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The synthesis and crystal structure of a new open-framework zincophosphate UiO-17

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A novel three-dimensional open-framework zincophosphate $2[N_2C_4H_{12}]^{2+}[Zn_7(H_2O)_2(PO_4)_6]^{4-}$ has been synthesised hydrothermally, and characterised by powder and single crystal X-ray diffraction, thermogravimetric analysis and solid state ^{31}P MAS and ^{13}C CP MAS NMR spectroscopy. The compound crystallises in the monoclinic space group $C2/c$ with $a = 16.134(3)$, $b = 8.241(2)$, $c = 22.860(5)$ Å, $\beta = 104.05(3)°$, $V = 2948.4(10)$ Å^3 and $Z = 4$. The open framework contains a two-dimensional staggered eight-membered ring channel system running along [001] and [011] in which diprotonated piperazinium cations reside. The framework consists of ZnO_4 and PO_4 tetrahedral units, in addition there are $ZnO_4(H_2O)$ trigonal bipyramids which together with Zn–O–Zn bonding lead to an interrupted framework rather than alternating ZnO_4 and PO_4 linkages. The framework is an example of symmetry matching between template and framework as a symmetry element of piperazine constrains the framework structure.

Introduction

Open framework zincophosphates synthesised in the presence of organic templates form a growing family of compounds. These materials are all obtained *via* hydrothermal synthesis, and are excellent examples of how a large number of metastable phases can be isolated. A common feature of these compounds is a negatively charged framework which is hydrogen bonded to charge compensating protonated amines. In many cases there appears to be a relation between the charge, shape and volume of the organic template and the architecture of the zincophosphate framework.

Structural diversity among organically templated zincophosphates is substantial. In these, the zinc coordination is tetrahedral and there exists just one example of a zeolite-like, tetrahedral, fully alternating Zn/P framework topology.[1] In all the other structures, the open framework is so called interrupted. The most common framework interruption is the presence of terminal P–OH or P=O groups[2–9] leading to structures with molar Zn/P ratios of <1. Interruption also arises by terminal water molecules being bonded to tetrahedral zinc atoms[2,4,10] and in one structure type[11] the interruption is by a terminal Zn–OH_2 unit. In addition Zn–O–Zn connections leading to formation of tetrahedral three-rings and infinite Zn–O–Zn chains can occur.[12–16] There are also examples of structures where nitrogen of the organic template is involved in coordination to zinc.[10,16]

The present paper reports on the synthesis and crystal structure of a new open framework zincophosphate templated by piperazine. Its structure contains terminal Zn–OH_2 units, Zn–O–Zn connections leading to tetrahedral three rings, and also five coordinate Zn, a hitherto unknown structural element in open-framework zincoposhates.

Experimental

Synthesis

Single crystals of UiO-17 were obtained by mixing zinc acetate (98%, Fluka), phosphoric acid (85 wt%, Fluka), piperazine hexahydrate (99%, Fluka) and water in a molar ratio 2.0 ZnO : 1.0 P_2O_5 : 1.5 piperazine : 50 H_2O. The mixture, with a pH of 5.2, was transferred to a Teflon-lined steel autoclave, and placed in an oven for 4 days at 180 °C. After the reaction the supernatant liquid had a pH of 4.65. The obtained product which was in the form of large crystals up to several millimeters in size, was filtered off, washed with water and dried at 80 °C overnight. The estimated yield based on Zn was *ca.* 41%.

Powder X-ray diffraction

The powder X-ray pattern was collected on a Siemens D5000 diffractometer in transmission geometry using a 0.5 mm borosilicate capillary. The diffractometer was equipped with a Ge primary monochromator giving Cu-Kα_1 radiation and a Brown PSD detector.

Thermogravimetric analysis (TGA)

TGA was performed on a Stanton Redcroft STA 625 instrument. The sample was heated from room temperature to 600 °C at a rate of 5 K min^{-1} in a nitrogen gas flow.

Solid state MAS NMR spectroscopy

Solid state ^{31}P MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a Bruker DMX-200 spectrometer. The recording conditions are given in Table 1.

Single crystal structure determination

A suitable single crystal was fixed to a thin glass fibre and mounted on a Siemens Smart CCD diffractometer. A total of

Table 1 Recording conditions for MAS NMR data

	^{13}C	^{31}P
Standard	$Si(CH_3)_4$	H_3PO_4, (85%)
Frequency/MHz	50.31	80.98
Pulse width/μs	6	7
Acquisition time/s	0.6554	1.0617
Repetition time/s	3	100
Contact time/ms	1	—
Sweep width/Hz	30864	50000
MAS spinning speed/kHz	8.0	8.0
Number of scans	15000	16

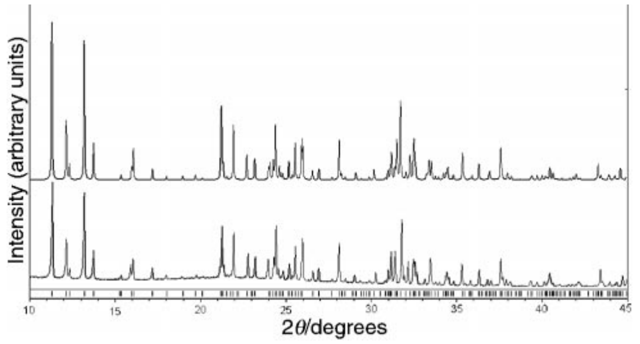

Fig. 1 Experimental (bottom) and simulated (top) powder X-ray diffraction patterns of UiO-17. Vertical bars represent positions for Bragg reflections.

1525 frames were collected at 150 K, thereby covering one hemisphere of the reciprocal space ($\Delta\theta = 0.3°$; 30 s per frame). Data reduction was carried out with the SAINT software,[17] and empirical absorption correction was carried out using the program SADABS.[18] The observed systematic absences were consistent with the space groups *Cc* and *C*2/*c*. The crystal structure was solved in space group *C*2/*c* by direct methods followed by difference Fourier methods. No hydrogen positions could be located. For the piperazinium cation hydrogen atoms were placed geometrically and refined in riding mode. All calculations were performed using the SHELXTL program package.[19] Final least squares refinements included extinction correction, anisotropic displacement parameters for non-hydrogen atoms and fixed isotropic displacement parameters for hydrogen atoms. A summary of experimental data and refinement parameters is given in Table 2. Atomic coordinates and displacement parameters are listed in Table 3, selected bond distances and angles are given in Table 4.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/189.

Table 2 Crystal data and parameters relevant for the structure refinement of UiO-17

Empirical formula	$Zn_7P_6O_{26}N_4C_8H_{28}$
Formula weight	1239.75
Temperature/K	150
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a/Å	16.134(3)
b/Å	8.241(2)
c/Å	22.860(5)
β/°	104.05(3)
V/Å^3	2948.4(10)
Z	4
D_c/g cm^{-3}	2.793
μ/mm^{-1}	6.039
$F(000)$	2448
Crystal size/mm^3	$0.1 \times 0.1 \times 0.15$
θ range for data collection/°	2.60–40.32
Index ranges, *hkl*	−29 to 29, −14 to 14, −41 to 40
Reflections collected	30302
Independent reflections (R_{int})	8890 (0.0410)
Reflections observed ($>2\sigma$)	8039
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	8890/0/233
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0344$ $wR_2 = 0.0909$
R indices (all data)	$R_1 = 0.0394$ $wR_2 = 0.0932$
Largest diff. peak, hole/e Å^{-3}	1.931, −1.166

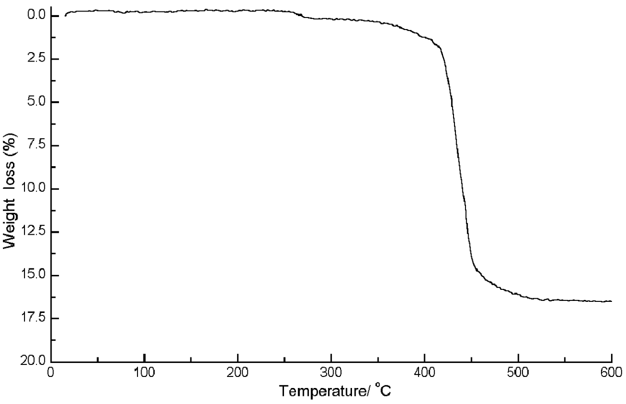

Fig. 2 TG curve for UiO-17, $2[N_2C_4H_{12}]^{2+}[Zn_7(H_2O)_2(PO_4)_6]^{4-}$, heated at a rate of 5 K min^{-1} in nitrogen flow.

See http://www.rsc.org/suppdata/jm/1999/3119/ for crystallographic files in .cif format.

Results

A comparison of the experimental powder X-ray pattern and that simulated on the basis of the single crystal structure determination using the POWDER CELL program,[20] shows a close correspondence (Fig. 1) and establishes that the crystal chosen for the X-ray analysis is representative of the bulk sample.

The TGA curve (Fig. 2) shows a weight loss of 16.55% at *ca.* 440 °C. This loss corresponds well to the release of two water molecules and two piperazinium cations (calculated loss 17.12%) with respect to the formula $2[N_2C_4H_{12}]^{2+}$-$[Zn_7(H_2O)_2(PO_4)_6]^{4-}$ as determined by the single-crystal analysis. The material became amorphous during decomposition. In addition there was a small weight loss of *ca.* 0.4% around 270 °C probably due to an impurity phase.

Crystal structure

The UiO-17 material, $2[N_2C_4H_{12}]^{2+}[Zn_7(H_2O)_2(PO_4)_6]^{4-}$ is a new open framework zincophosphate. The asymmetric unit of the structure contains four non-equivalent zinc atoms, three phosphate groups, one water molecule and two nitrogen and four carbon atoms belonging to the piperazinium cation. The coordination environments of Zn and P are shown in Fig. 3. One of the zinc atoms, Zn(4), is located on a twofold axis and is tetrahedrally coordinated by four oxygen atoms of the phosphate groups. The same coordination feature applies for

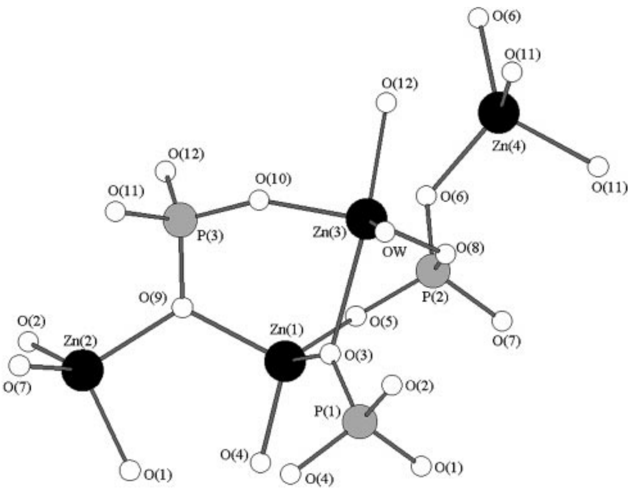

Fig. 3 Coordination environment for non-equivalent Zn and P atoms in UiO-17.

Table 3 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for UiO-17. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Calculated standard deviations in parentheses

Atom	x	y	z	U_{eq}
Zn(1)	0.1985(1)	0.1553(1)	0.0737(1)	0.005(1)
Zn(2)	−0.1489(1)	0.3507(1)	0.0725(1)	0.005(1)
Zn(3)	0.2363(1)	0.3836(1)	0.1941(1)	0.006(1)
Zn(4)	0.0000	0.3285(1)	0.2500	0.005(1)
P(1)	0.2682(1)	0.4894(1)	0.0455(1)	0.004(1)
P(2)	0.0512(1)	0.2897(1)	0.1325(1)	0.004(1)
P(3)	0.1807(1)	0.5104(1)	0.3105(1)	0.004(1)
O(1)	−0.1824(1)	0.4627(2)	−0.0041(1)	0.010(1)
O(2)	−0.1868(1)	0.1340(2)	0.0829(1)	0.010(1)
O(3)	0.2552(1)	0.3626(2)	0.0923(1)	0.008(1)
O(4)	0.1718(1)	0.0842(2)	−0.0090(1)	0.010(1)
O(5)	0.0901(1)	0.1592(2)	0.0976(1)	0.007(1)
O(6)	0.0239(1)	0.2014(2)	0.1841(1)	0.008(1)
O(7)	−0.0256(1)	0.3736(2)	0.0891(1)	0.007(1)
O(8)	0.1178(1)	0.4219(2)	0.1567(1)	0.007(1)
O(9)	0.2858(1)	−0.0055(2)	0.1188(1)	0.006(1)
O(10)	0.2956(1)	0.1781(2)	0.2080(1)	0.010(1)
O(11)	0.0849(1)	0.4832(2)	0.2950(1)	0.009(1)
O(12)	0.2273(1)	0.3789(2)	0.2822(1)	0.007(1)
OW	0.3182(1)	0.5668(2)	0.1989(1)	0.010(1)
N(1)	0.1098(1)	0.8566(2)	0.1495(1)	0.009(1)
N(2)	−0.0469(1)	0.7170(2)	0.0843(1)	0.012(1)
C(1)	−0.0425(1)	0.8153(2)	0.1399(1)	0.011(1)
C(2)	0.0453(1)	0.8009(2)	0.1820(1)	0.010(1)
C(3)	0.1065(1)	0.7613(2)	0.0933(1)	0.011(1)
C(4)	0.0183(1)	0.7724(2)	0.0515(1)	0.013(1)

the two zinc atoms, Zn(1) and Zn(2), in general positions. The tetrahedral Zn–O distances are in the range 1.92(1)–2.042(1) Å with the longest bond to three-coordinate O atoms. This corresponds to findings for similar zincophosphates.[13,15] The fourth zinc atom, Zn(3), is five-coordinate, and this type of coordination represents a new feature among the open framework zincophosphates. Five-coordinate zinc is known for dense zincophosphates like $Zn_2(OH)PO_4$[21] and $Zn_3(PO_4)_2 \cdot H_2O$,[22] but has not been reported for open framework zincophosphates. The coordination polyhedron is a distorted trigonal bipyramid which coordinates four phosphate oxygen atoms and one water molecule (Fig. 3). The long Zn(3)–O(3) bond [2.425(2) Å] is somewhat longer than the Zn–O bond of 2.305 Å observed for five-coordinate Zn in $Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$.[23] The P–O bonds of the phosphate tetrahedra fall within the range 1.515(1)–1.581(1) Å with the longest bonds again being associated with three-coordinate oxygen atoms. The phosphate tetrahedra are quite regular with O–P–O angles in the range 105.27(8)–112.40(8)°. The Zn–O tetrahedra are less regular with O–Zn–O in the range 97.19(6)–121.82(7)°. Bond valence analysis[24] (Table 5) gives calculated valences close to the expected values of two and five for zinc and phosphorus, respectively. The calculated bond valences for some of the oxygen atoms are rather low. Their valences are however fulfilled by hydrogen bonding contributions from the piperazinium cations and the water molecules (see below).

The three-dimensional framework is formed by connection of ZnO_4, $ZnO_4(H_2O)$ and PO_4 units into three-, four-, six- and eight-membered rings. The three-, four- and six-membered rings are connected edge-wise, forming infinite sheets in the *bc*-plane (Fig. 4). These sheets moreover are cross-linked by $P(2)O_4$ and $Zn(4)O_4$ tetrahedra to form a three-dimensional framework, which exhibits a two-dimensional staggered eight-ring channel system running along [001] and [011] [Fig. 5(a) and (b)]. The channel system can alternatively be described as voids containing two piperazinium cations, and having elliptical windows of approximate dimensions 4.8 × 8.6 Å. The piperazinium cations are diprotonated, and form hydrogen bonds to the framework oxygen atoms. The relevant hydrogen bonding contacts are d[N(1)···O(5)] = 2.75 Å, d[N(1)···O(12)] = 2.72 Å, d[N(2)···O(4)] = 2.83 Å and d [N(1)···O(7)] = 2.85 Å. The water molecule that coordinates to Zn(3) participates in hydrogen bonding to O(2) with d[OW···O(2)] = 2.69 Å and O(12) with d[OW···O(12)] = 2.72 Å.

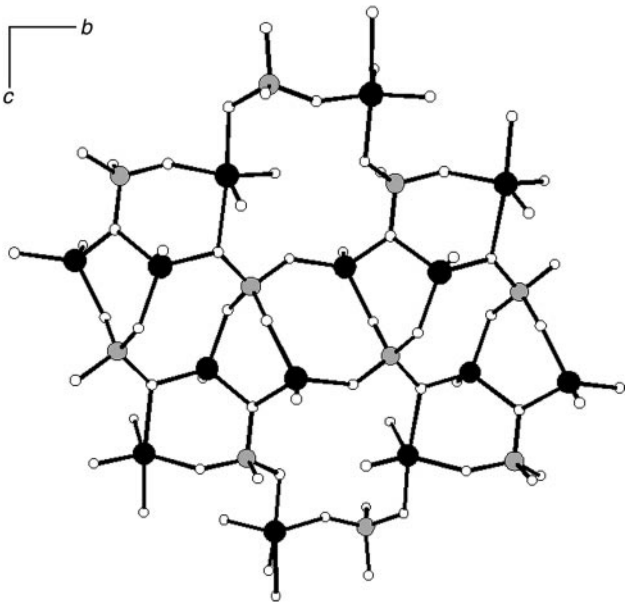

Fig. 4 Connection of corner sharing polyhedra into edge sharing three-, four- and six-membered rings.

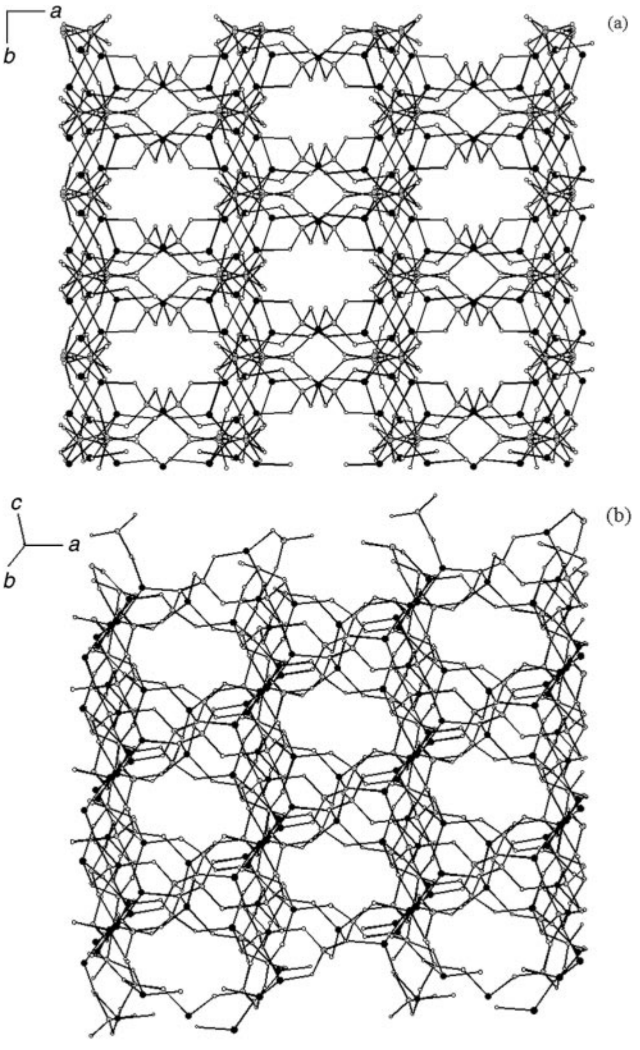

Fig. 5 The staggered eight-ring channel system in UiO-17, seen along (a) [001] and (b) [011].

Table 4 Bond distances (Å) and selected angles (°) for UiO-17. Calculated standard deviations in parentheses

Zn(1)–O(4)	1.926(1)	O(4)–Zn(1)–O(3)	117.69(6)
Zn(1)–O(3)	1.936(1)	O(4)–Zn(1)–O(5)	106.12(6)
Zn(1)–O(5)	1.954(1)	O(3)–Zn(1)–O(5)	109.35(6)
Zn(1)–O(9)	2.024(1)	O(4)–Zn(1)–O(9)	105.22(6)
		O(3)–Zn(1)–O(9)	103.43(6)
		O(5)–Zn(1)–O(9)	115.38(6)
Zn(2)–O(2)	1.922(1)	O(2)–Zn(2)–O(1)	121.82(7)
Zn(2)–O(1)	1.936(1)	O(2)–Zn(2)–O(7)	114.09(6)
Zn(2)–O(7)	1.941(1)	O(1)–Zn(2)–O(7)	100.30(6)
Zn(2)–O(9)	2.042(1)	O(2)–Zn(2)–O(9)	104.79(6)
		O(1)–Zn(2)–O(9)	97.19(6)
		O(7)–Zn(2)–O(9)	118.38(6)
Zn(3)–O(8)	1.922(1)	O(8)–Zn(3)–O(10)	128.04(6)
Zn(3)–O(10)	1.933(1)	O(8)–Zn(3)–OW	118.36(6)
Zn(3)–OW	1.992(1)	O(10)–Zn(3)–OW	111.11(7)
Zn(3)–O(12)	2.055(1)	O(8)–Zn(3)–O(12)	98.05(6)
Zn(3)–O(3)	2.425(2)	O(10)–Zn(3)–O(12)	88.38(6)
		OW–Zn(3)–O(12)	99.47(6)
		O(8)–Zn(3)–O(3)	85.86(6)
		O(10)–Zn(3)–O(3)	85.59(5)
		OW–Zn(3)–O(3)	82.56(5)
		O(12)–Zn(3)–O(3)	173.97(5)
Zn(4)–O(6)	1.948(1)	O(6)–Zn(4)–O(6)	114.97(8)
Zn(4)–O(6)	1.948(1)	O(6)–Zn(4)–O(11)	100.81(6)
Zn(4)–O(11)	1.969(1)	O(6)–Zn(4)–O(11)	120.55(6)
Zn(4)–O(11)	1.969(1)	O(6)–Zn(4)–O(11)	120.55(6)
		O(6)–Zn(4)–O(11)	100.81(6)
		O(11)–Zn(4)–O(11)	99.32(9)
P(1)–O(1)	1.528(2)	O(1)–P(1)–O(2)	112.18(9)
P(1)–O(2)	1.542(1)	O(1)–P(1)–O(3)	110.42(8)
P(1)–O(3)	1.545(1)	O(2)–P(1)–O(3)	105.27(8)
P(1)–O(4)	1.547(1)	O(1)–P(1)–O(4)	110.99(8)
		O(2)–P(1)–O(4)	109.32(8)
		O(3)–P(1)–O(4)	108.45(8)
P(2)–O(8)	1.536(1)	O(8)–P(2)–O(6)	111.45(8)
P(2)–O(6)	1.538(1)	O(8)–P(2)–O(7)	107.11(8)
P(2)–O(7)	1.549(1)	O(6)–P(2)–O(7)	111.62(8)
P(2)–O(5)	1.559(1)	O(8)–P(2)–O(5)	109.84(7)
		O(6)–P(2)–O(5)	107.03(8)
		O(7)–P(2)–O(5)	109.80(8)
P(3)–O(11)	1.515(1)	O(11)–P(3)–O(10)	112.40(8)
P(3)–O(10)	1.521(1)	O(11)–P(3)–O(12)	111.70(8)
P(3)–O(12)	1.549(1)	O(10)–P(3)–O(12)	109.83(8)
P(3)–O(9)	1.581(1)	O(11)–P(3)–O(9)	107.64(8)
		O(10)–P(3)–O(9)	108.23(7)
		O(12)–P(3)–O(9)	106.79(7)
N(1)–C(2)	1.491(2)	C(2)–N(1)–C(3)	112.5(1)
N(1)–C(3)	1.494(3)	C(1)–N(2)–C(4)	111.4(2)
N(2)–C(1)	1.494(3)	N(2)–C(1)–C(2)	110.0(2)
N(2)–C(4)	1.502(3)	N(1)–C(2)–C(1)	108.6(2)
C(1)–C(2)	1.512(3)	N(1)–C(3)–C(4)	110.1(2)
C(3)–C(4)	1.512(3)	N(2)–C(4)–C(3)	109.4(2)

MAS NMR

The ^{31}P MAS NMR spectrum [Fig. 6(a)] shows three peaks at δ 0.38, 4.15 and 7.54, with an intensity ratio of *ca.* 1 : 1 : 1 as expected on the basis of the crystal structure data with three crystallographically distinct P positions. The resonances fall inside the appropriate range (δ −30 to 12) reported for a large number of orthophosphates.[25] Müller *et al.*[26] have suggested an empirical correlation between the ^{31}P isotropic chemical shift and average P–O–Al bond angle in aluminophosphates where the chemical shift decreases with increasing average bond angle. If this approach is considered applicable also for the zincophosphates, the assignment of the ^{31}P peaks for UiO-17 is as follows:

δ 7.54 position P(2) with average angle P(2) − O − Zn 127.5°

δ 4.15 position P(1) with average angle P(1) − O − Zn 132.5°

δ 0.38 position P(3) with average angle P(3) − O − Zn 134.0°

It should, however, be pointed out that this assignment is based on an assumption that the empirical correlation for aluminophosphates can be extended to zincophosphates. We cannot, however, establish such a correlation unequivocably because there are too few ^{31}P NMR data available on zincophosphates. The additional weak peaks in the ^{31}P MAS NMR spectrum at δ *ca.* 3 and 7 can be attributed to an impurity phase, possibly the same as that responsible for the small weight loss in the TGA curve at *ca.* 270 °C.

The ^{13}C CP MAS NMR spectrum [Fig. 6(b)] shows a single peak at δ 41.78. This peak assigned to the carbon atoms in piperazine indicates that the resonances from the four non-equivalent carbon atoms in UiO-17 overlap. The chemical shift is shifted upfield compared to that for liquid phase piperazine (δ 47.34), presumably because of the lack of intermolecular interactions between the isolated template molecules in the voids.

Discussion

In addition to UiO-17, two other open framework zincophosphate structures templated by piperazine are known, $[C_4N_2H_{11}][Zn_2(PO_4)(H_2PO_4)_2]$ and $[C_4N_2H_{12}][Zn_2(H_2O)(PO_4)(HPO_4)]\cdot H_2O$,[4] which can be described as interrupted and expanded sodalites, respectively. Perturbation of the sodalite type structure takes place since the templating

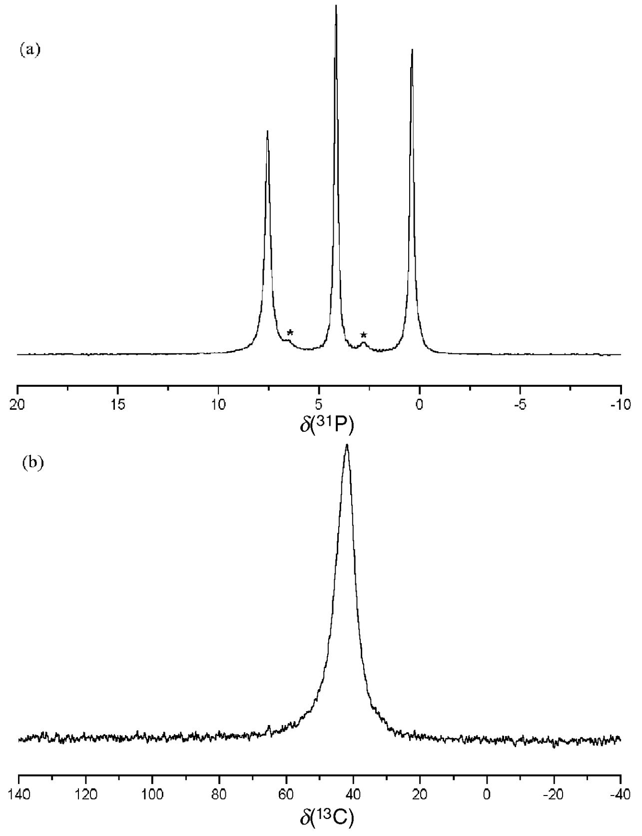

Fig. 6 ^{31}P MAS NMR spectrum (peaks marked * are due to impurities) (a) and ^{13}C CP MAS NMR spectrum (b) of UiO-17.

Table 5 Bond valence analysis for UiO-17

	Zn(1)	Zn(2)	Zn(3)	Zn(4)	P(1)	P(2)	P(3)	Σ
O(1)		0.53			1.27			1.80
O(2)		0.56			1.23			1.79
O(3)	0.53		0.14		1.21			1.88
O(4)	0.55				1.21			1.76
O(5)	0.51					1.17		1.68
O(6)				0.52 × 2		1.24		1.76
O(7)		0.53				1.20		1.73
O(8)			0.56			1.25		1.81
O(9)	0.42	0.40					1.10	1.92
O(10)			0.54				1.30	1.84
O(11)				0.49 × 2			1.32	1.81
O(12)			0.39				1.20	1.59
OW			0.46					0.46
Σ	2.01	2.02	2.08	2.01	4.92	4.85	4.92	

piperazinium cation has a charge of less than +3, which would be required to balance the charge of a zincophosphate sodalite. Interruption of the cage involves removal of a tetrahedrally coordinated atom from the sodalite cage, the negative charge is thereby reduced from −3 to −1, and can be charge balanced by a monoprotonated piperazinium cation in the cage. Expansion involves insertion of tetrahedrally coordinated atom groups into the framework, with a resulting charge lowering from −3 to −2 for the framework. This can then be compensated by a diprotonated piperazinium cation in the cage. UiO-17 has voids containing two diprotonated piperazinium cations, and a matching framework charge of −4. UiO-17 is however not related to the other compounds nor to the sodalite structure. Other structure modifying elements such as three-membered rings and five-coordinate zinc are introduced to the framework in order to match the charge of the two diprotonated piperazinium cations in the voids.

In addition to the host–guest charge matching principle as a factor in determining the product of a synthesis, the templating effect of the organic species can be important. In many cases the organic guest molecules have a lower symmetry than the inorganic framework. As a consequence the guest molecules are orientationally disordered to conform to the higher symmetry of the framework structure. Piperazine is however involved in several examples of the opposite situation where there is a symmetry matching between the template and the inorganic framework, *e.g.* in the sodalite variants mentioned above. Piperazine shows point symmetry $2/m$ with three individual symmetry elements (i, 2, m). In UiO-17 there is a twofold axis running through the voids relating the two piperazine molecules in each void. Thereby a symmetry element of the template molecule (piperazine) constrains the framework structure in UiO-17, and the structure is an example of symmetry matching.

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