Synthesis and Crystal Structures of Two Novel Anionic Aluminophosphates: A One-Dimensional Chain, UT-7 ($[Al_3P_5O_{20}H]^{5-}[C_7H_{13}NH_3^+]_5$), and a Layer Containing Two Cyclic Amines, UT-8 ($[Al_3P_4O_{16}]^{3-}[C_4H_7NH_3^+]_2[C_5H_{10}NH_2^+]$)

Scott Oliver, Alex Kuperman,† Alan Lough, and Geoffrey A. Ozin*

Materials Chemistry Research Group, Lash Miller Chemical Laboratories, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

Received April 26, 1996[⊗]

UT-7 and UT-8 (University of Toronto, structure numbers 7 and 8) are two novel aluminophosphate materials prepared under non-aqueous conditions. Their structures, extended in one and two dimensions, respectively, have been solved by single-crystal X-ray diffraction and characterized by a variety of methods including powder X-ray diffraction (PXRD), *insitu* high-temperature PXRD, thermogravimetric analysis (TGA), energy dispersive X-ray analysis (EDX), and scanning electron microscopy (SEM). UT-7 ($[Al_3P_5O_{20}H]^{5-}[C_7H_{13}NH_3^+]_5$, triclinic space group $P\bar{1}$, $Z = 2$, $a = 10.118(3)$ Å, $b = 15.691(4)$ Å, $c = 18.117(3)$ Å, $\alpha = 72.91(2)°$, $\beta = 85.18(2)°$, $\gamma = 79.49(2)°$) is built of polymeric one-dimensional chain units, hydrogen-bonded into anionic layers that are charge-compensated by interlamellar cycloheptylammonium cations. UT-7 is isostructural to our previously discovered UT-3 chain structure, isolated in the analogous cyclopentylamine system. UT-8 ($[Al_3P_4O_{16}]^{3-}$-$[C_4H_7NH_3^+]_2[C_5H_{10}NH_2^+]$, monoclinic space group $P2_1$, $Z = 2$, $a = 8.993(4)$ Å, $b = 14.884(8)$ Å, $c = 9.799(9)$ Å, $\beta = 103.52(3)°$) is a two-dimensional net isostructural to several previously reported $[Al_3P_4O_{16}]^{3-}$ layers. The interlayer region of UT-8 is occupied by two different cyclic organic amine species, namely piperidinium and cyclobutylammonium. To our knowledge, this is the first report of the crystal structure of an aluminophosphate material containing cyclobutylammonium or a mixture of cyclic amines. Interestingly, UT-7 is observed to thermally transform in the solid state to an as yet unknown layered material that can be independently synthesized in a similar synthetic system. In the same way as UT-3 transforms to the UT-4 layered phase, we believe UT-7 transforms to a layered material by means of a chain to layer transformation.

Introduction

The number of structurally and compositionally unique aluminophosphate materials continues to increase through ongoing synthetic work. While some possess framework molecular sieve structures,[1−4] more recent examples are of one-dimensional chains[5−7] or two-dimensional layered materials.[4,7−16] Many of these chain and layered aluminophosphates have been isolated using non-aqueous solvents. They represent a new class

Table 1. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters[a]

	UT-7	UT-8
empirical formula	$C_{35}H_{81}Al_3N_5O_{20}P_5$	$C_{13}H_{32}Al_3N_3O_{16}P_4$
M_r	1127.84	691.24
space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
temp, K	293(2)	173(2)
a, Å	10.118(3)	8.993(4)
b, Å	15.691(4)	14.884(8)
c, Å	18.117(3)	9.799(9)
α, deg	72.91(2)	90
β, deg	85.18(2)	103.52(3)
γ, deg	79.49(2)	90
V, A^3	2701.7(11)	1275(2)
Z	2	2
ρ_{obsd}, g cm^{-3}	not measured	not measured
ρ_{calcd}, g cm^{-3}	1.386	1.800
μ(MoKα), cm^{-1}	2.92	4.82
R_1 [$I > 2\sigma(I)$]	0.0774	0.0557
wR_2 (all data)	0.2206	0.1989

[a] Definition of R indices: $R_1 = \sum(F_o - F_c)/\sum(F_o)$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

† Current address: Catalysis Lab, The Dow Chemical Company, Midland, MI 48674.

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) (a) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146. (b) Wilson, S. T.; Lok, B. M.; Flanigen, E. M. U.S. Patent 4,310,440.
(2) Szostak, R. *Molecular Sieves: Principles of Synthesis and Identification*; Van Nostrand Reinhold: Toronto, Canada, 1989.
(3) (a) Huo, Q.; Xu, R.; Li, S.; Ma, Z.; Thomas, J. M.; Jones, R. H.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 875. (b) Jones, R. H.; Thomas, J. M.; Chen, J.; Xu, R.; Huo, Q.; Li, S.; Ma, Z.; Chippindale, A. M. *J. Solid State Chem.* **1993**, *102*, 204.
(4) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. Submitted for publication.
(5) Jones, R. H.; Thomas, J. M.; Xu, R.; Huo, Q.; Xu, Y.; Cheetham, A. K.; Bieber, D. *J. Chem. Soc., Chem. Commun.* **1990**, 1170.
(6) Tieli, W.; Long, Y.; Wengin, P. *J. Solid State Chem.* **1990**, *89*, 392.
(7) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A., *Chem. Mater*. **1996**, *8*, 2391.
(8) Jones, R. H.; Thomas, J. M.; Xu, R.; Huo, Q.; Cheetham, A. K.; Powell, A. V. *J. Chem. Soc., Chem. Commun*. **1991**, 1266.
(9) Thomas, J. M.; Jones, R. H.; Xu, R.; Chen, J.; Chippindale, A. M.; Natarajan, S.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun*. **1992**, 929.
(10) Chippindale, A. M.; Powell, A. V.; Bull, L. M.; Jones, R. H.; Cheetham, A. K.; Thomas, J. M.; Xu, R. *J. Solid State Chem.* **1992**, *96*, 199.
(11) Kuperman, A.; Nadimi, S.; Oliver, S.; Ozin, G. A.; Garces, J. M.; Olken, M. M. *Nature* **1993**, *365*, 239.
(12) (a) Jones, R. H.; Chippindale, A. M.; Natarajan, S.; Thomas, J. M. *J. Chem. Soc., Chem. Commun*. **1994**, 565. (b) Chippindale, A. M.; Natarajan, S.; Thomas, J. M.; Jones, R. H. *J. Solid State Chem*. **1994**, *111*, 18.
(13) Morgan, K.; Gainsford, G.; Milestone, N. *J. Chem. Soc., Chem. Commun*. **1995**, 425.
(14) Barrett, P. A.; Jones, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1979.
(15) Bruce, D. A.; Wilkinson, A. P.; White, M. G.; Bertrand, J. A. *J. Chem. Soc., Chem. Commun.* **1995**, 2059.
(16) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *J. Chem. Soc., Chem. Commun.* **1996**, 1761.

S0020-1669(96)00458-2 CCC: $12.00

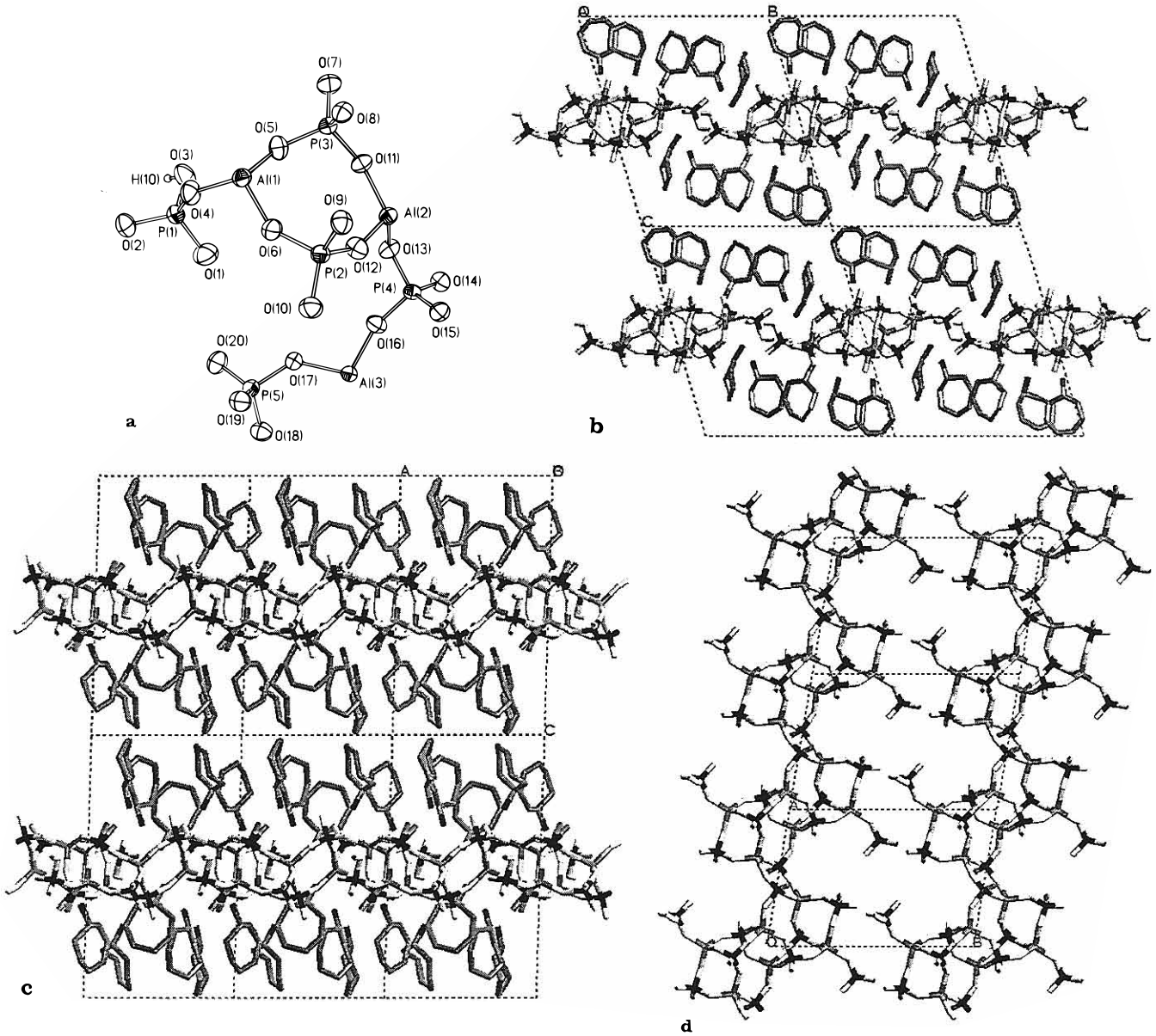

Figure 1. Cerius graphical representations of the UT-7 structure. The organic hydrogens have been omitted in parts b−d for clarity. Key: (a) thermal ellipsoids and naming scheme of the asymmetric unit; (b) [100]-projection, with an end-on projection of the chains and their connection into layers through terminal phosphate groups (note the bilayer-like arrangement of the cycloheptylammonium cations); (c) [010]-projection, showing a side-on view of the chains and the bilayer-like arrangement of cyclics; (d) [001]-projection, with a clear view of the chain structure. The organics have been omitted for clarity. Shading scheme: oxygen and hydrogen, white; phosphorus and nitrogen: black; aluminum and carbon: gray.

of aluminophosphate materials that is distinct to the strictly 1:1, Al:P framework $AlPO_4$-*n*'s. Consequently, these new materials are expected to have unique properties for potential use in intercalation or catalytic applications. Unlike the fully cross-linked $AlPO_4$-*n* frameworks, the presence of singly-, doubly-, and triply-bridged phosphate groups containing terminal oxygens intriguingly renders these materials potentially useful in self-assembly processes, by using them as a starting substrate or by the growth of the layered structures from monomeric sources or exfoliated layers.[17]

Most of the recently reported, non-framework aluminophosphates are layered. It is noteworthy that while over 12 layered structures have been reported, there are, in fact, only six structurally unique materials and, of these, there are only two unique layer stoichiometries. For example, seven materials possess the empirical formula $[Al_3P_4O_{16}]^{3-}$,[8,9,11−15] of which there are only three unique structure types. The isostructurality and stoichiometric equivalence of the layers is an indication of the thermodynamic stability of their structures, similar to the template-independence of many of the $AlPO_4$-*n* molecular sieves and aluminosilicate zeolites.[2] To date, there exist only three examples of chain aluminophosphates,[5−7] of which two are isostructural.[5,6]

Here, we increase the number of known aluminophosphates with the report of a new chain aluminophosphate, denoted UT-7, that is isomorphous with our previously reported chain UT-3 structure.[7] The thermal properties of the material have been investigated, and a transformation to a layered material is observed to occur. We believe this transformation to be analogous to the UT-3 to UT-4 chain to layer solid state transformation that we have previously reported.[7] We also report a new layered material UT-8, prepared in a mixed cyclic amine system.

(17) See, for example: (a) Hong, H.; Sackett, D. D.; Mallouk, T. E. *Chem. Mater*. **1991**, *3*, 521. (b) Kepley, L. J.; Sackett, D. D.; Bell, C. M.; Mallouk, T. E. *Thin Solid Films* **1992**, *208*, 132.

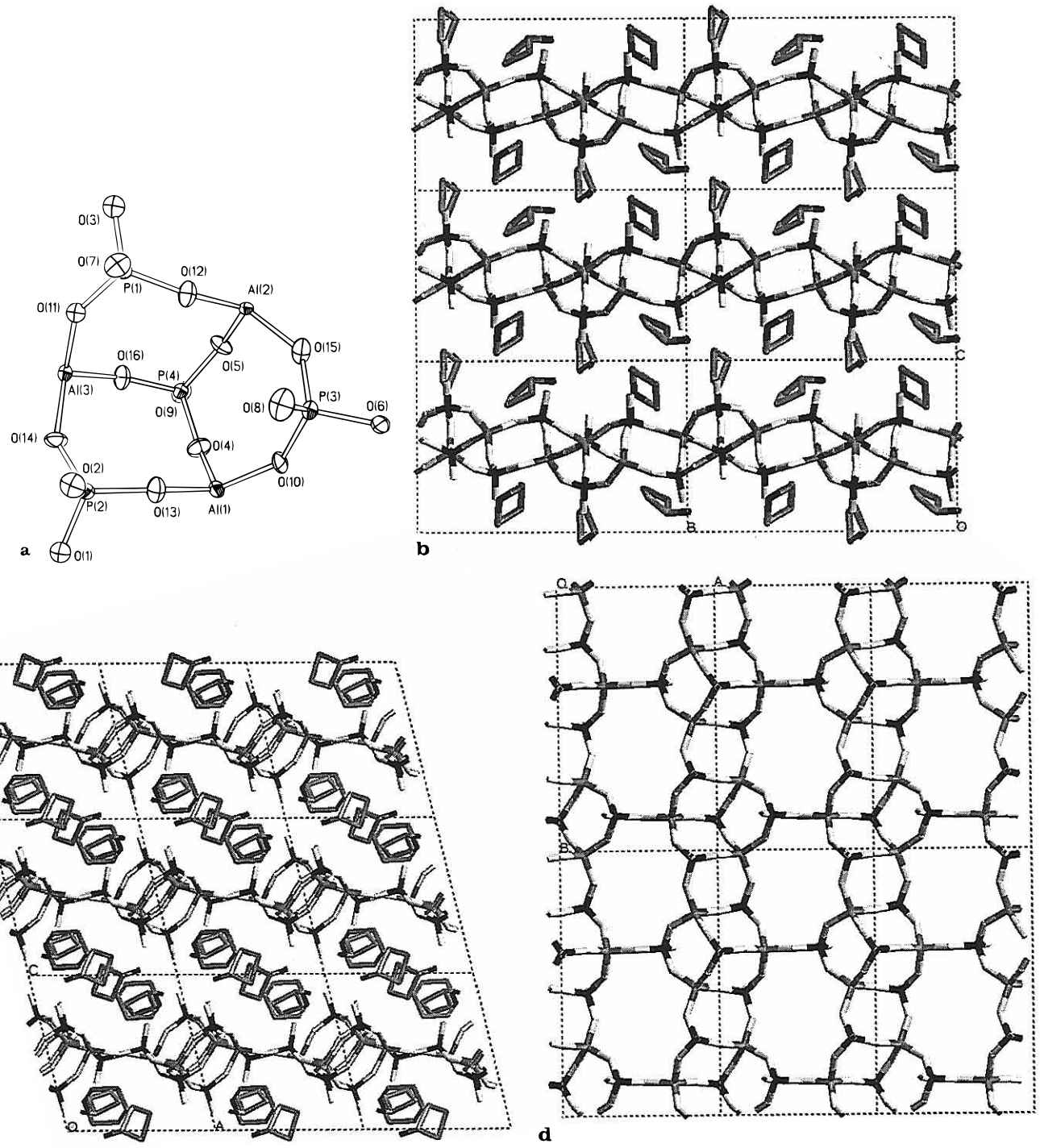

Figure 2. Cerius graphical representations of the UT-8 structure. Organic hydrogens in parts b−d have been omitted for clarity. Key: (a) Thermal ellipsoids and naming scheme of the asymmetric unit; (b) [100]-projection, side-on view of the layer; (c) [010]-projection (note the cage-like aggregation of the template molecules); (d) [001]-projection top view of the " capped $AlPO_4$-12 layer". The cyclic amines obstruct the eight-membered ring channels of the structure (omitted for clarity). Shading scheme is the same as for Figure 1.

Experimental Section

Synthesis of UT-7 and UT-8. The synthesis procedures for both structures is identical, with the exception of the final step when organic amine(s) is (are) added. Into a preweighed tetraethylene glycol (TEG) solvent (as-received, Aldrich), hydrated pseudoboehmite (Dispal 23N4−80, Aldrich) is dispersed, with magnetic stirring. Phosphoric acid (85 wt %) is then added dropwise with stirring, allowing the mixture to homogenize after each drop. Finally, the organic amine (as-received, Aldrich) is added, and the mixture rapidly gelates. It must be immediately stirred rigorously by hand to achieve homogeneity. After magnetic stirring for 15 min, the gel is loaded into 15 mL capacity Teflon-lined stainless steel autoclaves (constructed in-house) to a *ca.* 60% degree of filling. The autoclaves are placed in a forced-convection oven and statically treated at the synthesis temperature for the required time period. The ideal synthesis conditions for the materials are as follows: **UT-7**, 28TEG: 0.9 Al_2O_3·*n*H_2O:1.8P_2O_5:5.9cycloheptylamine ($C_7H_{13}NH_2$), 150 °C, 3 days; **UT-8**, 14TEG:0.9Al_2O_3·*n*H_2O:1.8P_2O_5:2.9cyclobutylamine ($C_4H_7NH_2$):2.9piperidine ($C_5H_{10}NH$), 180 °C, 6 days.

Sample Characterization. Powder X-ray diffraction (PXRD) patterns were collected on a Siemens D5000 diffractometer using Ni-filtered Cu Kα radiation (λ = 1.541 78 Å). The step size used was 0.030°, step time 1.0 s, and scan range 1−50° in 2θ. The detector in the instrument was a Kevex 2005−212 solid state detector. High-temperature (HT-) PXRD patterns were obtained by running samples *in situ* on the same instrument under a nitrogen flow, using a Siemens HTK 10 attachment. The heating rate typically used was 10 °C/min

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for UT-7

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Al(1)	−30(2)	−2926(1)	5548(1)	29(1)	C(16)	2687(9)	−1995(7)	2772(4)	74(3)
Al(2)	1289(2)	−327(1)	4206(1)	27(1)	C(17)	3291(7)	−2609(7)	3464(5)	80(3)
Al(3)	6513(2)	−1187(1)	4904(1)	25(1)	N(2)	7311(5)	226(4)	2760(3)	39(1)
P(1)	2201(2)	−4531(1)	5487(1)	34(1)	C(21)	7670(11)	458(6)	1927(5)	75(3)
P(2)	854(2)	−1313(1)	5980(1)	27(1)	C(22)	7454(29)	−208(9)	1591(7)	308(19)
P(3)	−750(1)	−1515(1)	4024(1)	27(1)	C(23)	8071(35)	−223(13)	854(8)	406(29)
P(4)	4141(1)	54(1)	3845(1)	25(1)	C(24)	7621(34)	499(12)	199(9)	304(19)
P(5)	6964(2)	−3147(1)	5898(1)	30(1)	C(25)	7455(29)	1424(13)	147(8)	233(12)
O(1)	3309(5)	−3998(4)	5429(3)	57(1)	C(26)	7642(31)	1769(13)	760(6)	273(16)
O(2)	2448(5)	−5461(3)	6035(3)	45(1)	C(27)	7240(19)	1389(7)	1547(6)	149(7)
O(3)	1908(6)	−4584(3)	4663(3)	52(1)	N(3)	3548(6)	−3213(4)	6609(3)	51(2)
O(4)	875(4)	−4003(3)	5720(3)	45(1)	C(31)	3167(10)	−3891(6)	7313(5)	84(3)
O(5)	−124(4)	−2440(3)	4552(2)	37(1)	C(32)	4077(14)	−4744(7)	7421(7)	122(5)
O(6)	714(4)	−2263(3)	5955(3)	40(1)	C(33)	4391(31)	−5325(14)	8183(8)	327(21)
O(7)	−1243(4)	−1621(3)	3310(3)	43(1)	C(34)	4309(19)	−5129(15)	8913(8)	240(14)
O(8)	−1886(4)	−1081(3)	4489(2)	33(1)	C(35)	3172(25)	−4619(16)	9210(11)	265(16)
O(9)	−584(4)	−823(3)	6105(2)	35(1)	C(36)	2279(23)	−4013(14)	8636(9)	265(15)
O(10)	1769(4)	−1406(3)	6606(2)	40(1)	C(37)	2862(21)	−3485(8)	7929(6)	218(12)
O(11)	336(4)	−905(3)	3832(2)	34(1)	N(4)	307(6)	−6348(4)	6431(3)	49(2)
O(12)	1358(4)	−777(3)	5194(2)	37(1)	C(41)	−297(8)	−6320(4)	7212(4)	55(2)
O(13)	2931(4)	−408(3)	3830(2)	34(1)	C(42)	−845(11)	−5393(5)	7195(5)	83(3)
O(14)	4542(4)	553(3)	3048(2)	37(1)	C(43)	−1533(20)	−5169(10)	7853(6)	187(9)
O(15)	3705(4)	695(3)	4347(2)	35(1)	C(44)	−1270(22)	−5622(14)	8643(7)	242(13)
O(16)	5303(4)	−679(3)	4220(2)	37(1)	C(45)	−276(19)	−6380(10)	8984(7)	182(9)
O(17)	6347(4)	−2320(3)	5231(2)	35(1)	C(46)	170(16)	−7079(8)	8612(5)	135(6)
O(18)	8405(4)	−2988(3)	5986(3)	41(1)	C(47)	617(10)	−6877(7)	7809(4)	93(3)
O(19)	6218(4)	−3114(3)	6642(3)	41(1)	N(5)	−2530(5)	−2057(4)	7204(3)	42(1)
O(20)	6941(5)	−3977(3)	5669(3)	53(1)	C(51)	−1867(8)	−2498(5)	7953(4)	59(2)
H(1O)	2349(82)	−5046(37)	4588(25)	113(40)	C(52)	−2862(12)	−2939(8)	8515(5)	108(4)
N(1)	5179(6)	−3401(4)	4314(3)	43(1)	C(53)	−2711(26)	−3084(15)	9346(7)	265(14)
C(11)	4656(7)	−2724(10)	3648(6)	135(6)	C(54)	−3041(19)	−2277(14)	9634(8)	177(9)
C(12)	5679(10)	−2347(9)	3117(5)	110(5)	C(55)	−2379(24)	−1469(13)	9341(10)	209(11)
C(13)	5647(13)	−2289(15)	2320(7)	210(10)	C(56)	−2117(16)	−1157(9)	8493(9)	170(9)
C(14)	4611(11)	−1794(13)	1804(7)	160(7)	C(57)	−1212(12)	−1834(7)	8175(6)	103(4)
C(15)	3253(11)	−1948(12)	2013(6)	149(6)					

[a] Defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. Coordinates for organic hydrogens have been omitted; see Supporting Information.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for UT-7

Al(1)−O(18)	1.716(4)	Al(1)−O(4)	1.722(4)	P(3)−O(5)	1.541(4)	P(3)−O(8)	1.543(4)
Al(1)−O(6)	1.739(4)	Al(1)−O(5)	1.745(5)	P(4)−O(14)	1.489(4)	P(4)−O(15)	1.530(4)
Al(2)−O(12)	1.723(4)	Al(2)−O(11)	1.733(4)	P(4)−O(16)	1.533(4)	P(4)−O(13)	1.538(4)
Al(2)−O(13)	1.738(4)	Al(2)−O(9)	1.756(4)	P(5)−O(20)	1.482(5)	P(5)−O(19)	1.500(5)
Al(3)−O(16)	1.727(4)	Al(3)−O(15)	1.729(4)	P(5)−O(18)	1.553(4)	P(5)−O(17)	1.563(4)
Al(3)−O(17)	1.736(4)	Al(3)−O(8)	1.743(4)	N(1)−C(11)	1.420(10)	C(11)−C(17)	1.415(7)
P(1)−O(1)	1.495(5)	P(1)−O(2)	1.495(5)	C(11)−C(12)	1.438(7)	C(12)−C(13)	1.421(8)
P(1)−O(4)	1.539(4)	P(1)−O(3)	1.576(5)	C(13)−C(14)	1.421(8)	C(14)−C(15)	1.439(8)
P(2)−O(10)	1.481(4)	P(2)−O(12)	1.525(4)	C(15)−C(16)	1.430(7)	C(16)−C(17)	1.442(7)
P(2)−O(6)	1.537(4)	P(2)−O(9)	1.549(4)	N(2)−C(21)	1.476(9)	N(3)−C(31)	1.475(10)
P(3)−O(7)	1.488(4)	P(3)−O(11)	1.539(4)	N(4)−C(41)	1.503(9)	N(5)−C(51)	1.485(9)

O(4)−Al(1)−O(5)	108.6(2)	O(6)−Al(1)−O(5)	109.8(2)	O(12)−P(2)−O(6)	109.8(3)	O(10)−P(2)−O(9)	113.3(3)
O(4)−Al(1)−O(6)	111.4(2)	O(18)−Al(1)−O(5)	111.8(2)	O(12)−P(2)−O(9)	106.1(2)	O(6)−P(2)−O(9)	106.6(2)
O(18)−Al(1)−O(4)	108.8(2)	O(18)−Al(1)−O(6)	106.5(2)	P(1)−O(4)−Al(1)	141.8(3)	P(3)−O(5)−Al(1)	135.0(3)
O(12)−Al(2)−O(11)	109.8(2)	O(12)−Al(2)−O(13)	107.6(2)	P(2)−O(6)−Al(1)	148.2(3)	P(3)−O(8)−Al(3)	142.6(3)
O(11)−Al(2)−O(13)	111.7(2)	O(12)−Al(2)−O(9)	114.7(2)	P(2)−O(12)−Al(2)	153.8(3)	P(4)−O(13)−Al(2)	135.4(3)
O(11)−Al(2)−O(9)	107.0(2)	O(13)−Al(2)−O(9)	106.1(2)	C(17)−C(11)−N(1)	120.7(7)	N(1)−C(11)−C(12)	113.5(7)
O(1)−P(1)−O(2)	114.4(3)	O(1)−P(1)−O(4)	109.3(3)	C(17)−C(11)−C(12)	124.2(8)	C(13)−C(12)−C(11)	120.0(12)
O(2)−P(1)−O(4)	109.6(3)	O(1)−P(1)−O(3)	110.1(3)	C(14)−C(13)−C(12)	126.7(14)	C(13)−C(14)−C(15)	118.5(12)
O(2)−P(1)−O(3)	109.9(3)	O(4)−P(1)−O(3)	103.0(3)	C(16)−C(15)−C(14)	121.9(11)	C(15)−C(16)−C(17)	123.3(9)
O(10)−P(2)−O(12)	112.4(3)	O(10)−P(2)−O(6)	108.6(2)	C(11)−C(17)−C(16)	125.1(8)		

between scans, and 1 °C/min during data collection. Quick scans were run from 1 to 37° (2θ), with 0.050° step size and 0.7 s step time.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer 7 Series Analyzer, under nitrogen atmosphere and with a 5 °C/min heating rate.

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were performed on a JEOL 840 SEM, with accelerating conditions of 10^{-10}A and 5kV.

SCXRD Structure Determination. A summary of selected crystallographic data is given in Table 1. Data for both compounds were collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The intensities of three standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects and for absorption.[18]

The structures were solved using the SHELXTL\PC V5.0 package[19] and refined by full-matrix least-squares methods on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms**.** In UT-7, the H atom of the P−OH group was refined with an isotropic thermal

(18) Sheldrick, G. M. SHELXA-90, Program for Absorption Correction. University of Göttingen, Germany, 1990.

(19) Sheldrick, G. M. SHELXTL/PC Version 5.0. Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1995.

Table 4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for UT-8

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Al(1)	−1466(3)	5123(2)	4361(3)	16(1)	O(14)	2709(7)	4710(5)	6159(7)	24(2)
Al(2)	−1503(3)	2348(2)	4111(2)	13(1)	O(15)	−3082(7)	2856(5)	4540(7)	25(2)
Al(3)	2922(2)	3741(3)	5271(2)	14(1)	O(16)	1630(5)	3711(7)	3645(5)	25(1)
P(1)	1542(2)	2100(2)	6557(2)	15(1)	N(1)	2393(9)	3591(8)	−312(8)	38(2)
P(2)	1613(2)	5318(2)	6748(2)	14(1)	C(1)	3696(29)	3416(17)	22(31)	147(12)
P(3)	−3509(2)	3669(2)	5330(2)	14(1)	C(2)	4881(33)	3953(34)	−601(26)	199(17)
P(4)	52(2)	3797(2)	2645(2)	13(1)	C(3)	5891(17)	3994(17)	1124(29)	133(12)
O(1)	2080(6)	6293(5)	6519(6)	22(1)	C(4)	4788(37)	3820(25)	1560(19)	161(12)
O(2)	1688(7)	5127(5)	8259(6)	23(2)	N(2)	1298(7)	−117(5)	1204(7)	21(2)
O(3)	2111(6)	1194(5)	6120(6)	24(1)	C(5)	2181(10)	729(9)	1103(10)	37(3)
O(4)	−741(8)	4626(5)	3056(7)	26(2)	C(6)	2015(19)	1472(11)	2081(18)	73(5)
O(5)	−910(8)	2960(5)	2826(6)	23(2)	C(7)	3588(26)	1629(31)	2547(30)	212(22)
O(6)	−5259(4)	3712(6)	4970(5)	20(1)	C(8)	3935(16)	687(15)	1839(27)	116(10)
O(7)	1444(7)	2094(5)	8062(6)	22(2)	N(3)	1671(8)	6954(7)	1929(8)	37(2)
O(8)	−2811(6)	3611(6)	6884(5)	30(2)	C(9)	4364(12)	6151(14)	1385(14)	81(6)
O(9)	169(5)	3862(6)	1140(5)	21(2)	C(10)	3575(15)	6999(16)	568(13)	87(6)
O(10)	−2983(7)	4525(5)	4691(7)	24(2)	C(11)	1897(13)	7010(12)	497(11)	51(3)
O(11)	2651(7)	2814(5)	6285(6)	20(1)	C(12)	2407(11)	6121(8)	2696(11)	36(3)
O(12)	−37(6)	2292(5)	5612(6)	25(2)	C(13)	4088(14)	6112(12)	2766(14)	58(4)
O(13)	−35(7)	5176(5)	5895(6)	25(2)					

[a] Defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. Coordinates for organic hydrogens have been omitted; see Supporting Information.

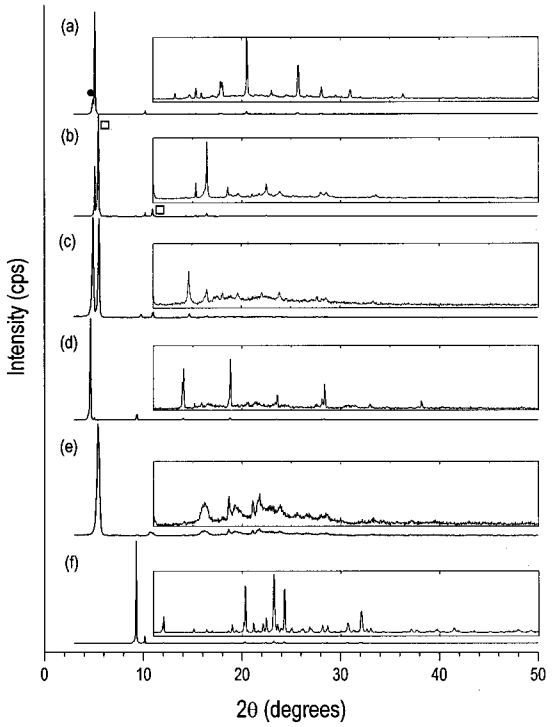

Figure 3. Representative examples of PXRD patterns of the synthesis products. An expansion of the higher-angle region in the insets shows the degree of crystallinity of the phases. (a) The pattern for UT-7, with a minor amount of an unknown material formed, is shown (●). (b) Use of 220 °C synthesis temperature changes the product to a second unknown material (□), mixed with a significant amount of UT-7. (c) Addition of 20 molar equiv of water to the UT-7 synthesis yields approximately equal amounts of the two unknown materials and no UT-7. (d) Further addition of water (89.5 moles) isolates the first unknown material, with a trace amount of UT-7. (e) Pattern of the product obtained by thermally treating UT-7 (material of Figure 3a) at 150 °C in air, for 4 h. The UT-7 chain structure has completely transformed to the second unknown phase; (f) The pattern for UT-8 is shown. The material is obtained phase-pure.

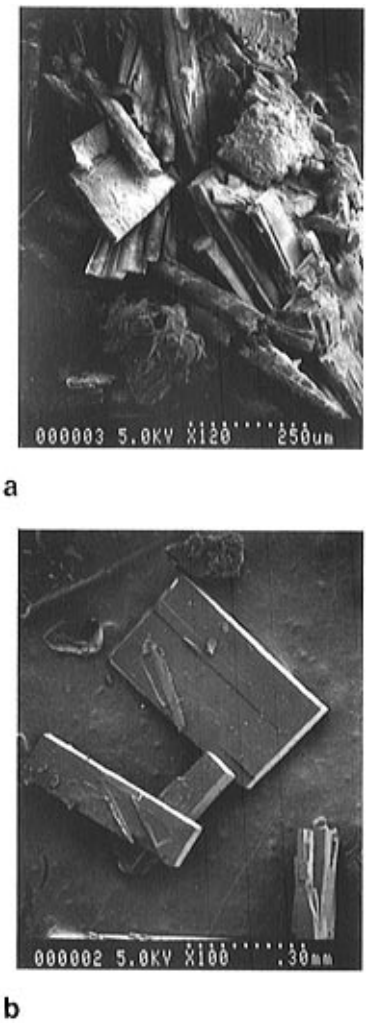

Figure 4. SEM micrographs of the product crystals: (a) UT-7; (b) UT-8.

parameter. In both UT-7 and UT-8 structures, the C atoms of the template cycloheptylamine and cyclobutylamine molecules have large anisotropic displacement parameters, and this may suggest that these molecules are disordered. Attempts to model the cycloheptylamine and cyclobutylamine molecules as disordered rigid groups did not give as satisfactory a refinement as allowing all C atoms of the molecules to refine freely with anisotropic thermal parameters.

Results and Discussion

The thermal ellipsoids, atom labeling scheme, and crystallographic projections of the UT-7 and UT-8 structures are shown in Figures 1 and 2, respectively. Selected atomic coordinates and bond lengths and angles of UT-7 are given in Tables 2 and 3 and for UT-8 in Tables 4 and 5. Anisotropic displacement

Table 5. Selected Bond Lengths (Å) and Angles (deg) for UT-8

Al(1)−O(10)	1.721(7)	Al(1)−O(3)	1.725(8)	P(3)−O(8)	1.507(5)	P(3)−O(6)	1.531(4)
Al(1)−O(4)	1.731(7)	Al(1)−O(13)	1.737(6)	P(3)−O(15)	1.533(8)	P(3)−O(10)	1.541(7)
Al(2)−O(1)	1.723(7)	Al(2)−O(12)	1.732(6)	N(1)−C(1)	1.17(2)	C(1)−C(2)	1.57(3)
Al(2)−O(5)	1.736(7)	Al(2)−O(15)	1.744(7)	C(1)−C(4)	1.71(3)	C(2)−C(3)	1.72(3)
P(1)−O(7)	1.498(6)	P(1)−O(11)	1.523(7)	C(3)−C(4)	1.20(3)	N(3)−C(11)	1.467(12)
P(1)−O(12)	1.530(6)	P(1)−O(3)	1.537(7)	N(3)−C(12)	1.518(14)	C(9)−C(10)	1.57(3)
P(2)−O(2)	1.494(6)	P(2)−O(13)	1.536(6)	C(9)−C(13)	1.43(2)	C(10)−C(11)	1.49(2)
P(2)−O(1)	1.542(7)	P(2)−O(14)	1.546(7)	C(12)−C(13)	1.50(2)		

O(10)−Al(1)−O(3)	107.4(3)	O(10)−Al(1)−O(4)	111.7(4)	O(8)−P(3)−O(6)	113.4(3)	O(8)−P(3)−O(15)	111.7(4)
O(3)−Al(1)−O(4)	110.7(3)	O(10)−Al(1)−O(13)	108.7(3)	O(6)−P(3)−O(15)	106.3(4)	O(8)−P(3)−O(10)	111.3(4)
O(3)−Al(1)−O(13)	109.2(4)	O(4)−Al(1)−O(13)	109.1(3)	O(6)−P(3)−O(10)	105.6(4)	O(15)−P(3)−O(10)	108.1(3)
O(1)−Al(2)−O(12)	111.4(3)	O(1)−Al(2)−O(5)	109.7(3)	P(2)−O(1)−Al(2)	147.2(4)	P(1)−O(3)−Al(1)	140.8(4)
O(12)−Al(2)−O(5)	109.8(3)	O(1)−Al(2)−O(15)	106.7(3)	P(4)−O(4)−Al(1)	145.1(5)	P(4)−O(5)−Al(2)	141.2(4)
O(12)−Al(2)−O(15)	108.5(3)	O(5)−Al(2)−O(15)	110.7(4)	P(3)−O(6)−Al(3)	157.5(3)	P(3)−O(10)−Al(1)	146.6(5)
O(7)−P(1)−O(11)	111.6(4)	O(7)−P(1)−O(12)	109.7(3)	N(1)−C(1)−C(2)	120(3)	N(1)−C(1)−C(4)	120(2)
O(11)−P(1)−O(12)	108.5(4)	O(7)−P(1)−O(3)	111.7(4)	C(2)−C(1)−C(4)	82(2)	C(1)−C(2)−C(3)	84(2)
O(11)−P(1)−O(3)	106.8(3)	O(12)−P(1)−O(3)	108.5(4)	C(4)−C(3)−C(2)	93(2)	C(3)−C(4)−C(1)	97(2)
O(2)−P(2)−O(13)	109.1(4)	O(2)−P(2)−O(1)	111.8(4)	C(11)−N(3)−C(12)	112.2(9)	C(13)−C(9)−C(10)	110.8(12)
O(13)−P(2)−O(1)	108.2(4)	O(2)−P(2)−O(14)	111.9(4)	C(11)−C(10)−C(9)	111(2)	N(3)−C(11)−C(10)	108.6(9)
O(13)−P(2)−O(14)	109.6(4)	O(1)−P(2)−O(14)	106.1(3)	C(13)−C(12)−N(3)	110.4(10)	C(9)−C(13)−C(12)	110.6(10)

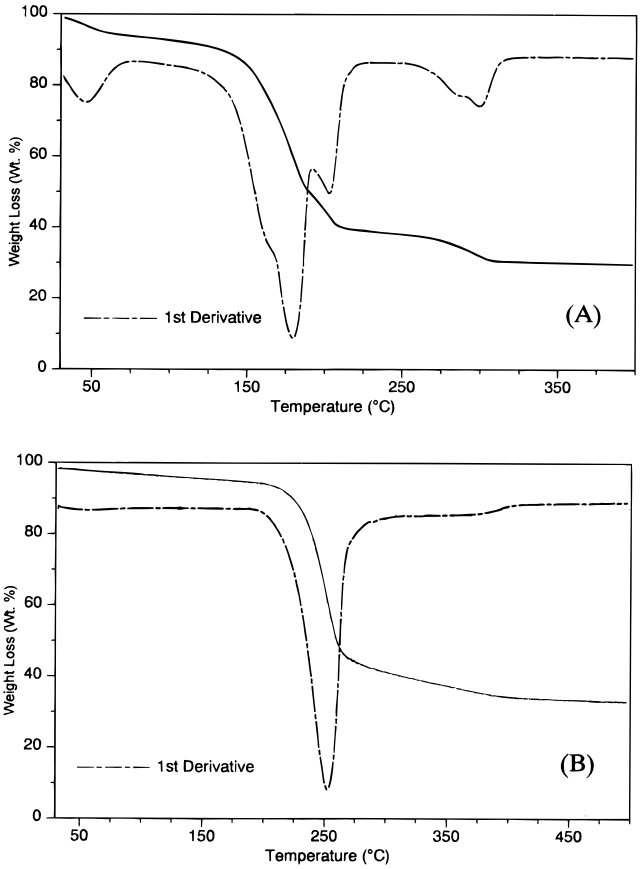

Figure 5. TGA plots of the materials. (a) UT-7 displays at least two thermal events at approximately 225 and 250 °C, corresponding to a total loss of ca. 60 wt %. The first peak appears to be due to a chain to layer solid state transformation, while the second is the decomposition of the new crystalline layer to an open, amorphous, layered material, which collapses at ca. 350 °C, giving rise to the small peak in the first derivative curve. (b) UT-8, which appears to simply break down to $AlPO_4$-tridymite at ca. 350°, is also reflected in the *in situ* HT-PXRD.

parameters and coordinates of carbon hydrogens have been submitted as Supporting Information. PXRD patterns, SEM micrographs, TGA plots, and HT-PXRD patterns are displayed in Figures 3−6, respectively. The micrographs show the relatively large crystal sizes of the materials that allowed their SCXRD structure determination.

The polymeric structure of UT-7 contains $[Al_3P_5O_{20}H]^{5-}$ chains infinitely extended along the *a*-axis (Figure 1d). The chains are comprised of alternating tetrahedral aluminum and phosphorus atoms connected through bridging oxygens. All of the aluminums are four-connected with respect to phosphorus ($Al-O_{av}$ 1.734(1) Å), while three of the five crystallographically distinct phosphorus atoms possess three bridging oxygens ($P-O_{av}$ 1.537(1) Å) and one terminal phosphonyl oxygen ($P{=}O_{av}$ 1.486(1) Å). The fourth phosphate group is doubly-bridging (P−O distances 1.553(4) and 1.563(4) Å), with two terminal oxygens (P═O distances 1.482(4), 1.500(5) Å). The remaining fifth phosphorus is only connected to one aluminum (P−O 1.539(4) Å) and contains three terminal oxygens, of which one is protonated (P═O distances 1.495(5) and 1.495(5) Å, P−OH 1.576(5) Å).

The protonated phosphate group donates a hydrogen-bond to the terminal oxygen of a triply-bridged phosphate group on an adjacent chain (P−OH···O−P 1.72 Å). This holds the chains together to define a hydrogen-bonded layer, Figure 1d. This layer should be thought of as a layer of chains and not as a layered material, which has a strictly covalently bonded structure within each layer. All other terminal phosphate oxygens of the chains accept at least one hydrogen-bond from the head groups of the interlamellar cycloheptylammonium cations. The cyclic amines interact with only one of the two adjacent layers and reside in a bilayer-like arrangement, delineating a hydrophobic interlayer region and the overall bonding structure in three dimensions, Figure 1b,c.

The inorganic architecture of the individual chain units may be considered as a linear polymer that contains alternating sections of three corner-sharing four-rings of T-atoms (T = Al, P) and five edge-sharing four-rings, where the latter are connected in a double-crankshaft cis−trans conformation.[20] We had previously theoretically predicted such a structure to exist[21] and believe it to be a key discovery in our model for the formation of aluminophosphate materials. The entire UT-7 structure is isomorphous with UT-3, our recently discovered chain structure containing interlamellar cyclopentylammonium.[7] The unit cells of these two structures are of very similar dimensions, with a corresponding increase of 2.381(3) Å in the interlayer distance of UT-7 to accomodate the larger rings of the cycloheptylammonium ions.

The chain structure of UT-7 and UT-3 represents many "firsts" for a crystalline aluminophosphate. These materials provide the first example of an aluminophosphate structure that contains a singly-bridged, triply-terminated phosphate group. They are the first example of an aluminophosphate material that has a 5:3 P:Al stoichiometric ratio, and are the first nonframework aluminophosphates to contain a primary cyclic amine in their structures. UT-7 and UT-3 are also the only chain aluminophosphates known to contain a six T-atom ring (T =

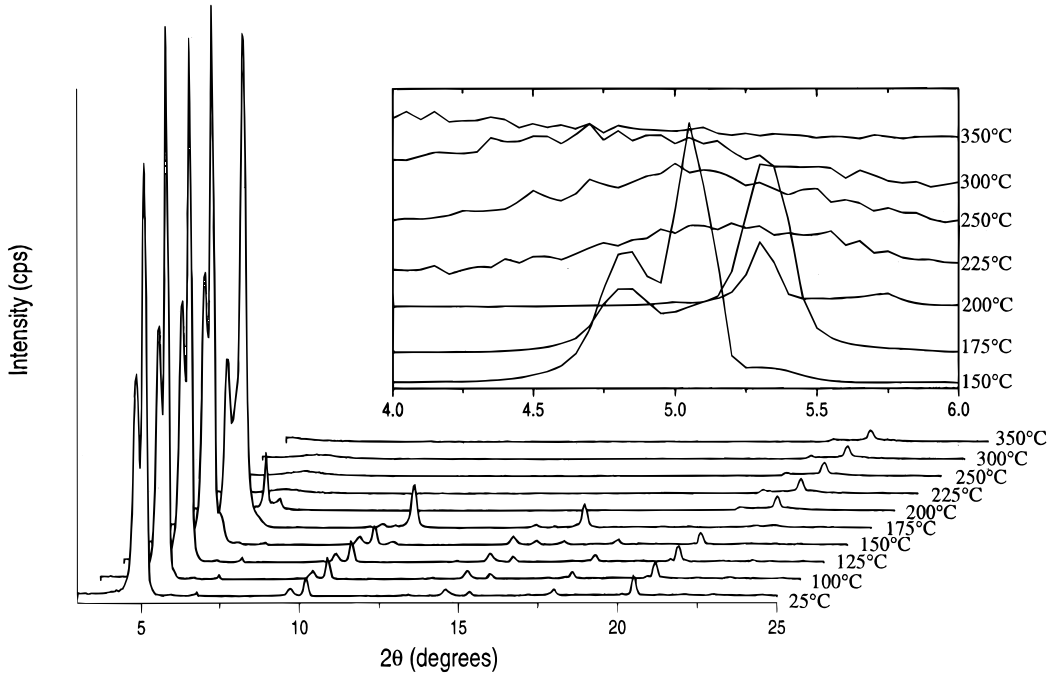

Figure 6. *In situ* HT-PXRD of UT-7. As observed for the thermally treated sample of Figure 3e, the chain structure transforms in the 175 °C region to a material with a pattern comparing well with the unknown material of smaller *d*-spacing in Figure 3b,c. All materials decompose at approximately 200 °C to $AlPO_4$-tridymite and an amorphous layered material, which collapses by 350 °C (inset).

Al, P), edge-sharing four-rings, or triply-bridged, singly-terminated phosphate groups. In fact, they represent only the second structural example of a one-dimensional chain aluminophosphate.

As observed for many of our other TEG synthesis systems, a second phase, unknown in this case, coprecipitates in the product (Figure 3a). Changing the synthesis conditions also forms another unknown phase, as observed by increasing the synthesis temperature (Figure 3b) or mole fraction of water (Figures 3c). Further increase of water content results in the first unknown as a majority phase and a small amount of UT-7 (Figure 3d). Varying the synthesis conditions between these examples alters the ratio of these three phases, and each phase may thereby be formed as a pure-phase or in a desired ratio. UT-7 (Figure 3a) was thermally treated in air at 150 °C (2-h ramp, 2-h soak), transforming it to a low-crystallinity material that compares to the second unknown phase (Figure 3e).

This result is corroborated by the TGA (Figure 5a) and HT-PXRD results (Figure 6), which are very similar to the behavior of UT-3 when it transforms to the layered UT-4.[7] The unknown pattern which appears at 175 °C in the HT-PXRD, Figure 6, also compares well to that in Figure 3b, leading us to believe that the UT-7 chain structure undergoes the identical chain to layer transformation. Further work is underway to obtain the crystal structure of the as yet unknown cylcoheptylammonium material into which UT-7 transforms.

The $[Al_3P_4O_{16}]^{3-}$ UT-8 layered structure, Figure 2, is a three-connected two-dimensional net of alternating tetrahedral aluminum and phosphorus centres connected by doubly-bridging oxygens (P−O_{av} 1.535(1) Å, Al−O_{av} 1.732(1) Å), defining an array of edge-sharing four-, six-, and eight-rings, Figure 2d. This arrangement is identical to that of the *ab* plane of the frameworks $AlPO_4$-12 or $AlPO_4$-25.[2] However, in UT-8, the fourth oxygen of the phosphorus atoms is not linked to another layer, but rather exists as terminal phosphonyl groups (P═O_{av} 1.501(1) Å). The six-rings are capped above and below the plane of this two-dimensional $AlPO_4$-12-like layer by a triply-bridged phosphate group, as observed for the capped six-rings of the $AlPO_4$-5-like layered structures.[9,11,14] UT-8 is isostructural to the layer reported by Thomas *et al*., which contains one interlamellar diprotonated 1,5-diaminopentane and one piperidinium.[12] UT-8, however, contains two crystallographically independent cyclobutylammoniums and one piperidinium in the interlayer region. These two structures are in turn isostructural to another $[Al_3P_4O_{16}]^{3-}$ layer reported by Thomas *et al*. containing protonated interlamellar ethylenediamine and ethylene glycol,[8] as well as the recently reported $[Al_3P_4O_{16}]^{3-}$ layer containing octahedral cobalt complexes.[15]

Each terminal oxygen of the phosphate groups accepts two hydrogen-bonds from the template ammoniums (NH···OP 1.92−2.35 Å). The piperidiniums reside in the same position and conformation with respect to the inorganic layers as in the material reported by Thomas *et al*.,[12] with the secondary ammonium groups interacting with the same layer. Interestingly, two cyclobutylammoniums in the present structure play the same role as the one pentane-1,5-diammonium of the other. Consequently, each cyclobutylammonium donates one hydrogen-bond to one layer and two to the adjacent layer, as for each end of the diamine. The inorganic layers are therefore held together by not only weak hydrophobic interactions, as in other chain and layered structures, but also directly by the hydrogen-bonds of the primary amines. This, however, does not increase the thermal stability of the material, as revealed in the TGA, Figure 5. The layer collapses to $AlPO_4$-tridymite at approximately 225 °C, confirmed by HT-PXRD. This is to be expected, as the nature of the "direct" layer connection *via* the cyclobutylammoniums involves only weak hydrogen-bonds and hydrophobic interactions, as for other layered aluminophosphates.

Finally, it is interesting to note the somewhat accidental way in which the mixed-amine UT-8 and Thomas *et al*.[12] $[Al_3P_4O_{16}]^{3-}$ layers were initially discovered. UT-8 was discovered when conducting synthetic experiments in the TEG system, with either

(20) (a) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A.; Garces, J. M.; Olken, M. M.; Rudolf, P. *Stud. Surf. Sci. Catal*. **1994**, *84A*, 219. (b) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A.; Garces, J. M.; Olken, M. M.; Rudolf, P. Poster presentation at the 10th International Zeolite Conference, Garmisch-Partenkirchen, Germany, July 17−22, 1994.

(21) Oliver, S.; Kuperman, A.; Ozin, G. A. Submitted for publication.

cyclobutylamine or piperidine as the organic additive. Both experiments yielded crystals displaying an unknown PXRD pattern, but not of a sufficient size to allow their structure determination by SCXRD methods. Leftover gels of the cyclobutylamine and piperidine experiments were combined and treated at the synthesis temperature of 180 °C, resulting in the first isolation of the UT-8 material. For the $[Al_3P_4O_{16}]^{3-}$ layer of Thomas *et al*., the material was crystallized using only 1,5-diaminopentane as template, which partially decomposed and ring-closed to form piperidine.

Conclusions

UT-7 and UT-8 represent two new members of the non-framework aluminophosphates. UT-7 is a one-dimensional chain structure that thermally transforms to a material which appears to be layered in nature. This would be only the second example of a chain to layer solid state aluminophosphate transformation. This type of transformation may play a role in the formation of $AlPO_4$-based molecular sieves.[21] UT-8 is a layered material that belongs to the family of layered aluminophosphates with common formula $[Al_3P_4O_{16}]^{3-}$, and contains two interlamellar cyclic ammonium species. It should be possible using other mixed amine synthetic systems to obtain new aluminophosphate based materials.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada in support of this work is acknowledged. S.O. expresses his appreciation to the Ontario Graduate Scholarship program in partial support of his research. We thank Dr. Neil Coombs (Imagetek Analytical Imaging, Toronto) for scanning electron microscopy, and Dr. David Young for informative discussions.

Supporting Information Available: Text giving experimental details of the structure determination and listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atomic coordinates (13 pages). Ordering information is given on any current masthead page.

IC960458V