

Ambient-Temperature Synthesis of New Layered AlPOs and GaPOs in Silica Gels

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A method for synthesising open-framework phosphates under less-severe conditions than those employed in conventional solvothermal processes is described. Two new layered aluminum phosphates containing pyridine and imidazole templates and their gallium analogues have been grown in silica gel at room temperature, and the structures determined by single-crystal X-ray diffraction. Crystal data: general formula $(C_5NH_6)[M(HPO_4)_2(H_2O)_2]$, triclinic, space group $P\bar{1}$, lattice parameters $a = 6.994(1)$, $b = 7.2208(7)$, $c = 12.114(1)$ Å, $\alpha = 105.080(8)$, $\beta = 104.85(1)$, $\gamma = 90.39(1)^\circ$ when $M = Al$; $a = 7.056(1)$, $b = 7.315(1)$, $c = 12.165(1)$ Å, $\alpha = 105.32(1)$, $\beta = 105.49(1)$, $\gamma = 90.25(1)^\circ$ when $M = Ga$. General formula $(C_3N_2H_5)[M(HPO_4)_2(H_2O)_2]$, monoclinic, space group $C2/c$, $a = 21.893(1)$, $b = 7.1830(3)$, $c = 6.9890(5)$ Å, $\beta = 104.164(5)^\circ$ when $M = Al$; $a = 22.002(2)$, $b = 7.262(1)$, $c = 7.047(1)$ Å, $\beta = 105.11(1)^\circ$ when $M = Ga$. The four structures are closely related and contain MO_6 ($M = Al, Ga$) and PO_4 polyhedra linked to form corrugated layers. The pyridinium or imidazolium cations occupy sites between these layers and are linked through hydrogen bonding to one or two adjacent layers, respectively.

Introduction

There has recently been much interest in the synthesis and characterization of layered aluminum and gallium phosphates because of their potential uses in areas such as ion exchange, catalysis, and separation science. To date, solvothermal methods have been employed under aqueous and nonaqueous conditions to produce low-dimensional AlPOs and GaPOs. Two series of layered AlPOs with P:Al ratios of 4:3^{1–9} and 3:2^{10–12} in which the interlamellar spaces are occupied by either organic amine cations or metal complexes such as Co(en)₃³⁺ or Co(tn)₃³⁺ (en = ethylenediamine, tn = 1,3-diaminopropane) have been characterized together with

one layered GaPO containing ethylenediamine which has a P:Ga ratio of 1:1.¹³ We have been investigating the room-temperature synthesis of microporous phosphates in silica gels with the intention of using templates that are unstable at the temperatures and pressures employed under solvothermal conditions. Silica gels have been used previously in the growth of crystals of a wide range of materials including metal oxalates, tartrates, and hydrogen phosphates.¹⁴ The main advantage of the gel growth method is that the number of accessible nucleation centers is reduced within the gel¹⁴ and so large, high-quality single crystals can be grown from solutions of reactants which, in the absence of gel, would otherwise produce amorphous or microcrystalline products. Two techniques are commonly adopted: namely, either the diffusion of one or more reactants into a preformed silica gel or the mixing of all components prior to gel formation. Both methods were explored in the 1960s and 1970s for the ambient-temperature growth of large single crystals of sodium-containing zeolites,^{15–17} but neither has yet been investigated for the synthesis of organically templated framework materials. We here report the synthesis of four organically templated layered aluminum and gallium phosphates: $(C_5NH_6)[Al(HPO_4)_2(H_2O)_2]$ (I), $(C_5NH_6)[Ga(HPO_4)_2(H_2O)_2]$ (II), $(C_3N_2H_5)[Al(HPO_4)_2(H_2O)_2]$ (III) and $(C_3N_2H_5)[Ga(HPO_4)_2(H_2O)_2]$ (IV). In

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Table 1. Summary of Synthetic Conditions^a

compound	I	II	III	IV
gel composition	1Al(NO ₃) ₃ :9.2py: 11H ₃ PO ₄ :3.4TEOS: 350H ₂ O	1Ga(NO ₃) ₃ :6.2py: 18H ₃ PO ₄ :1.9TEOS: 260H ₂ O	1Al(NO ₃) ₃ :11imid: 11H ₃ PO ₄ :5.1TMOS: 350H ₂ O	1Ga(NO ₃) ₃ :6.1imid: 18H ₃ PO ₄ :1.9TEOS: 260H ₂ O
initial gel pH	2	2	2	2
gel setting time	1 week	1 week	1 week	1 week
time of appearance of crystals	3 weeks	3 weeks	3 weeks	10 days
time at which crystals removed for X-ray study	4 weeks	4 weeks	3 weeks	3 weeks

^a py = pyridine; imid = imidazole; TEOS = tetraethyl orthosilicate; TMOS = tetramethyl orthosilicate.

Table 2. Combustion and Energy-Dispersive X-ray Analyses

compound		C (%)	H (%)	N (%)	M:P ratio
I	obsd	17.61	3.38	4.14	1:1.95(8)
	calcd for (C ₅ NH ₆)[AlH ₆ P ₂ O ₁₀]	17.92	3.61	4.18	1:2
II	obsd	15.84	3.45	3.56	1:2.1(2)
	calcd for (C ₅ NH ₆)[GaH ₆ P ₂ O ₁₀]	15.90	3.20	3.71	1:2
III	obsd	10.81	3.60	8.34	1:2.05(7)
	calcd for (C ₃ N ₂ H ₅)[AlH ₆ P ₂ O ₁₀]	11.12	3.42	8.64	1:2
IV	obsd	10.06	3.31	7.72	1:2.1(1)
	calcd for (C ₃ N ₂ H ₅)[GaH ₆ P ₂ O ₁₀]	9.82	3.02	7.64	1:2

Table 3. Summary of Crystallographic Data for Compounds I–IV

compound	I	II	III	IV
formula of asym unit	C ₅ H ₁₂ AlNP ₂ O ₁₀	C ₅ H ₁₂ GaNP ₂ O ₁₀	C _{3/2} H _{11/2} Al _{1/2} NPO ₅	C _{3/2} H _{11/2} Ga _{1/2} NPO ₅
<i>M_r</i>	335.08	377.82	162.03	183.40
crystal size (mm)	0.03 × 0.09 × 0.12	0.10 × 0.20 × 0.20	0.03 × 0.15 × 0.15	0.10 × 0.20 × 0.25
crystal habit	square plate	square plate	square plate	hexagonal plate
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	6.994(1)	7.056(1)	21.893(1)	22.002(2)
<i>b</i> (Å)	7.2208(7)	7.315(1)	7.1830(3)	7.262(1)
<i>c</i> (Å)	12.114(1)	12.165(1)	6.9890(5)	7.047(1)
α (deg)	105.080(8)	105.32(1)	90	90
β (deg)	104.85(1)	105.49(1)	104.164(5)	105.11(1)
γ (deg)	90.39(1)	90.25(1)	90	90
vol (Å ³)	569.2	581.8	1065.6	1087.0
<i>Z</i>	2	2	8	8
radiation wavelength (Å)	0.71069	1.5418	1.5418	1.5418
ρ_{Calc} (g cm ⁻³)	1.955	2.157	2.020	2.241
μ (cm ⁻¹)	4.989	64.175	5.105	68.688
$\theta_{\text{min}}, \theta_{\text{max}}$ (deg)	2, 25	2, 74	2, 74	2, 74
$h_{\text{min}}, h_{\text{max}}$	-9, 8	-8, 8	-26, 26	-26, 26
$k_{\text{min}}, k_{\text{max}}$	-8, 8	-8, 8	0, 8	0, 9
$l_{\text{min}}, l_{\text{max}}$	0, 15	0, 14	0, 8	0, 8
measured data	2957	2427	1180	2478
unique data	2474	2119	1047	1107
obsd data (<i>I</i> > 3 σ (<i>I</i>))	1344	1928	944	1064
<i>R</i> _{merge}	0.024	0.015	0.020	0.028
no. of parameters refined	176	143	106	101
resid electron density (e Å ⁻³)	-0.38, 0.37	-0.73, 0.85	-0.46, 0.41	-0.77, 1.02
<i>R</i> , <i>R</i> _w	0.037, 0.036	0.029, 0.034	0.031, 0.034	0.043, 0.055

addition to the novel method of their synthesis, these phases are unusual in that they have a metal:phosphorus ratio of 1:2, a stoichiometry previously unknown for layered AlPOs or GaPOs containing organic cations.

Experimental Section

Synthesis. To prepare the silica gels described in this work, 0.5 g of aluminum nitrate nonahydrate or gallium nitrate hydrate (18.8% Ga by mass) was dissolved in an appropriate quantity of deionized water (Table 1). Aqueous phosphoric acid (85% w/w) was added, and the solution stirred until homogeneous. Tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) was added, and the resultant mixture shaken until the orthosilicate ester had dissolved. This required ca. 30 min of shaking when TEOS was used, while TMOS dissolved after ca. 5 min. The organic template was then added and the mixture again stirred until homogeneous. The solution was placed in a soda-glass test tube, stoppered

tightly, and allowed to stand undisturbed at ambient temperature until a firm gel had formed. After a period of typically several weeks colorless crystals began to form within the gel. Reactions I–III led to the formation of transparent square plates, some of which aggregated to form spherical masses. Reaction IV resulted in the formation of transparent hexagonal plates, again with some spherical aggregates. When the crystals had reached sizes suitable for single-crystal X-ray diffraction, a sample of the gel was removed and stirred vigorously in deionized water. The resultant suspension of finely divided silica gel was decanted from the solid product, which was then washed further and dried in air at 60 °C for 24 h. Mixing the reagents together in the absence of either orthosilicate ester produced white powdery precipitates after several days. X-ray diffraction showed these products to be amorphous.

Characterization of the Products. Combustion analysis was used to determine the carbon, hydrogen, and nitrogen contents of the products. The results are summarized in Table

Table 4. Fractional Atomic Coordinates and Isotropic Thermal Parameters of Refined Atoms of Compound I

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Al(1)	1.0	0.5	1.0	0.0094
Al(2)	0.5	0.0	1.0	0.0092
P(1)	0.7989(2)	0.0610(1)	0.84952(9)	0.0094
P(2)	0.2990(1)	0.3049(1)	0.84842(9)	0.0091
O(1)	0.6587(5)	0.1030(4)	0.7346(3)	0.0176
O(2)	0.9525(4)	-0.0601(4)	0.8044(3)	0.0132
O(3)	0.8846(4)	0.2503(4)	0.9376(3)	0.0140
O(4)	0.6757(4)	-0.0546(4)	0.9002(3)	0.0118
O(5)	0.1638(4)	0.1579(4)	0.7338(3)	0.0164
O(6)	0.4472(4)	0.3947(4)	0.8003(3)	0.0132
O(7)	0.1751(4)	0.4596(4)	0.8996(3)	0.0122
O(8)	0.3973(4)	0.1973(4)	0.9366(3)	0.0132
O(9)	0.8061(4)	0.5808(4)	0.8817(3)	0.0125
O(10)	0.3013(4)	-0.1847(4)	0.8820(3)	0.0129
N(1)	0.3221(6)	0.5550(7)	0.6236(4)	0.0293
C(1)	0.2628(8)	0.4052(7)	0.5300(5)	0.0309
C(2)	0.1974(9)	0.4292(9)	0.4182(5)	0.0371
C(3)	0.1950(9)	0.6131(8)	0.4056(5)	0.0355
C(4)	0.256(1)	0.7658(8)	0.5051(6)	0.0368
C(5)	0.3219(8)	0.7331(8)	0.6138(5)	0.0342
H(1)	0.568(8)	0.197(8)	0.746(6)	0.05
H(2)	0.086(8)	0.076(8)	0.752(5)	0.05
H(3)	0.793(9)	0.712(6)	0.888(6)	0.05
H(4)	0.678(7)	0.522(8)	0.862(6)	0.05
H(5)	0.176(7)	-0.129(9)	0.862(6)	0.05
H(6)	0.268(9)	-0.302(7)	0.891(6)	0.05

Table 5. Fractional Atomic Coordinates and Isotropic Thermal Parameters of Refined Atoms of Compound II

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Ga(1)	1.0	0.5	1.0	0.0112
Ga(2)	0.5	0.0	1.0	0.0111
P(1)	0.79701(7)	0.05861(7)	0.84772(4)	0.0115
P(2)	0.29688(7)	0.30473(7)	0.84570(4)	0.0116
O(1)	0.6573(2)	0.1042(2)	0.7342(1)	0.0208
O(2)	0.9503(2)	-0.0582(2)	0.8016(1)	0.0166
O(3)	0.8818(2)	0.2434(2)	0.9405(1)	0.0180
O(4)	0.6757(2)	-0.0607(2)	0.8954(1)	0.0149
O(5)	0.1635(2)	0.1528(2)	0.7331(1)	0.0199
O(6)	0.4432(2)	0.3901(2)	0.7968(1)	0.0156
O(7)	0.1723(2)	0.4597(2)	0.8933(1)	0.0162
O(8)	0.3971(2)	0.2071(2)	0.9382(1)	0.0185
O(9)	0.7963(2)	0.5794(2)	0.8775(1)	0.0160
O(10)	0.2927(2)	-0.1878(2)	0.8769(1)	0.0149
N(1)	0.3197(3)	0.5526(4)	0.6207(2)	0.0321
C(1)	0.2574(5)	0.4060(4)	0.5251(3)	0.0409
C(2)	0.1948(5)	0.4332(5)	0.4150(3)	0.0403
C(3)	0.1957(5)	0.6174(5)	0.4054(2)	0.0371
C(4)	0.2605(5)	0.7659(4)	0.5059(3)	0.0404
C(5)	0.3232(5)	0.7314(4)	0.6138(3)	0.0376
H(1)	0.579(5)	0.206(4)	0.761(3)	0.05
H(2)	0.083(5)	0.067(5)	0.755(3)	0.05
H(3)	0.775(6)	0.715(3)	0.892(3)	0.05
H(4)	0.669(3)	0.516(5)	0.862(3)	0.05
H(5)	0.263(6)	-0.309(3)	0.888(3)	0.05

2 and support the results of the single-crystal X-ray structure determinations.

Energy-dispersive X-ray analyses of the products were carried out using a JEOL 2000FX analytical electron microscope, with the α -quartz polymorphs of AlPO₄ and GaPO₄ used as calibration standards.¹⁸ Ten crystallites of each product were analyzed, and the results are summarized in Table 2. There was no detectable amount of silicon present in any of the crystallites studied. The metal:phosphorus ratios of ca. 1:2 and the absence of silicon are again consistent with the results of the single-crystal X-ray structure determinations.

Single-Crystal X-ray Diffraction Structure Determinations. Suitable crystals were selected from the solid products of reactions I–IV. These were mounted on thin glass capillaries using cyanoacrylate adhesive. X-ray diffraction

Table 6. Fractional Atomic Coordinates and Isotropic Thermal Parameters of Refined Atoms of Compound III

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Al(1)	0.75	0.25	0.0	0.0151
P(1)	0.66930(2)	0.12484(5)	0.30506(5)	0.0150
O(1)	0.60873(6)	0.0311(2)	0.1693(2)	0.0249
O(2)	0.64383(6)	0.2320(2)	0.4566(2)	0.0204
O(3)	0.71562(5)	-0.0251(2)	0.3966(2)	0.0201
O(4)	0.69773(6)	0.2602(2)	0.1823(2)	0.0190
O(5)	0.81295(6)	0.1164(2)	0.1909(2)	0.0185
N(1)	0.5475(1)	0.4812(4)	0.3167(3)	0.0445
C(1)	0.5	0.3819(5)	0.25	0.0553
C(2)	0.5323(1)	0.6622(5)	0.2948(4)	0.0493
H(1)	0.622(1)	-0.063(4)	0.094(4)	0.0500
H(2)	0.802(2)	-0.003(4)	0.208(5)	0.0500
H(3)	0.826(1)	0.180(4)	0.316(4)	0.0500

Table 7. Fractional Atomic Coordinates and Isotropic Thermal Parameters of Refined Atoms of Compound IV

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Ga(1)	0.75	0.25	0.0	0.0117
P(1)	0.66838(3)	0.12655(8)	0.30153(9)	0.0119
O(1)	0.60846(9)	0.0281(3)	0.1658(3)	0.0205
O(2)	0.6425(1)	0.2297(2)	0.4505(3)	0.0162
O(3)	0.71703(9)	-0.0158(3)	0.3937(3)	0.0187
O(4)	0.6945(1)	0.2640(2)	0.1779(3)	0.0162
O(5)	0.81524(9)	0.1159(2)	0.2015(3)	0.0149
N(1)	0.5471(2)	0.4852(6)	0.3129(5)	0.0425
C(1)	0.5	0.3865(9)	0.25	0.0579
C(2)	0.5320(2)	0.6654(7)	0.2915(8)	0.0465
H(1)	0.619(2)	-0.062(5)	0.072(6)	0.05
H(2)	0.809(2)	-0.019(2)	0.220(7)	0.05
H(3)	0.828(2)	0.190(7)	0.325(5)	0.05

data were measured at 293 K on an Enraf-Nonius CAD4 Mark II diffractometer (graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å)) for compound I and an Enraf-Nonius Mach III diffractometer (graphite-monochromated Cu K α radiation ($\lambda = 1.5418$ Å)) for compounds II–IV. Unit-cell dimensions were determined from the measurement of the positions of 25 well-centered reflections. All intensity data were measured using a ω - 2θ scan technique. Three standard reflections were monitored hourly, and no significant crystal decay was detected during any of the data collections. X-ray absorption was monitored in each case by measurement of a ψ -scan through 360° using a reflection with $\chi \approx 90^\circ$. Data reduction and correction for absorption were carried out using the program RC93.¹⁹ The unit cells of compounds I and II were found to be triclinic (space group $P\bar{1}$), whereas those of compounds III and IV were found to be monoclinic (space group $C2/c$). Crystallographic data for the four compounds are summarized in Table 3.

The structures of compounds I–III were solved by direct methods using the program SIR92,²⁰ which located all the non-hydrogen atoms. Hydrogen atoms were then located in difference Fourier maps. All Fourier calculations and subsequent full-matrix least-squares refinements of the structures were carried out using the CRYSTALS suite of programs.²¹ Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.²² In the final cycles of each refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters. In addition, the positions of the hydrogen atoms of the framework hydroxyl groups were refined with O–H bond lengths restrained to be 1.00(5) Å. The template hydrogen atoms were positioned geometrically after each cycle

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Table 8. Selected Bond Lengths and Angles of Compounds I and II

	length in compound I (M = Al) (Å)	length in compound II (M = Ga) (Å)
M(1)–O(3)	1.852(3)	1.921(1)
M(1)–O(7)	1.910(3)	1.973(1)
M(1)–O(9)	1.919(3)	1.987(2)
M(2)–O(4)	1.910(3)	1.976(1)
M(2)–O(8)	1.854(3)	1.926(2)
M(2)–O(10)	1.928(3)	1.999(1)
P(1)–O(1)	1.586(3)	1.584(2)
P(1)–O(2)	1.511(3)	1.514(2)
P(1)–O(3)	1.506(3)	1.512(1)
P(1)–O(4)	1.531(3)	1.535(1)
P(2)–O(5)	1.580(3)	1.579(1)
P(2)–O(6)	1.527(3)	1.526(1)
P(2)–O(7)	1.520(3)	1.526(2)
P(2)–O(8)	1.510(3)	1.510(2)
N(1)–C(1)	1.320(7)	1.327(4)
C(1)–C(2)	1.370(8)	1.362(5)
C(2)–C(3)	1.372(9)	1.383(5)
C(3)–C(4)	1.377(9)	1.370(5)
C(4)–C(5)	1.361(9)	1.360(4)
C(5)–N(1)	1.322(7)	1.333(4)

	angle in compound I (deg)	angle in compound II (deg)
O(3)–M(1)–O(7)	87.2(1)	85.97(6)
O(3)–M(1)–O(9)	89.9(1)	89.09(6)
O(7)–M(1)–O(9)	89.9(1)	88.83(6)
O(4)–M(2)–O(8)	87.7(1)	86.93(6)
O(4)–M(2)–O(10)	89.9(1)	89.03(6)
O(8)–M(2)–O(10)	88.9(1)	87.83(6)
O(1)–P(1)–O(2)	104.3(2)	104.34(9)
O(1)–P(1)–O(3)	108.5(2)	109.03(9)
O(2)–P(1)–O(3)	113.7(2)	113.86(9)
O(1)–P(1)–O(4)	108.5(2)	108.79(9)
O(2)–P(1)–O(4)	110.2(2)	110.07(9)
O(3)–P(1)–O(4)	111.3(2)	110.48(9)
O(5)–P(2)–O(6)	103.1(2)	103.54(8)
O(5)–P(2)–O(7)	109.7(2)	109.93(9)
O(6)–P(2)–O(7)	109.3(2)	109.13(9)
O(5)–P(2)–O(8)	109.3(2)	109.55(9)
O(6)–P(2)–O(8)	112.7(2)	112.47(9)
O(7)–P(2)–O(8)	112.2(2)	111.89(9)
M(1)–O(3)–P(1)	160.7(2)	156.3(1)
M(2)–O(4)–P(1)	136.7(2)	134.25(9)
M(1)–O(7)–P(2)	139.7(2)	137.53(9)
M(2)–O(8)–P(2)	161.3(2)	157.2(1)
C(5)–N(1)–C(1)	121.8(5)	122.0(3)
N(1)–C(1)–C(2)	120.9(5)	120.8(3)
C(1)–C(2)–C(3)	118.5(5)	118.4(3)
C(2)–C(3)–C(4)	119.2(5)	119.5(3)
C(3)–C(4)–C(5)	119.7(5)	120.0(3)
C(4)–C(5)–N(1)	119.9(5)	119.4(3)

of refinement. The isotropic thermal parameters of all the framework and template hydrogen atoms were fixed at 0.05 Å². A three-term Chebychev polynomial weighting scheme was applied.²³ Fractional atomic coordinates and isotropic thermal parameters of refined atoms of compounds I–III are given in Tables 4–6, respectively.

Direct methods failed to solve the structure of compound IV correctly, and this structure was instead solved by Patterson methods using the program SHELXS-86.²⁴ This located the gallium and phosphorus atoms. The remaining non-hydrogen atoms were located in observed Fourier maps and the hydrogen atoms located in difference Fourier maps.

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Table 9. Selected Bond Lengths and Angles of Compounds III and IV

	length in compound III (M = Al) (Å)	length in compound IV (M=Ga) (Å)
M(1)–O(3)	1.853(1)	1.923(2)
M(1)–O(4)	1.911(1)	1.967(2)
M(1)–O(5)	1.923(1)	1.991(2)
P(1)–O(1)	1.580(1)	1.583(2)
P(1)–O(2)	1.521(1)	1.517(2)
P(1)–O(3)	1.510(1)	1.508(2)
P(1)–O(4)	1.526(1)	1.532(2)
N(1)–C(1)	1.253(4)	1.243(6)
N(1)–C(2)	1.342(4)	1.350(7)
C(2)–C(2)	1.399(6)	1.37(1)

	angle in compound III (deg)	angle in compound IV (deg)
O(3)–M(1)–O(4)	87.65(5)	86.55(8)
O(3)–M(1)–O(5)	89.40(5)	88.49(8)
O(4)–M(1)–O(5)	89.94(5)	88.70(8)
O(1)–P(1)–O(2)	103.70(7)	103.7(1)
O(1)–P(1)–O(3)	109.17(7)	109.7(1)
O(2)–P(1)–O(3)	112.88(7)	113.2(1)
O(1)–P(1)–O(4)	109.36(7)	109.1(1)
O(2)–P(1)–O(4)	109.79(7)	109.6(1)
O(3)–P(1)–O(4)	111.61(7)	111.2(1)
M(1)–O(3)–P(1)	162.53(9)	158.1(1)
M(1)–O(4)–P(1)	138.04(7)	135.7(1)
C(1)–N(1)–C(2)	110.4(2)	111.1(4)
N(1)–C(1)–N(1)	110.6(4)	109.6(6)
N(1)–C(2)–C(2)	104.3(2)	104.1(3)

Table 10. Hydrogen-Bonding Distances (Å) Present in Compounds I and II

	compound I	compound II
O(1)···O(6)	2.652(4)	2.653(2)
O(5)···O(2)	2.590(4)	2.583(2)
O(9)···O(4)	2.766(4)	2.741(2)
O(9)···O(6)	2.660(4)	2.652(2)
O(10)···O(2)	2.634(4)	2.622(2)
O(10)···O(7)	2.788(4)	2.784(2)
N(1)···O(6)	2.651(5)	2.668(3)

Table 11. Hydrogen-Bonding Distances (Å) Present in Compounds III and IV

	compound III	compound IV
O(1)···O(2)	2.633(2)	2.638(3)
O(2)···O(5)	2.648(2)	2.636(3)
O(4)···O(5)	2.737(2)	2.719(2)
N(1)···O(2)	2.757(2)	2.779(4)

Subsequent refinement of the structure was carried out in the same manner as described for compounds I–III. It was necessary to correct the data for the effects of secondary extinction using the method of Larsen.²⁵ Fractional atomic coordinates and isotropic thermal parameters of refined atoms are summarized in Table 7.

Selected bond lengths and angles for the compounds I and II are presented in Table 8 and for compounds III and IV in Table 9. Short nonbonded O···O and N···O distances which indicate the presence of hydrogen bonds are listed in Tables 10 and 11. Figure 1 shows the local coordination of the asymmetric units of compounds I and II, while Figure 2 shows the local coordination of the asymmetric units of compounds III and IV.

Discussion

The four compounds described in this work all have isostructural corrugated metal–phosphate layers, with

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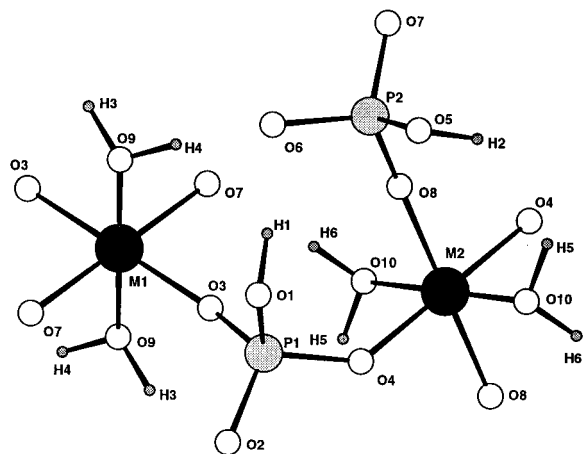


Figure 1. Local coordination of the asymmetric units of compounds I and II, showing numbering scheme (compound I, M = Al; compound II, M = Ga). Drawing package CAMERON.²⁶

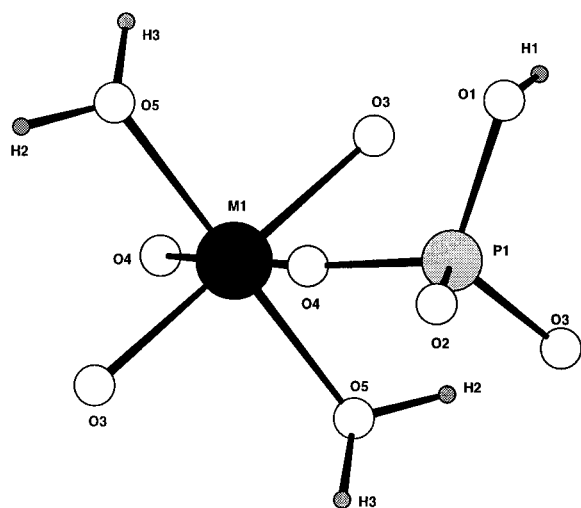


Figure 2. Local coordination of the asymmetric units of Compounds III and IV, showing numbering scheme (compound III, M = Al; compound IV, M = Ga).

the differences in unit-cell dimensions and symmetry being due to varying arrangements of template cations. The topology of the layers, which is based solely on eight-membered rings of polyhedra, is unlike that of any previously reported aluminophosphate.

Compound I has anionic layers constructed from alternating AlO_6 octahedra and PO_4 tetrahedra (Figure 3). There are two distinct Al sites, both of which are located on crystallographic centers of inversion. There are no significant differences between the local geometries of the two sites. Each aluminum atom is coordinated to four phosphate groups and two water molecules. There is however considerable difference between the two Al–O_{phosphate} bond lengths around each Al (Al(1)–O(3) 1.852(3) Å, cf. Al(1)–O(7) 1.910(3) Å; Al(2)–O(8) 1.854(3) Å, cf. Al(2)–O(4) 1.910(3) Å) resulting from hydrogen bonding as described below.

There are also two distinct phosphorus sites, both of which have no crystallographic symmetry. Each phosphorus is coordinated to four oxygen atoms, with no significant difference in the local geometries of the phosphate groups. The phosphate ions have two oxygens coordinated to aluminum (O(3) and O(4); O(7) and O(8)), with bond lengths typical of those found previ-

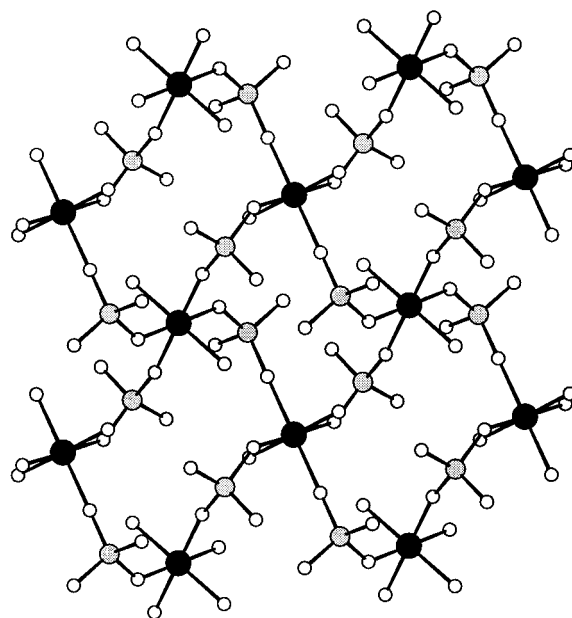


Figure 3. View of one aluminophosphate layer of compound I along the *c* axis showing eight-membered rings of polyhedra. Framework hydrogen atoms have been omitted for clarity. Key: black spheres = Al, gray spheres = P, white spheres = O.

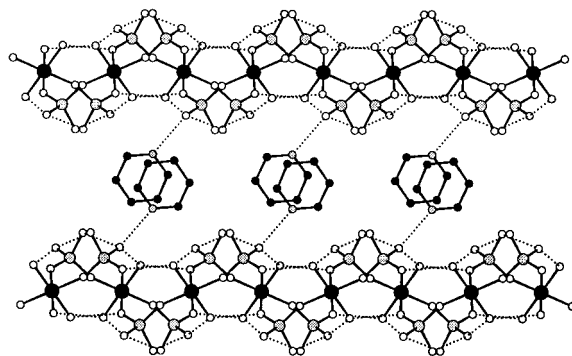


Figure 4. View of compound I along the *a* axis showing pyridinium cations occupying sites between the corrugated aluminophosphate layers. Hydrogen bonds are shown as dotted lines. All hydrogen atoms have been omitted. Key: large black spheres = Al, large gray spheres = P, white spheres = O, small black spheres = C, small gray spheres = N.

ously in other aluminophosphate materials.¹⁰ One of the remaining P–O bond lengths of each phosphate group is considerably longer than the other (P(1)–O(1) 1.586(3) Å; P(2)–O(5) 1.580(3) Å), consistent with the presence of distinct P–OH groups. This assignment is supported by the location of H(1) and H(2) in difference Fourier maps and by bond-valence calculations.²⁷ The remaining P–O lengths (P(1)–O(2) 1.511(3) Å, P(2)–O(6) 1.527(3) Å) are rather short, suggesting some multiple-bond character.

There is a complex network of hydrogen bonds within each aluminophosphate layer (Table 10), but no direct hydrogen bonds between adjacent layers (Figure 4). The two P–OH groups are each hydrogen bonded to a different phosphoryl oxygen (O(1)⋯O(6) 2.652(4) Å,

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O(5)⋯O(2) 2.590(4) Å), as is one hydroxyl group of each water molecule (O(9)⋯O(6) 2.660(4) Å, O(10)⋯O(2) 2.634(4) Å). The second hydroxyl group is hydrogen bonded to a P–O–Al bridging oxygen (O(9)⋯O(4) 2.766(4) Å, O(10)⋯O(7) 2.788(4) Å), which results in the elongation of the Al(1)–O(7) and Al(2)–O(4) bond lengths mentioned above.

The pyridinium template cations occupy sites between the layers and balance the overall negative electrostatic charge of the AlPO layers. The nitrogen atom of each template molecule is hydrogen bonded to the oxygen of only one of the two phosphoryl groups in the adjacent aluminophosphate layer (N(1)⋯O(6) 2.651(5) Å), but there is no such bonding to the other neighboring layer (Figure 4).

Compound II is isostructural with compound I, and the only significant differences between the structures are due to the slightly longer Ga–O bond lengths compared with the Al–O bond lengths (Table 8). The geometries of the phosphate groups, the hydrogen bonding within the layers (Table 10), and the position of the template cations are all essentially unchanged compared with those of compound I.

The metal–phosphate layers of compounds III and IV are isostructural with those of compounds I and II. The former compounds have additional crystallographic symmetry, however, with the result that there is only one crystallographically distinct metal site and one distinct phosphate site within the structures. The intralayer hydrogen bonding in each case is similar to that present in compounds I and II (Table 11), but the imidazolium template is hydrogen bonded to phosphoryl oxygen atoms of both adjacent metal–phosphate layers (Figure 5). This leads to additional symmetry within the structure but does not result in any substantial change in template location or metal–phosphate layer stacking.

Conclusion

This work has demonstrated that silica gels can be used to grow high-quality large single crystals of organically templated aluminum and gallium phosphates at room temperature. The products are interesting in themselves—they are the first reported examples of organically templated layered aluminum or gallium phosphates with metal:phosphorus ratios of 1:2. The previously reported examples of aluminophosphates

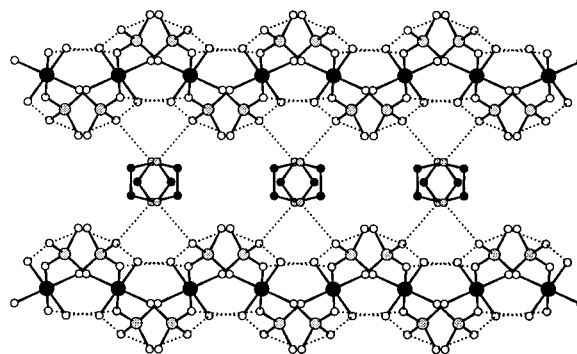


Figure 5. View of compound II along the *c* axis showing the more symmetric environment of the cations in comparison to those in compound I. Key as for Figure 4.

phosphates with metal:phosphorus ratio 1:2, for example, (Et₃NH)[H₂AlP₂O₈],²⁸ (C₁₀N₂H₉)[Al(PO₄)(H₂PO₄)],²⁹ and [H₃N(CH₂)_{*n*}NH₃][Ga(PO₄)(HPO₄)] (*n* = 3,³⁰ 4³¹), all have one-dimensional fibrous structures. Previously reported layered aluminophosphates have Al:P ratios of 3:4, for example, 1.5(H₃NC₄H₈NH₃)[Al₃(PO₄)₄],² or 2:3, for example, (C₅H₅NH)[Al₂(PO₄)(HPO₄)₂].¹⁰ The latter has pyridine as template but is structurally unrelated to the phases described in this work.

To our knowledge this is the first use of silica gels as growth media for organically templated metal phosphates. There is considerable potential to extend this technique to encompass other systems such as those containing thermally unstable templates and this is currently under investigation.

Acknowledgment. A.M.C. thanks the University of Oxford for a Glasstone Research Fellowship, and M.A.L. and A.R.C. thank the EPSRC for studentships.

Supporting Information Available: Tables listing coordinates of geometrically placed hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms (9 pages); tables of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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