715i/>

**Table 1** Experimental conditions and relevant data for the Rietveld refinements of dittmarite, UiO-24-EN and UiO-24-DAB. Calculated standard deviations in parentheses

	Dittmarite	UiO-24-EN	UiO-24-DAB
Pattern range $2\theta/^\circ$	8–90	8–90	5–90
Step size $\Delta 2\theta/^\circ$	0.015552 <sup>a</sup>	0.015552 <sup>a</sup>	0.015552 <sup>a</sup>
Wavelength/ $\text{\AA}$	1.540598	1.540598	1.540598
Space group	$Pmn2_1$	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	5.61120(3)	5.66319(5)	5.60237(5)
$b/\text{\AA}$	8.76358(7)	19.2965(2)	27.8965(3)
$c/\text{\AA}$	4.78963(3)	4.79259(4)	4.78115(4)
$\beta/^\circ$		92.4407(7)	91.9697(8)
$Z$	2	4	4
$V/\text{\AA}^3$	235.526(3)	523.257(9)	746.792(13)
No. of observations	5257	5257	5450
No. of reflections	132	440	626
No. of refined parameters	58	90	97
$R_{\text{wp}}$	0.0403	0.0540	0.0394
$R_{\text{F}}^2$	0.0417	0.0354	0.0531

<sup>a</sup>Defined by the PSD setting.

collected in 16 scans with repetition times of 300 s. The chemical shifts are defined relative to an 85%  $\text{H}_3\text{PO}_4$  standard.

### Ion-exchange experiments

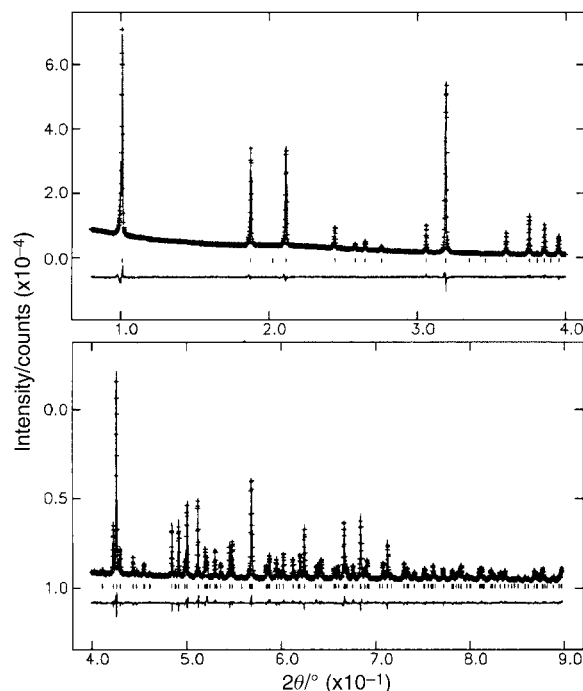
Ion-exchange reactions were attempted by stirring *ca.* 0.1 g of either UiO-24-EN or UiO-24-DAB in 2 M aqueous solutions of the appropriate metal salt at room temperature and at 70 °C for 48 h. Metals used were  $\text{Na}^+$  (NaCl),  $\text{K}^+$  ( $\text{KNO}_3$ ),  $\text{Co}^{2+}$  ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) and  $\text{Ni}^{2+}$  ( $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ). After the experiments, powder XRD experiments were performed on the samples.

### Structure solution

The powder diffraction patterns were indexed on the basis of the 20 first well-resolved Bragg reflections using the program TREOR90.<sup>11</sup> For UiO-24-EN the best solution gave a monoclinic unit cell:  $a=5.662 \text{ \AA}$ ,  $b=19.293 \text{ \AA}$ ,  $c=4.792 \text{ \AA}$  and  $\beta=92.432^\circ$  ( $M_{20}=112$ ). The systematic absences were consistent with space group  $P2_1/n$  ( $h0l$  absent for  $h+l=2n+1$ , and  $0k0$  absent for  $k=2n+1$ ). Also UiO-24-DAB was found to take a monoclinic unit cell:  $a=5.6076 \text{ \AA}$ ,  $b=27.923 \text{ \AA}$ ,  $c=4.783 \text{ \AA}$  and  $\beta=91.971^\circ$  ( $M_{20}=48$ ), and the systematic absences indicated again space group  $P2_1/n$ . Dittmarite was indexed on an orthorhombic unit cell:  $a=5.609 \text{ \AA}$ ,  $b=8.761 \text{ \AA}$  and  $c=4.788 \text{ \AA}$  ( $M_{20}=174$ ). The systematic absences were consistent with space group  $Pmn2_1$  ( $h0l$  absent for  $h+l=2n+1$ ).

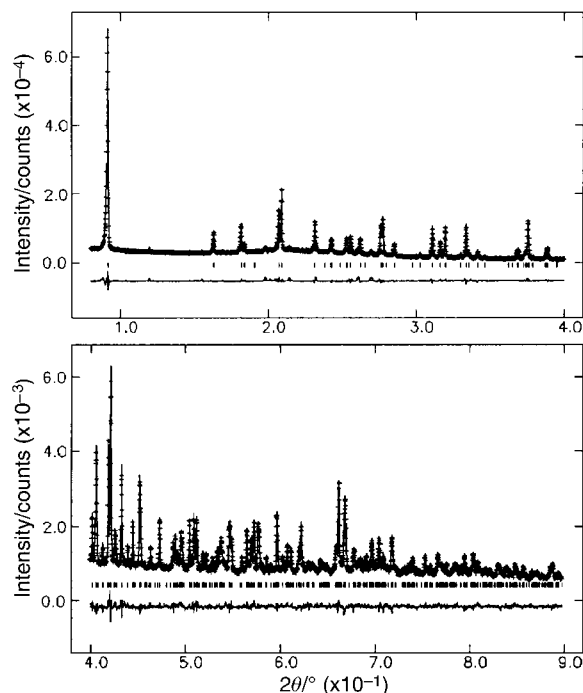
The crystal structure solution of UiO-24-EN,  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{MgPO}_4 \cdot \text{H}_2\text{O}]$ , and UiO-24-DAB,  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}[\text{MgPO}_4 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$  followed almost exactly the same procedure. The intensities were extracted by means of EXTRA<sup>12</sup> using the LeBail method.<sup>13</sup> These were transferred to the direct methods program SIRPOW92<sup>14</sup> by means of EXPO,<sup>15</sup> which connects the two programs. In both cases, all atoms could be located in the E-map with the highest figure-of-merit. For dittmarite, a starting model for the refinement was built on the basis of the single-crystal structure of  $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ .<sup>16</sup>

Rietveld refinements for the three structures were carried out using the program GSAS.<sup>17</sup> Initial profile parameters were in all cases obtained by fitting the observations according to the LeBail method.<sup>13</sup> Initially the refinements included scale, background, zero-point and lattice parameters. The atomic coordinates were thereafter refined with soft constraints included:  $d(\text{P}-\text{O})=1.54 (\pm 2)$  and  $d(\text{Mg}-\text{O})=2.10 (\pm 5) \text{ \AA}$  in all three structures and in addition  $d(\text{C}-\text{N})=1.48 (\pm 2)$  and  $d(\text{C}-\text{C})=1.52 (\pm 2) \text{ \AA}$  for UiO-24-EN and UiO-24-DAB. Common isotropic displacement parameters were



**Fig. 1** Observed, calculated and difference diffraction profiles for dittmarite.

adopted for the O atoms of the phosphate tetrahedra and likewise for the C and N of the template molecules for UiO-24-EN and UiO-24-DAB. The soft constraint weight could be lifted completely as the refinement progressed. In all three cases, the displacement parameters of the interlamellar species came out negative. Hydrogen atoms were therefore placed geometrically for these species and refined with soft constraints  $d(\text{C}-\text{H})=1.07 (\pm 1)$ ,  $d(\text{O}-\text{H})=1.03 (\pm 1)$  and  $d(\text{N}-\text{H})=1.03 (\pm 1) \text{ \AA}$ . A constant common displacement parameter of 0.03 was given to the hydrogen atoms. All three refinements converged to satisfactory residual factors. Details of the refinements are given in Table 1. Final Rietveld plots for the



**Fig. 2** Observed, calculated and difference diffraction profiles for UiO-24-EN.

**Table 2** Atomic coordinates and isotropic displacement parameters for dittmarite,  $\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$ . Calculated standard deviations in parentheses. Space group  $Pmm2_1$ . O3, H3 and H4 in 4b sites, the remaining in 2a sites

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/\text{\AA}^2$
P	0	0.8099(2)	0.8833(11)	0.022(1)
Mg	0	0.0210(2)	0.4482(10)	0.025(1)
O1	0	0.6354(4)	0.8211(12)	0.021(1)
O2	0	0.8332(4)	0.2023(10)	0.021(1)
O3	0.2184(4)	0.8858(3)	0.7421(10)	0.021(1)
OW	0	0.2034(5)	0.7477(12)	0.025(1)
N	0	0.4747(7)	0.3258(13)	0.030(2)
H1	0	0.501(5)	0.543(4)	0.03 <sup>a</sup>
H2	0	0.531(4)	0.137(5)	0.03 <sup>a</sup>
H3	0.367(4)	0.601(3)	0.781(6)	0.03 <sup>a</sup>
H4	0.353(4)	0.842(3)	0.344(6)	0.03 <sup>a</sup>

<sup>a</sup>Fixed, see text.

refinements are shown in Figs. 1–3. Atomic coordinates, isotropic displacement parameters and selected bond distances and angles are given in Tables 2–7.

## Results and discussion

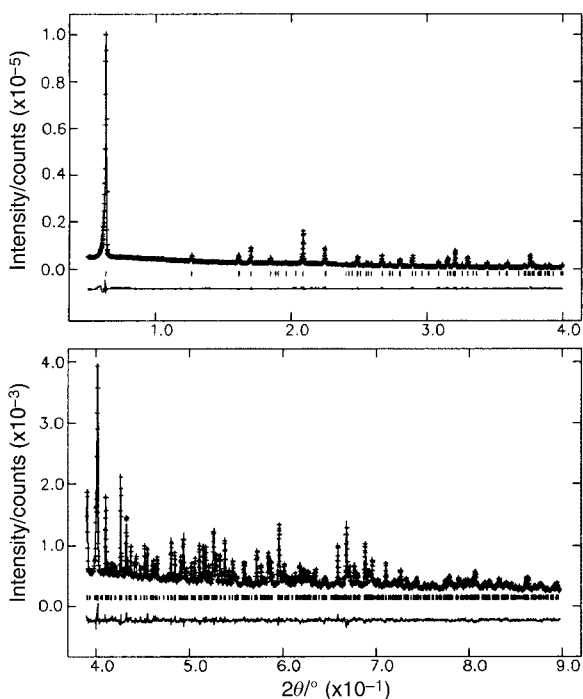
### Crystal structures

Dittmarite was found to be isostructural with ammonium phosphates having the general formula  $\text{NH}_4\text{M}^{\text{II}}\text{PO}_4\cdot\text{H}_2\text{O}$  ( $\text{M}^{\text{II}}=\text{Mn, Fe, Ni, Co}$ ),<sup>6</sup> and it exhibits a layered structure with magnesium phosphate sheets separated by  $\text{NH}_4^+$  cations (Fig. 4a). The inorganic layers are formed by corner sharing magnesium octahedra crosslinked by phosphate tetrahedra (Fig. 5). The magnesium octahedra are distorted with  $d(\text{Mg}-\text{O})$  in the range 2.024(4)–2.211(3) Å and  $\angle(\text{O}-\text{Mg}-\text{O})$  in the range 67.34(15)–101.92(17)° and 162.71(15)–173.67(21)°. Five of the vertices in the octahedra are connected to the  $\text{PO}_4$  groups whereas the last terminal vertex is a water molecule. The phosphate tetrahedra are more regular with  $d(\text{P}-\text{O})$  in the range 1.542(3)–1.558(4) Å and  $\angle(\text{O}-\text{P}-\text{O})$  in the range 104.52(19)–112.06(14)°. They are bridged *via* corner and edge sharing by three oxygen atoms to the magnesium octahedra, see Fig. 5. The fourth oxygen is terminal, and is directed

towards the interlayer space. Here its valence is fulfilled by being recipient of four hydrogen-bonding interactions from the ammonium ion [ $2 \times d(\text{N}\cdots\text{O}1)=2.81(4)$  and  $2 \times d(\text{N}\cdots\text{O}1)=2.98(4)$  Å].

The UiO-24 compounds represent layered structures with magnesium phosphate sheets stacked along [010], separated by organic species and water molecules, and are monoclinic distortions of the orthorhombic dittmarite structure, see Figs. 4b and 4c. The organic template introduces geometrical constraints and lowers the symmetry. However, the crystal structure of the inorganic magnesium phosphate layers  $\text{MgPO}_4\cdot\text{H}_2\text{O}^-$  for the UiO-24 compounds is essentially identical to that in dittmarite. The symmetry reduction results in more irregular Mg octahedra. In dittmarite the four equatorial Mg–O3 bonds are paired in two,  $d(\text{Mg}-\text{O})=2.034(2)$  and  $d(\text{Mg}-\text{O})=2.211(3)$  Å. In both UiO-24 compounds, the equatorial bonds relate to two non-equivalent oxygen atoms, O3 and O4, and the bond distances are in the range 2.046(4)–2.330(4) Å in UiO-24-EN and 2.038(5)–2.300(5) Å in UiO-24-DAB, see Tables 5 and 7.

In the UiO-24 compounds, the organic species have quite different orientations relative to the inorganic layers. In UiO-24-EN the ethylenediamine molecules are oriented almost parallel to the inorganic magnesium phosphate layers, Fig. 4b. They are most probably doubly protonated with three hydrogen bonding contacts between each nitrogen and the terminal oxygen of the phosphate tetrahedra;  $d(\text{N}\cdots\text{O}1)=2.71(4)$ , 2.72(4) and 2.91(4) Å. In UiO-24-DAB on the other hand, the orientation of the 1,4-diaminobutane molecules are almost perpendicular to the inorganic layers, Fig. 4c. Each nitrogen of the molecules has just two hydrogen bonding contacts to the terminal oxygen atoms;  $d(\text{N}\cdots\text{O}1)=2.80(5)$  and 2.81(5) Å. The third H connected to N is directed towards OW1;  $d(\text{N}\cdots\text{O}1)=3.27(5)$  Å.



**Fig. 3** Observed, calculated and difference diffraction profiles for UiO-24-DAB.

**Table 3** Selected bond distances (Å) and angles (°) for dittmarite,  $\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$ . Calculated standard deviations in parentheses

P–O1	1.558(4)	O2–Mg–O3	86.24(14)
P–O2	1.542(3)	O3–Mg–O3	101.92(17)
P–O3	1.550(3) × 2	O2–Mg–O3	92.52(11)
		O3–Mg–OW	91.46(13)
Mg–O2	2.024(4)	O2–Mg–OW	173.67(21)
Mg–O3	2.211(3) × 2	O3–Mg–O3	67.34(15)
Mg–O3	2.034(2) × 2	O3–Mg–O3	162.71(15)
Mg–OW	2.147(5)	O3–Mg–OW	88.49(13)
		O3–Mg–O3	95.37(6)
O1–P–O2	108.62(18)	O3–Mg–O3	162.71(15)
O1–P–O3	109.75(13) × 2		
O2–P–O3	112.06(14) × 2		
O3–P–O3	104.52(19)		

**Table 4** Atomic coordinates and isotropic displacement parameters for UiO-24-EN,  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_2\text{NH}_3]^{2+} [\text{MgPO}_4 \cdot \text{H}_2\text{O}]$ . Calculated standard deviations in parentheses. Space group  $P2_1/n$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/\text{\AA}^2$
P	0.0616(3)	0.1637(1)	0.3135(4)	0.022(1)
Mg	0.0651(4)	0.2603(1)	0.8733(4)	0.024(1)
O1	0.0725(6)	0.0850(2)	0.2560(9)	0.018(1)
O3	0.8302(6)	0.1954(2)	0.1735(7)	0.018(1)
O2	0.0664(6)	0.1751(2)	0.6298(7)	0.018(1)
O4	0.2711(6)	0.1991(2)	0.1827(7)	0.018(1)
OW	0.0625(7)	0.3409(2)	0.1783(7)	0.021(1)
N	0.7296(9)	0.4763(3)	0.2866(10)	0.022(1)
C	0.9744(12)	0.4985(3)	0.3406(12)	0.022(1)
H1	0.381(6)	0.4806(15)	0.739(8)	0.03 <sup>a</sup>
H2	0.351(6)	0.5540(17)	0.560(6)	0.03 <sup>a</sup>
H3	0.280(7)	0.5474(18)	0.905(5)	0.03 <sup>a</sup>
H4	0.036(9)	0.4505(12)	0.758(10)	0.03 <sup>a</sup>
H5	0.895(5)	0.5301(17)	0.765(8)	0.03 <sup>a</sup>
H6	0.408(5)	0.1633(23)	0.787(8)	0.03 <sup>a</sup>
H7	0.679(6)	0.1698(22)	0.840(7)	0.03 <sup>a</sup>

<sup>a</sup>Fixed, see text.

### Thermogravimetric analysis

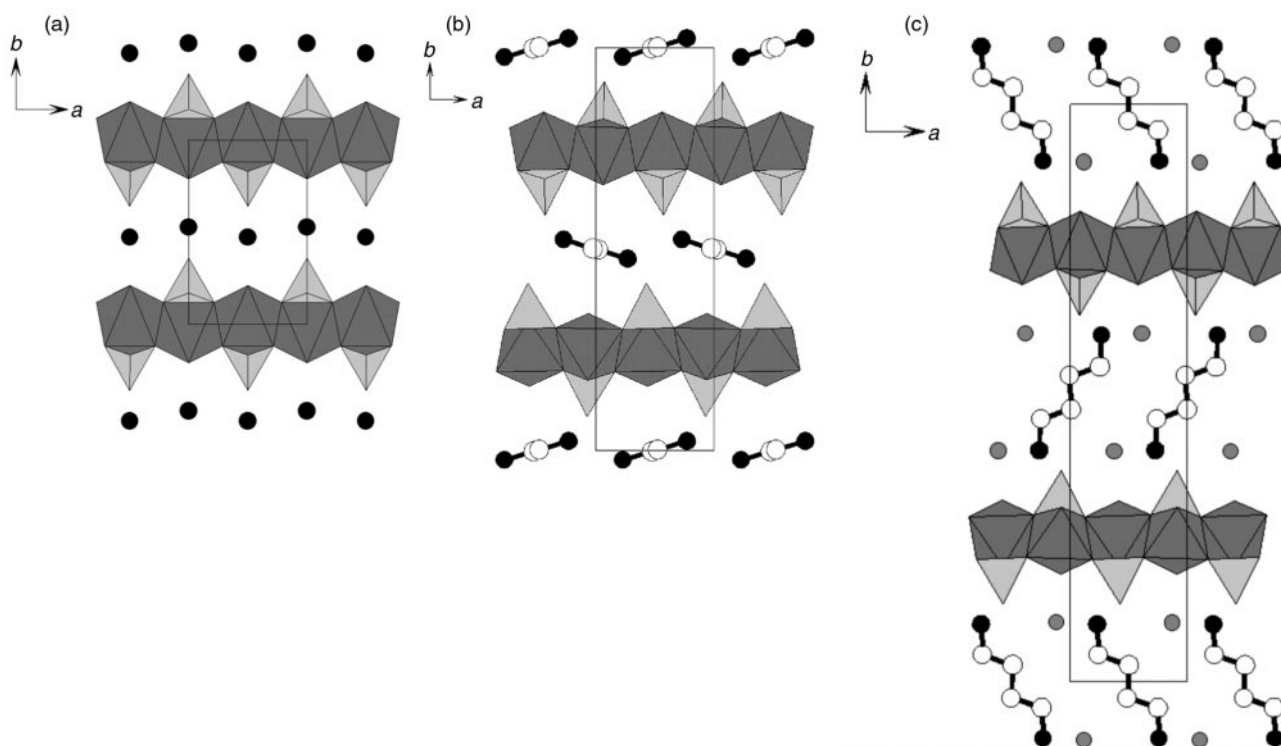
The TG curves for the three compounds are presented in Fig. 6. Dittmarite shows a single weight loss of 22.9% in the range 190–325 °C. This is consistent with the loss of water and ammonia molecules in the structure (calc. 22.6%). The further gradual weight loss reflects phosphate group dimerisation, which finally results in magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , at temperatures above 650 °C.

Both UiO-24 compounds show a two step weight loss, Fig. 6. The first step of 10.0% for UiO-24-EN and 17.3% for UiO-24-DAB below 190 °C is attributed to the loss of the water molecules (calc. 10.7 and 18.5%, respectively). Powder X-ray diffraction data for the residual products show poorly crystalline materials, and the powder patterns could not be indexed. The second weight loss of 16.2 and 21.7% for UiO-24-EN and -DAB, respectively, above 290 °C corresponds to the loss of the

organic templates (calc. 18.4 and 22.0%, respectively). This results first in amorphisation of the materials, thereafter a continued weight loss occurs prior to crystallization of magnesium pyrophosphate at around 750 °C.

### Solid-state $^{31}\text{P}$ MAS NMR

The solid-state  $^{31}\text{P}$  MAS NMR spectra for all three compounds (Fig. 7) exhibit one resonance in accordance with just one crystallographic P site in each compound. The isotropic chemical shift values of 6.2, 4.3 and 6.5 ppm for dittmarite, UiO-24-EN and UiO-24-DAB, respectively, are within the range (–30 to 12 ppm) reported for a large number of orthophosphates.<sup>18</sup> Other magnesium phosphates like holtedahlite and newberyite also have  $\text{PO}_4$  groups with one terminal oxygen. Since the latter represent protonated  $\text{HPO}_4$  groups, the



**Fig. 4** Polyhedral representation along [001] of (a) dittmarite, (b) UiO-24-EN and (c) UiO-24-DAB.  $\text{MgO}_6$  octahedra with darker shading,  $\text{PO}_4$  tetrahedra with lighter shading, C atoms with open circles, O atoms with light shading and N atoms with closed circles.

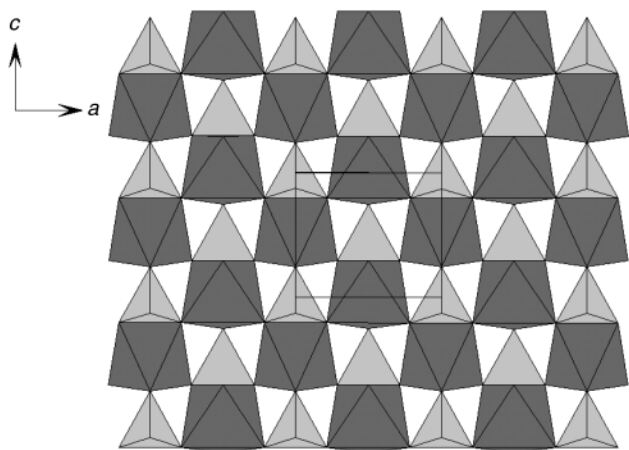
**Table 5** Selected bond distances (Å) and angles (°) for UiO-24-EN  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_2\text{NH}_3]^{2+}[\text{MgPO}_4 \cdot \text{H}_2\text{O}]^-$ . Calculated standard deviations in parentheses

P–O1	1.546(3)	O3–Mg–O3	163.98(20)
P–O2	1.529(3)	O3–Mg–O2	86.29(16)
P–O3	1.530(4)	O3–Mg–O4	65.40(14)
P–O4	1.527(3)	O3–Mg–O4	91.37(15)
		O3–Mg–OW	87.07(15)
Mg–O2	2.016(4)	O3–Mg–O2	92.77(16)
Mg–O3	2.046(4)	O3–Mg–O4	98.59(15)
Mg–O3	2.330(4)	O3–Mg–O4	104.64(17)
Mg–O4	2.192(3)	O3–Mg–OW	92.46(18)
Mg–O4	2.023(3)	O2–Mg–O4	86.44(15)
Mg–OW	2.136(5)	O2–Mg–O4	94.47(15)
		O2–Mg–OW	172.17(19)
N–C	1.462(7)	O4–Mg–O4	156.67(21)
C–C	1.544(12)	O4–Mg–OW	87.02(15)
		O4–Mg–OW	89.83(18)
O1–P–O2	110.68(24)		
O1–P–O3	108.57(21)	N–C–C	108.9(6)
O1–P–O4	109.19(21)		
O2–P–O3	110.92(22)		
O2–P–O4	106.31(19)		
O3–P–O4	111.15(22)		

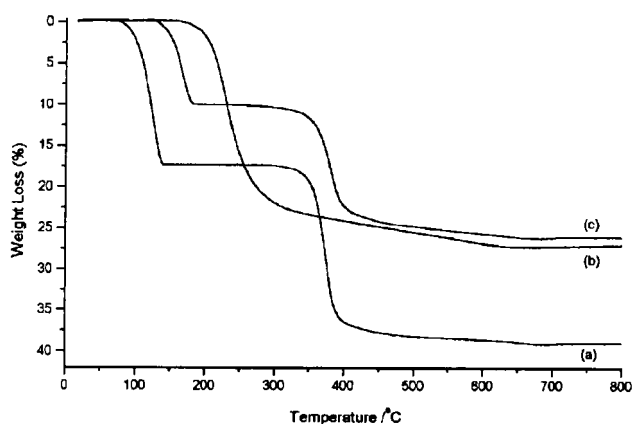
**Table 6** Atomic coordinates and isotropic displacement parameters for UiO-24-DAB  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}[\text{MgPO}_4 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ . Calculated standard deviations in parentheses. Space group  $P2_1/n$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/\text{Å}^2$
P	0.4138(5)	0.18956(10)	0.0495(6)	0.0180(9)
Mg	0.4186(6)	0.25652(12)	−0.3839(7)	0.0203(11)
O1	0.4235(10)	0.13464(21)	−0.0036(13)	0.0170(10)
O2	0.4224(10)	0.19784(22)	0.3620(11)	0.0170(10)
O3	0.1891(10)	0.21191(18)	−0.0907(12)	0.0170(10)
O4	0.6256(10)	0.21443(18)	−0.0864(12)	0.0170(10)
OW1	0.9142(10)	0.18707(23)	0.4273(12)	0.0146(19)
OW2	−0.1187(10)	0.10140(21)	0.9594(12)	0.0290(23)
N	0.2426(15)	0.09784(29)	0.4893(17)	0.0259(17)
C1	0.2476(16)	0.0449(4)	0.4981(22)	0.0259(17)
C2	0.5055(18)	0.02860(31)	0.4957(21)	0.0259(17)
H1	0.274(10)	0.1104(13)	0.296(5)	0.03 <sup>a</sup>
H2	0.315(11)	0.1126(13)	0.662(6)	0.03 <sup>a</sup>
H3	0.114(8)	0.0350(23)	0.339(8)	0.03 <sup>a</sup>
H4	0.148(9)	0.0429(24)	0.686(6)	0.03 <sup>a</sup>
H5	0.636(8)	0.0377(23)	0.659(7)	0.03 <sup>a</sup>
H6	0.585(9)	0.0390(22)	0.303(6)	0.03 <sup>a</sup>
H7	0.773(7)	0.1967(22)	0.552(11)	0.03 <sup>a</sup>
H8	0.872(12)	0.1507(7)	0.405(12)	0.03 <sup>a</sup>
H9	0.061(11)	0.1100(26)	0.525(15)	0.03 <sup>a</sup>

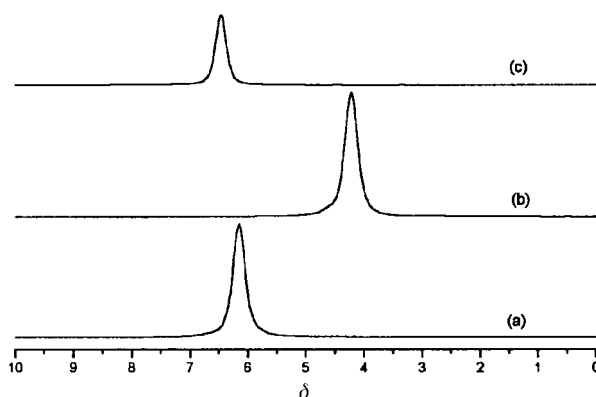
<sup>a</sup>Fixed, see text.



**Fig. 5** Polyhedral representation of dittmarite along [010] showing infinite chains of MgO<sub>6</sub> octahedra crosslinked by PO<sub>4</sub> tetrahedra. MgO<sub>6</sub> octahedra with darker shading and PO<sub>4</sub> tetrahedra with lighter shading.



**Fig. 6** TG curves of (a) UiO-24-DAB, (b) dittmarite and (c) UiO-24-EN. Heating rate 5 K min<sup>−1</sup> in an N<sub>2</sub> atmosphere.



**Fig. 7** <sup>31</sup>P MAS NMR spectra of (a) dittmarite, (b) UiO-24-EN and (c) UiO-24-DAB.

**Table 7** Selected bond distances (Å) and angles (°) for UiO-24-DAB,  $0.5 \cdot [\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}[\text{MgPO}_4 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ . Calculated standard deviations in parentheses

P–O1	1.554(6)	O2–Mg–O3	86.92(26)
P–O2	1.511(6)	O2–Mg–O3	91.99(26)
P–O3	1.538(6)	O2–Mg–O4	86.53(28)
P–O4	1.538(5)	O2–Mg–O4	93.46(25)
		O2–Mg–OW1	173.19(32)
Mg–O2	2.039(6)	O3–Mg–O3	165.96(31)
Mg–O3	2.300(5)	O3–Mg–O4	66.54(23)
Mg–O3	2.038(5)	O3–Mg–O4	92.67(24)
Mg–O4	2.152(6)	O3–Mg–OW1	87.40(24)
Mg–O4	2.045(6)	O3–Mg–O4	99.42(26)
Mg–OW1	2.166(7)	O3–Mg–O4	101.37(27)
		O3–Mg–OW1	92.61(29)
N–C1	1.479(12)	O4–Mg–O4	159.20(33)
C1–C2	1.515(12)	O4–Mg–OW1	87.77(25)
C2–C2	1.597(17)	O4–Mg–OW1	90.55(27)
O1–P–O2	108.20(34)	N–C1–C2	108.4(8)
O1–P–O3	111.16(35)	C1–C2–C2	105.2(10)
O1–P–O4	110.1(4)		
O2–P–O3	111.5(4)		
O2–P–O4	110.51(35)		
O3–P–O4	105.35(33)		

chemical shift values are shifted to lower values,<sup>19</sup> with  $-7.2$  ppm for newberyite<sup>18</sup> and  $-7.0$  ppm for holtedahlite.<sup>20</sup>

### Ion-exchange experiments

UiO-24-EN and UiO-24-DAB showed no ion-exchange behaviour towards Na<sup>+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>. The powder XRD patterns of the samples after the ion-exchange experiments at room temperature were identical to the original patterns of

UiO-24-EN and UiO-24-DAB. Experiments at 70 °C resulted in amorphisation of the samples. The ion-exchange experiments using  $K^+$  resulted in formation of the compound  $KMgPO_4 \cdot 6H_2O^{21}$  which is composed of  $K^+$  cations and unconnected  $PO_4$  tetrahedra and  $Mg(H_2O)_6$  octahedra.

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