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Syntheses and structures of the open-framework phases $(CH_3NH_3)_3\cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3\cdot Zn_4O(PO_4)_3$ related to the $M_3Zn_4O(XO_4)_3\cdot nH_2O$ family

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The solution-mediated syntheses and single crystal structures of the new open-framework phases $(CH_3NH_3)_3\cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3\cdot Zn_4O(PO_4)_3$ are reported. These compounds are built up from vertex-sharing three-dimensional "OZn_4" + ZnO_4 + AsO_4/PO_4 tetrahedral frameworks encapsulating methylammonium cations in three-dimensional channel systems. These phases are closely related to the zeolite-like $M_3Zn_4O(XO_4)_3\cdot nH_2O$ family of phases.

Introduction

Over the last few years, innumerable new open-framework materials built up from fused polyhedra have been prepared by solution-mediated reactions.[1] A frequently used concept in seeking systematic trends in this area of materials chemistry is that of *templating*[2]—the tendency of a cation to direct the reaction to form a particular product, or at least one containing a distinct structural feature. Small organic molecules, particularly those containing protonated amino groups, have played an outstanding role in templating novel networks.[3] However, slight variations on the same reaction can generate completely different crystal structures,[4] indicating the extreme sensitivity of such preparations to the (sometimes poorly defined) reaction conditions, and the importance of a systematic approach to identifying and controlling the reacting species.[5]

We have recently reported[6] the syntheses and characterisation of a new family of open-framework zincophosphate/arsenate phases of stoichiometry $M_3Zn_4O(XO_4)_3\cdot nH_2O$ (M = Na, K, Rb, Cs; X = P, As; $n = 3.5$–6). The unusual zinc-rich 4 : 3 ratio Zn : X framework stoichiometry arises due to the presence of novel "OZn_4" tetrahedral building units as well as vertex-linked ZnO_4 and XO_4 tetrahedra. Unlike many zincophosphate framework structures, which collapse or transform upon dehydration or template removal,[7,8] several of these $M_3Zn_4O(XO_4)_3\cdot nH_2O$ materials show post-dehydration thermal stability to ≈500–600 °C. Facile, "zeolitic" ion-exchange of the guest cations is also possible for these phases.[6]

In this paper we report the solution-mediated syntheses and single crystal structures of $(CH_3NH_3)_3\cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3\cdot Zn_4O(PO_4)_3$. These phases are built up from a new monoclinic modification of the $[Zn_4O(XO_4)_3]^{3-}$ framework encapsulating methylammonium cations in place of the combination of inorganic cations + water molecules as seen in the $M_3Zn_4O(XO_4)_3\cdot nH_2O$ structures.[6] This represents a notable example of a complex open framework structure type which is unusually *insensitive* to the templating effect of either inorganic cations of various sizes + water molecules or organic cations.

Experimental

Synthesis of $(CH_3NH_3)_3\cdot Zn_4O(AsO_4)_3$

Initially, $CH_3NH_2\cdot H_3AsO_4$ was prepared, as follows: 19.78 g (100 mmol) As_2O_3 (ACS primary standard, Fisher) was heated to solution with 100 ml H_2O and 34 g (300 mol) H_2O_2, (30% in water, Fisher). The resulting H_3AsO_4 solution was diluted to 200 ml in a volumetric flask and titrated with 15 ml (200 mmol) CH_3NH_2, (40% in water, Aldrich) using bromcresol green as the indicator. The solution was boiled until viscous, taken up in *ca.* 200 ml methanol, and reboiled. Absolute ethanol was added until the solution was turbid; the vessel was placed in an ice bath and stirred until precipitation was complete. The white crystalline powder $CH_3NH_2\cdot H_3AsO_4$ product (**1**) was filtered and dried in a 60 °C oven.

1.63 g (20 mmol) ZnO (J.T. Baker), 6.92 g (40 mmol) **1**, 11.36 g (146.6 mmol) H_3CNH_2 (40% in water), and 14.76 g (820 mmol) H_2O were heated in a closed PTFE bottle at 90 °C for 16 h, after which the ZnO completely dissolved. 1.00 g additional ZnO was added, and the bottle was reheated to 90 °C for 24 h. The fine white powder product (0.74 g) was recovered by filtration and was washed with water, then methanol. The resulting powder pattern bore some resemblance to those of the $M_3Zn_4O(XO_4)_3\cdot nH_2O$ structures,[6] suggesting that $(CH_3NH_3)_3\cdot Zn_4O(AsO_4)_3$ had been prepared. However, it was evidently of lower symmetry than the cubic and trigonal phases previously studied, and a suitable starting model for Rietveld refinement could not be developed.

Single crystals of $(CH_3NH_3)_3\cdot Zn_4O(AsO_4)_3$ were prepared by a modified method, as follows: *ca.* 50 g ZnO (St. Joseph's) were pressed at ≈8000 psi in a 28.6 mm die for 30 s. This bar was sintered for 30 min at 1150 °C, cooled to ambient, then sliced into 3.2 mm thick, 25 mm diameter ZnO pellets (**2**) using a diamond saw. Then, 0.81 g (10 mmol) of ZnO powder (St. Joseph's) was added to a solution containing 3.46 g (20 mmol) of **1**, 5.68 g (73.3 mmol) of CH_3NH_2 (40% in water) and 7.38 g H_2O. This yielded a starting ratio of 4.667 $(CH_3NH_2)_2O$: 1 ZnO : 1 As_2O_5 : 60 H_2O. The mixture was placed in a HDPE bottle in a 70 °C oven. After 3 h, all of the ZnO had dissolved, and a pellet of **2** weighing 0.79 g was added to the solution, which was returned to the 70 °C oven. After 5 days, the pellet had nearly corroded through, and crystals (up to 0.5 mm in size) were seen at the bottom of the bottle. The pellet was removed, and the bottle contents were filtered and dried. The pH of the mother liquors was 12. The yield of crystals was 1.27 g (24% based on As). Elemental analysis data for $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ (Galbraith Laboratories, Knoxville, Tennessee, USA) were in good agreement with the proposed stoichiometry: Zn (obs. weight% = 32.7, calc. = 33.1), As (28.7, 28.4), N (5.4, 5.3), C (4.8, 4.6), H (2.5, 2.3). We may speculate that the ZnO pellet dissolves more slowly than ZnO powder, reducing the Zn^{2+} concentration in solution, thus retarding the nucleation rate and increasing the crystallite size of the $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ product.

Synthesis of $(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$

0.81 g (10 mmol) of ZnO powder (St. Joseph's) was added to a solution containing 7.23 g (47 mmol) of CH_3NH_2, 2.30 g 85% H_3PO_4 (10 mmol) and 5.60 g H_2O. This yielded a starting ratio of 4.667 $(CH_3NH_2)_2O$: 1 ZnO : 1 P_2O_5 : 60 H_2O. The mixture was placed in a HDPE bottle in a 70 °C oven for 13 days. The bottle contents were vacuum filtered and dried in air. The pH of the mother liquors was 12.5. The yield of tiny (<0.02 mm maximum linear dimension) crystals was 1.30 g (59% based on Zn). Elemental analysis data for $(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$: P (obs. 13.5%, calc. 14.1%), N (6.3, 6.4), C (5.2, 5.5), H (2.8, 2.8). The ZnO "pellet method" was also tried for the phosphate, but did not lead to an appreciable increase in the size of the resulting $(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$ crystals.

Physical characterisation

X-Ray powder diffraction data (Stoe STADI P automated diffractometer, Cu-Kα_1 radiation, $\lambda = 1.54054$ Å) were recorded for well ground crystals of $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$. A simulation of the monoclinic single crystal structure indicated phase purity and *hkl*-to-peak assignments were made on this basis (Table 1). Least-squares cell parameter optimisation was carried out with UNITCELL,[9] resulting in refined cell parameters of $a = 7.804(2)$ Å, $b = 15.479(4)$ Å, $c = 7.805(2)$ Å, and $\beta = 92.88(2)°$. TGA data for both phases were recorded on a TA Instruments STD2960 simultaneous DTA–TGA instrument (ramp at 10 °C min^{-1} in air).

$(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ structure determination

Initially, a metrically *C*-centred orthorhombic unit cell [$a = 10.771(2)$ Å, $b = 11.338(2)$ Å, $c = 15.511(2)$ Å, $V = 1894.2(4)$ Å^3] was established by standard procedures. However, data collection based on this cell did not result in any reasonable structure solutions.

The crystal was re-examined and a primitive monoclinic cell (Table 2) was established and data were recollected. Absorption was monitored by ψ scans (range of equivalent transmission factors: 0.508–0.605). The 2600 raw intensities were reduced and merged to 2413 observations ($R_{Int} = 0.031$), with 2301 of these considered observed according to the criterion $I > 3\sigma(I)$. The systematic absences in the reduced data ($0k0$, $k \neq 2n$) indicated space groups $P2_1$ or $P2_1/m$.

Direct methods[10] revealed a sufficient fragment of the structure (Zn, As, some O) in space group $P2_1$ (No. 4) to enable the remainder of the non-hydrogen atoms to be located from Fourier difference maps, and the refinement proceeded to the $R \approx 10\%$ stage (isotropic thermal parameters). No model could be established in $P2_1/m$ and this space group was not considered further. However, the ZnO_4 and AsO_4 moieties appeared to be unrealistically distorted, and anisotropic refinement led to non-positive-definite thermal factors for many of the atoms. Difference Fourier syntheses appeared to indicate substantial disorder.

Table 1 X-Ray powder data for $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$

h	*k*	*l*	d_{obs}/Å	d_{calc}/Å	Δd	I_{rel}
0	0	1	7.793	7.795	−0.002	100
0	1	1	6.965	6.962	0.002	8
1	2	−1	4.566	4.566	0.000	19
1	2	1	4.418	4.417	0.001	13
0	0	2	3.897	3.898	−0.001	8
2	1	0	3.778	3.779	−0.001	11
1	3	1	3.723	3.723	0.000	19
1	0	−2	3.557	3.558	−0.001	3
2	1	−1	3.466	3.468	−0.001	12
1	1	2	3.338	3.338	0.000	3
1	2	−2	3.232	3.233	0.000	17
1	4	−1	3.192	3.194	−0.001	9
1	2	2	3.128	3.127	0.000	8
1	3	−2	2.931	2.929	0.001	3
0	5	1	2.877	2.877	0.000	3
2	3	1	2.849	2.849	0.000	7
2	0	−2	2.828	2.828	0.000	3
2	4	0	2.746	2.746	0.000	10
1	5	1	2.687	2.683	0.003	3
2	1	2	2.650	2.649	0.000	7
1	4	−2	2.620	2.619	0.000	7
2	4	1	2.562	2.562	0.000	7
3	1	−1	2.469	2.471	−0.002	6
0	6	1	2.448	2.449	0.000	5
1	1	3	2.399	2.399	0.000	8
3	2	−1	2.385	2.381	0.003	6
1	6	−1	2.347	2.347	0.000	4
2	4	−2	2.283	2.283	0.000	5
3	3	−1	2.250	2.252	−0.001	3
0	7	1	2.127	2.127	0.000	3
2	7	0	1.9228	1.9232	−0.0004	3
4	1	2	1.6989	1.6986	0.0003	2
2	3	−4	1.6829	1.6820	0.0009	3
4	2	2	1.6683	1.6687	−0.0003	3
0	5	4	1.6485	1.6492	−0.0007	3

Table 2 Crystallographic parameters

	$(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$	$(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$
Formula weight	790.47	658.63
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
μ/cm^{-1}	104.1	57.8
$R(F)$	0.030	0.081
$R_w(F)$	0.040	0.096
a/Å	7.814(3)	7.6569(5)
b/Å	15.498(6)	15.241(1)
c/Å	7.813(3)	7.6589(5)
β/°	92.91(2)	92.740(1)
V/Å^3	945.1(9)	892.7(5)
T/°C	25(2)	25(2)
Z	2	2
Measured data	2600	5706
Observed data[a]	2301	2694
R_{Int}	0.031	0.043

[a] $I > 3\sigma(I)$ after data merging.

A much better refinement was obtained in $P2_1$ by assuming rotational merohedral twinning[11] about [010], with a transformation matrix of

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & \bar{1} & 0 \\ 1 & 0 & 0 \end{pmatrix} \qquad (1)$$

relating the two twin components. Refinement of their relative fractions, d_i, subject to the constraint $d_1 + d_2 = 1.00$, resulted in a 0.743(2) : 0.257(2) domain ratio in the crystal studied here. This model (final $R = 3.01\%$) allowed for the refinement[12] of anisotropic thermal factors for all atoms and reasonable geometrical parameters resulted. No hydrogen atoms could be located from difference maps. Assuming that N–H···O hydrogen bonds are present (*vide infra*), these links are probably disordered over several conformations. Crystallographic data are summarised in Table 2.

$(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ structure determination

A very small crystal (transparent cuboid, dimensions $\approx 0.01 \times 0.01 \times 0.01$ mm) was examined on a Siemens SMART CCD diffractometer [graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 25(2)$ °C]. A similar monoclinic cell to that observed for $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ was established (Table 2), although all the crystals examined showed signs of split and/or multiple peaks. Intensity data were collected in narrow-slice ω-scan mode,[13] resulting in 5706 observations ($-10 \leqslant h \leqslant 10$, $-20 \leqslant k \leqslant 14$, $-10 \leqslant l \leqslant 10$) for $2° \leqslant 2\theta \leqslant 55°$. Data merging resulted in 3112 unique reflections ($R_{Int} = 0.043$) of which 2694 were considered observed according to the criterion $I > 3\sigma(I)$. Absorption and incident beam decay corrections were applied using SADABS,[14] with a resulting correction factor range of 0.94–0.97.

The crystal structure model for $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ was developed from that of $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ (P replacing As) in space group $P2_1$ using CRYSTALS. Considering the small crystal size, and assuming a similar twinning law to that seen for the $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ structure, this refined tolerably well. The untwinned $P2_1$ model had much higher residuals. However, even for the best twinned model, there were some significant difference Fourier peaks (up to 5 e Å^{-3}) in the vicinity of the Zn and P atoms and anisotropic thermal parameter refinement led to some non-positive definite ellipsoids. Refinement of the domain fractions, d_i, subject to the constraint $d_1 + d_2 = 1.00$ resulted in a 0.499(5) : 0.501(5) ratio in the individual crystal studied. No H atoms could be located. Crystallographic data for $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ are summarised in Table 2.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Information for Authors', *J. Mater. Chem.*, Issue 1, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/190.

See http://www.rsc.org/suppdata/jm/1999/3087/ for crystallographic files in .cif format.

Results

Crystal structure of $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$

This material forms a new open-framework zincoarsenate phase built up from tetrahedral ZnO_4 and AsO_4 building blocks, connected *via* Zn–O–Zn and Zn–O–As bonds, encapsulating cavities and channels occupied by extra-framework methylammonium cations. Final atomic co-ordinates and thermal parameters for $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ are presented in Table 3, with selected geometrical data in Table 4. An ORTEP-3[15] view of the building unit of $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ is shown in Fig. 1, and the complete crystal structure is illustrated in Fig. 2.

The four distinct zinc atoms in $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ are tetrahedrally co-ordinated by their O atom neighbours with typical[6,7] average zinc–oxygen bond distances of 1.966(8) Å for Zn1, 1.958(8) Å for Zn2, 1.952(8) Å for Zn3, and 1.950(8) Å for Zn4. Each zinc atom makes three Zn–O–As bonds and one Zn–O1 bond. The O1 atom is tetrahedrally co-ordinated (as μ_4-O) by one each of the four Zn atoms. There are three crystallographically distinct AsO_4 tetrahedra [d_{av}(As1–O) = 1.682(7) Å, d_{av}(As2–O) = 1.681(7) Å, d_{av}(As3–O) = 1.680(7) Å] in $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$: each of these groups make four As–O–Zn links. An average bond angle of 125.8° results for the 12 distinct Zn–O–As links. The framework stoichiometry of $Zn_4As_3O_{13}$ [or $ZnO \cdot (ZnAsO_4)_3$] has a charge of -3. We assume that this is charge balanced by the three crystallographically distinct extra-framework methylammonium cations. Each protonated NH_3 group makes four N···O contacts of $\approx$2.8–3.1 Å (Fig. 3) to framework Zn–O–As atoms, and the N–H···O hydrogen bonding links are probably disordered over several conformations. In this case, all 12 of the Zn–O–As bridging oxygen atoms serve as H bond acceptors. This is supported by the average bond valence sum (BVS)[16] of these oxygen atoms of 1.76 (range of values 1.68–1.82), based on O–Zn and O–As links, which is significantly less than the expected value of 2.00. BVS calculations yielded the following values for the tetrahedral atoms: Zn1 1.97, Zn2 2.01, Zn3 2.07, Zn4 2.06,

Table 3 Atomic co-ordinates/thermal factors for $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$

Atom	x	y	z	U_{eq}[a]
Zn1	0.19629(19)	0.30381(14)	−0.08337(19)	0.0110
Zn2	−0.0694(2)	0.29781(13)	0.21827(19)	0.0118
Zn3	0.19654(19)	0.45889(12)	0.19510(19)	0.0110
Zn4	−0.11700(18)	0.43457(13)	−0.08566(19)	0.0121
As1	0.08583(17)	0.38666(12)	−0.43461(18)	0.0119
As2	−0.00052(19)	0.12729(12)	−0.01458(18)	0.0127
As3	0.54844(17)	0.35986(12)	0.09467(18)	0.0126
O1	0.0513(11)	0.3740(6)	0.0653(11)	0.0111
O2	0.4146(12)	0.2762(7)	0.0417(14)	0.0181
O3	0.2508(12)	0.3630(7)	−0.2964(12)	0.0175
O4	0.0701(15)	0.1992(7)	−0.1530(14)	0.0207
O5	0.0379(14)	0.2969(7)	0.4484(11)	0.0198
O6	−0.3114(13)	0.3248(8)	0.2522(12)	0.0216
O7	−0.0495(16)	0.1735(7)	0.1685(13)	0.0214
O8	0.1413(14)	0.4688(8)	0.4358(13)	0.0207
O9	0.1761(13)	0.5761(7)	0.1062(14)	0.0207
O10	0.4399(13)	0.4431(8)	0.1687(17)	0.0313
O11	−0.3476(12)	0.3874(9)	−0.0782(13)	0.0256
O12	−0.0845(12)	0.4184(8)	−0.3295(12)	0.0227
O13	−0.1568(14)	0.5541(7)	−0.0271(17)	0.0265
N1	0.5068(18)	0.1009(9)	0.058(2)	0.0276
N2	−0.057(2)	0.6142(11)	0.483(2)	0.0413
N3	−0.4103(17)	0.3250(9)	0.5832(18)	0.0297
C1	0.574(3)	0.0712(14)	0.232(3)	0.0396
C2	−0.241(4)	0.581(2)	0.444(5)	0.0871
C3	−0.362(3)	0.2357(14)	0.636(3)	0.0457

[a] $U_{eq}/Å^2 = 1/3[U_1 + U_2 + U_3]$.

Table 4 Selected bond distance(Å)/angle(°) data for $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$

Zn1–O1	1.99(1)	Zn1–O2	1.97(1)
Zn1–O3	1.97(1)	Zn1–O4	1.961(11)
Zn2–O1	1.96(1)	Zn2–O5	1.946(9)
Zn2–O6	1.97(1)	Zn2–O7	1.974(11)
Zn3–O1	1.983(9)	Zn3–O8	1.96(1)
Zn3–O9	1.948(11)	Zn3–O10	1.939(11)
Zn4–O1	1.960(8)	Zn4–O11	1.95(1)
Zn4–O12	1.95(1)	Zn4–O13	1.937(11)
As1–O3	1.679(9)	As1–O5	1.695(11)
As1–O8	1.697(11)	As1–O12	1.67(1)
As2–O4	1.667(11)	As2–O7	1.66(1)
As2–O9	1.71(1)	As2–O13	1.692(11)
As3–O2	1.70(1)	As3–O6	1.70(1)
As3–O10	1.663(12)	As3–O11	1.67(1)
N1–C1	1.50(3)	N2–C2	1.55(4)
N3–C3	1.49(3)		
Zn1–O1–Zn2	109.5(5)	Zn1–O1–Zn3	109.5(4)
Zn2–O1–Zn3	111.6(4)	Zn1–O1–Zn4	107.2(4)
Zn2–O1–Zn4	109.1(4)	Zn3–O1–Zn4	109.8(5)
Zn1–O2–As3	117.4(6)	Zn1–O3–As1	117.0(5)
Zn1–O4–As2	123.4(6)	Zn2–O5–As1	124.5(6)
Zn2–O6–As3	124.1(6)	Zn2–O7–As2	127.9(6)
Zn3–O8–As1	126.2(7)	Zn3–O9–As2	129.1(6)
Zn3–O10–As3	130.9(7)	Zn4–O11–As3	127.6(6)
Zn4–O12–As1	131.6(6)	Zn4–O13–As2	124.3(6)

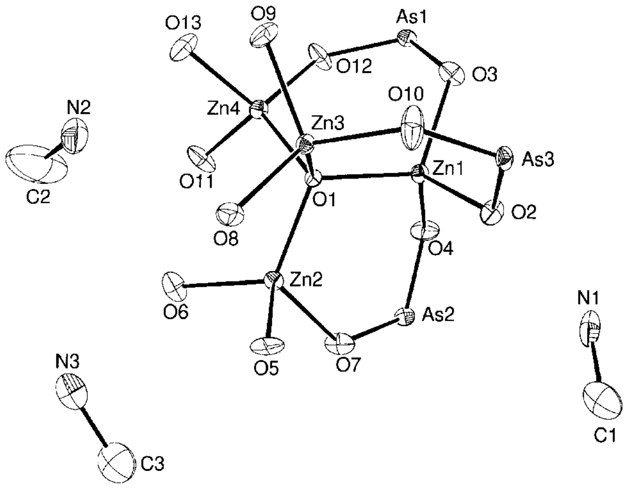

Fig. 1 View of a fragment of the $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ crystal structure showing the atom-labelling scheme (50% thermal ellipsoids).

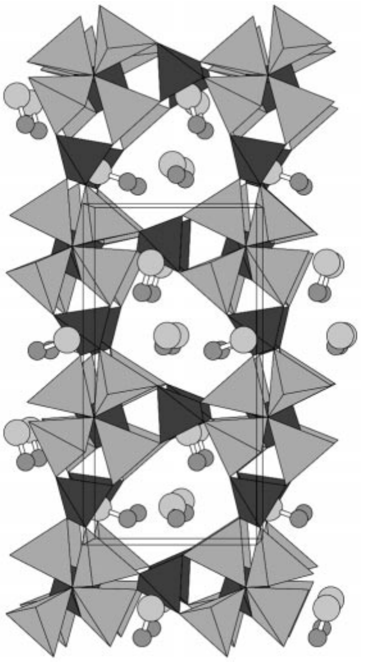

Fig. 2 Polyhedral view approximately down [100] of the $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ crystal structure (ZnO_4 tetrahedra light shading, AsO_4 tetrahedra dark shading, N atoms large circles, C atoms small circles).

As1 5.04, As2 5.07, As3 5.08, which are in good agreement with the expected values of 2.00 for Zn and 5.00 for As.

The polyhedral connectivity in $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ leads to the three-dimensional open-framework network shown in Fig. 2. Because of the involvement of the μ_4-O1 species, an unusual topology[6] of tetrahedral three-rings and eight-rings makes up the zincoarsenate framework. Intersecting eight-ring channels of approximate dimensions $\approx 5.4 \times 5.5$ Å propagate in essentially orthogonal directions, along [100], [010], and [001]. These intersecting channels define roughly spherical cages, of approximate atom-to-atom diameter 6.5 Å. Every eight-ring window is occupied by an NH_3^+ group of a methylammonium cation, and every cage contains three CH_3 groups. Non-bonding (van der Waals') C···C contacts of 3.73(3), 4.03(3), and 4.12(3) Å result, for the methyl groups in each cage. In the polar *y* direction, the $[C1H_3N1H_3]^+$ cations adopt a zigzag ordering pattern which results in a doubled unit cell repeat length for *b* (two cages) compared to the single cage repeat distance for the *a* and *c* directions.

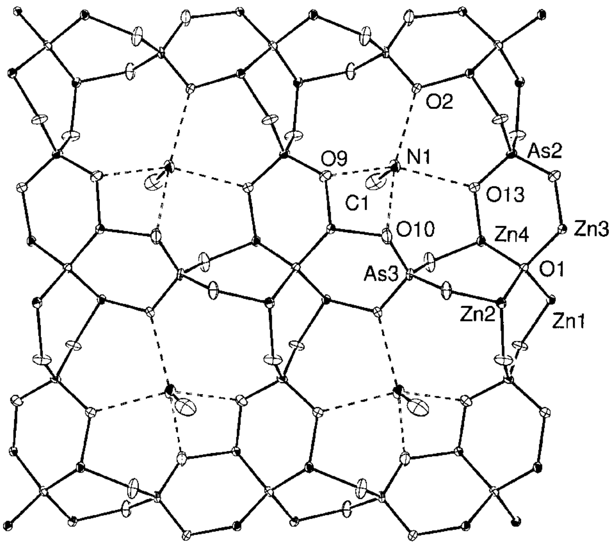

Fig. 3 View approximately down [001] of a slab of the $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$ structure showing the presence of tetrahedral 3-rings and 8-rings. The proposed disordered N–H···O hydrogen bonding links are indicated by dotted lines linking the N and O species (which do not imply that the N–H···O bond is linear).

Crystal structure of $(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$

This phase is isostructural with $(CH_3NH_3)_3{\cdot}Zn_4O(AsO_4)_3$, with tetrahedral ZnO_4 and PO_4 building blocks, connected *via* Zn–O–Zn and Zn–O–P bonds, making up the framework. The refinement is of poor quality, but the distinction between the arsenate and the phosphate is quite clear from the geometrical data. Final atomic co-ordinates and thermal parameters are presented in Table 5, with selected geometrical data in Table 6.

Average geometrical data for $(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$ are as follows: d_{av}(Zn1–O) = 1.954(9) Å, d_{av}(Zn2–O) = 1.951(9) Å, d_{av}(Zn3–O) = 1.949(9) Å, d_{av}(Zn4–O) = 1.960(9) Å, d_{av}(P1–O) = 1.541(9) Å, d_{av}(P2–O) = 1.536(9) Å, d_{av}(P3–O) = 1.546(9) Å, and θ_{av}(Zn–O–As) = 129.5°. Bond valence data (Zn1 2.04, Zn2 2.05, Zn3 2.07, Zn4 2.00, P1 4.92, P2 4.99, P3 4.85) are typical for the tetrahedral species. As with

Table 5 Atomic co-ordinates/thermal factors for $(CH_3NH_3)_3{\cdot}Zn_4O(PO_4)_3$

Atom	*x*	*y*	*z*	U_{iso}/Å^2
Zn1	0.1934(4)	0.3000(3)	−0.0934(4)	0.0133 (6)
Zn2	−0.0815(3)	0.2954(3)	0.2100(4)	0.0122(7)
Zn3	0.1932(4)	0.4560(2)	0.1920(4)	0.0126(5)
Zn4	−0.1207(3)	0.4357(2)	−0.0969(3)	0.0133(6)
P1	0.0776(8)	0.3826(5)	−0.4434(9)	0.0139(14)
P2	−0.0016(9)	0.1256(4)	−0.0116(9)	0.015(1)
P3	0.5448(9)	0.3620(5)	0.0828(9)	0.0135(14)
O1	0.048(2)	0.3715(9)	0.055(2)	0.013(3)
O2	0.422(2)	0.2850(12)	0.033(2)	0.017(4)
O3	0.231(2)	0.3572(12)	−0.314(2)	0.014(3)
O4	0.072(2)	0.1896(12)	−0.141(2)	0.019(4)
O5	0.023(2)	0.3016(14)	0.447(2)	0.019(4)
O6	−0.326(2)	0.3289(13)	0.232(2)	0.021(4)
O7	−0.069(3)	0.1730(14)	0.148(3)	0.026(4)
O8	0.133(2)	0.4567(14)	0.435(2)	0.021(4)
O9	0.155(2)	0.5751(12)	0.106(2)	0.023(4)
O10	0.441(2)	0.4411(15)	0.156(3)	0.026(4)
O11	−0.357(2)	0.3892(12)	−0.077(2)	0.018(4)
O12	−0.080(2)	0.4156(12)	−0.346(2)	0.017(4)
O13	−0.143(3)	0.5603(14)	−0.047(3)	0.033(5)
N1	0.508(4)	0.103(2)	0.059(4)	0.034(7)
N2	−0.056(4)	0.608(3)	−0.524(4)	0.05(1)
N3	−0.415(3)	0.3270(13)	−0.427(3)	0.029(4)
C1	0.585(4)	0.067(3)	0.238(4)	0.035(8)
C2	−0.241(7)	0.581(4)	−0.556(7)	0.078(15)
C3	−0.359(5)	0.240(2)	−0.360(5)	0.046(7)

Table 6 Selected bond distance(Å)/angle(°) data for $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$

Zn1–O1	1.959(19)	Zn1–O2	1.975(18)
Zn1–O3	1.932(17)	Zn1–O4	1.949(19)
Zn2–O1	1.963(19)	Zn2–O5	1.951(19)
Zn2–O6	1.959(19)	Zn2–O7	1.93(2)
Zn3–O1	1.968(13)	Zn3–O8	1.936(17)
Zn3–O9	1.948(18)	Zn3–O10	1.942(19)
Zn4–O1	1.961(12)	Zn4–O11	1.955(18)
Zn4–O12	1.972(18)	Zn4–O13	1.95(2)
P1–O3	1.551(19)	P1–O5	1.54(2)
P1–O8	1.54(2)	P1–O12	1.532(17)
P2–O4	1.516(19)	P2–O7	1.53(2)
P2–O9	1.556(18)	P2–O13	1.54(2)
P3–O2	1.54(2)	P3–O6	1.56(2)
P3–O10	1.56(2)	P3–O11	1.525(18)
N1–C1	1.57(5)	N2–C2	1.49(6)
N3–C3	1.48(4)		

Zn1–O1–Zn2	109.9(7)	Zn1–O1–Zn3	110.6(8)
Zn2–O1–Zn3	110.7(8)	Zn1–O1–Zn4	108.0(8)
Zn2–O1–Zn4	108.3(8)	Zn3–O1–Zn4	109.2(7)
Zn1–O2–P3	123.3(11)	Zn1–O3–P1	122.1(10)
Zn1–O4–P2	128.6(11)	Zn2–O5–P1	129.3(13)
Zn2–O6–P3	126.4(11)	Zn2–O7–P2	132.6(13)
Zn3–O8–P1	131.6(13)	Zn3–O9–P2	135.6(11)
Zn3–O10–P3	131.3(13)	Zn4–O11–P3	130.9(11)
Zn4–O12–P1	133.5(11)	Zn4–O13–P2	128.2(13)

$(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$, the framework stoichiometry of $Zn_4P_3O_{13}$ in $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ has a charge of -3, which is balanced by the three extra-framework methylammonium cations. These species occupy essentially the same positions as their equivalent species in the arsenate congener, with disordered N–H···O hydrogen bonding presumably occurring [range of N···O contacts = 2.72(4)–3.15(4) Å, average = 2.91 Å]. The average bond valence of the Zn–O–P bridge oxygen atoms is 1.75 (range of values 1.67–1.83), which is consistent with all of these species acting as H bond acceptors. The μ_4-O1 atom has a bond valence of 1.99 (Fig. 4).

Physical data

TGA for $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ showed no weight loss until ≈300 °C, followed by a two-step loss of 15.3% over the range 300–470 °C. A further weight loss of 7.1% (based on the starting weight) occurred at 500–650 °C. X-Ray powder data for the post-TGA residue indicated the presence of $Zn_2As_2O_7$, ZnO, and other unidentified phases.[17]

TGA for $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ showed a weight loss of ≈17% over the broad range ≈320–600 °C, in fair agreement with a possible decomposition pathway of

$$(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3 \rightarrow \text{“}Zn_4P_3O_{11.5}\text{”} \qquad (2)$$

involving the loss of all the N, C, H, and 1.5 O (calc. weight loss = 18.2%).

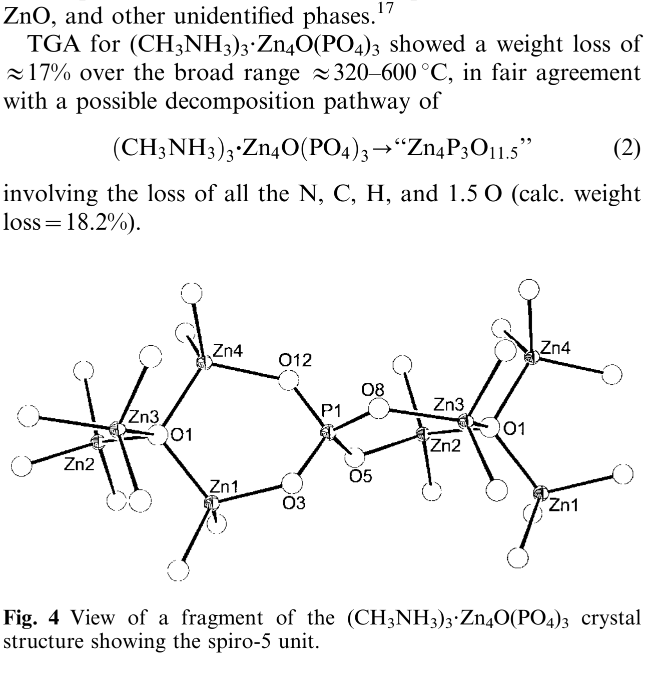

Fig. 4 View of a fragment of the $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ crystal structure showing the spiro-5 unit.

Discussion

Two new methylammonium zinc arsenate/phosphate phases, $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$, have been prepared as single crystals in reasonable yields and high purity and characterised by single-crystal diffraction methods. Problems of pseudo-symmetry and twinning had to be overcome before satisfactory structure solutions emerged. The title compounds have the same framework configuration as the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ family,[6] with methylammonium cations replacing the alkali metals seen previously. The $(CH_3NH_3)_3 \cdot Zn_4O(XO_4)_3$ phases are significantly less thermally stable than some other members of the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ family,[6] and the framework does not survive template removal, at least by the simple thermal methods explored to date.

The open-framework nature of $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ is emphasised by a PLATON[18] analysis (CALC SOLV option with default parameters) of the fraction of the unit cell volume *not* occupied by the framework Zn, As, and O atoms, assuming typical van der Waals' radii for these species. This showed that 359.7 Å^3 (38% of the unit cell volume) is "solvent accessible." However, when the methylammonium cations were included in the calculation, there was no residual volume, indicating that the organic species are well packed in the pores of this framework. A similar analysis for $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ showed 337.9 Å^3 (37.9% of the unit cell volume) to be solvent accessible for the empty $Zn_4O(PO_4)_3$ framework.

$(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ both crystallise as a new monoclinic modification of the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ structure type.[6] The geometries of the component tetrahedral species in each phase are unexceptional. The average Zn–O–As bond angle in $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ is some 4° less than the average Zn–O–P bond angle in $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$, which is consistent with a similar trend seen in other isostructural phases such as the sodalite types $Na_3(ZnAsO_4)_3 \cdot 4H_2O$ [θ(Zn–O–As) = 123.8°] and $Na_3(ZnPO_4)_3 \cdot 4H_2O$ [θ(Zn–O–P) = 126.1°].[19]

The simplest structural model for the $[Zn_4O(XO_4)_3]^{3-}$ framework component of this family can be established in the cubic space group $P\bar{4}3m$, with a unit cell parameter $a_0 \approx 7.2$–7.9 Å, depending on chemical composition.[6] Because of distortions of the $[Zn_4O(XO_4)_3]^{3-}$ framework and guest cation ordering, real $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ frameworks show superstructures, most commonly a $a_s \approx 2a_0$ face-centred cube, space group $F\bar{4}3c$. Tetragonal [*e.g.* $Cs_3Zn_4O(AsO_4)_3 \cdot 4H_2O$] and rhombohedral [*e.g.* $Na_3Zn_4O(PO_4)_3 \cdot 6H_2O$] distortions of the $F\bar{4}3c$ structure occur, which may be empirically correlated with the size and bonding requirements of the alkali metal cation involved.[20] The structures of monoclinic $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ correspond to a new superstructure of the $P\bar{4}3m$ cube with $a_m \approx a_0$, $b_m \approx 2b_0$, $c_m \approx c_0$, and $\beta \sim 90°$ (m refers to the monoclinic cell). The doubled monoclinic *b* dimension is accounted for by the zigzag ordering pattern of the H_3C1N1H_3 species noted above.

The previously described $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ phases, and $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ represent a notable example of a complex non-aluminosilicate open framework structure that is unusually *insensitive* to the nature of the templating species. Both metal cations + water molecules and organic cations lead to the same tetrahedral topology, albeit with different crystal symmetries. The structures of many organically templated framework structures may be partially rationalised in terms of strongly directional guest–framework H-bonding interactions.[21] It is notable that the hydrogen bonding patterns in $(CH_3NH_3)_3 \cdot Zn_4O(AsO_4)_3$ and $(CH_3NH_3)_3 \cdot Zn_4O(PO_4)_3$ appear to be *not* particularly specific, and probably involve multiple disorder of the N–H···O bonds, as discussed above. As is typical of hydrothermal synthesis, little insight into the mechanism of formation of these unusual phases can be gleaned from the present study.

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