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Aluminophosphate Chain-to-Layer Transformation

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

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The synthesis and characterization of two novel aluminophosphate materials, obtained from the same nonaqueous tetraethylene glycol−cyclopentylamine system, is reported. The first material, $[Al_3P_5O_{20}H]^{5-}\cdot 5[C_5H_9NH_3^+]$, denoted UT-2, has a 1-D chain structure with a P:Al ratio of 5:3, rather than 1:1 as found in the aluminophosphate $AlPO_4$-n molecular sieves. The UT-2 chains are hydrogen-bonded together by terminal phosphate groups and organized into a layered structure. The second material, $[Al_2P_3O_{12}H]^{2-}\cdot 2[C_5H_9NH_3^+]$, denoted UT-3, has a 2-D layer structure with a P:Al ratio of 3:2. Both materials have bilayers of charge-balancing cyclopentylammonium cations interdisposed between anionic aluminophosphate sheets. Variable-temperature in situ PXRD establishes a clean solid-state structural transformation, at 200 °C, of UT-2 to UT-3. The discovery of this chain-to-layer conversion suggests a new paradigm for the templated assembly of 1-D chain, 2-D layer, and 3-D open-framework aluminophosphates.

Introduction

The synthesis of inorganic materials with novel structures and properties provides opportunities for the development of new technologies. An excellent example of this synergism is found in the aqueous synthesis of the family of microporous aluminophosphates denoted $AlPO_4$-n.[1,2] Some of these materials are isostructural with zeolite frameworks, while others are structurally unique. The microporosity, hydrophobicity and acidity of the $AlPO_4$-n and their metal-substituted MeAPO-n open frameworks renders them useful in a diverse range of catalytic and separation processes.

In this context, a series of related 2-D layered aluminophosphates has recently been reported.[3−8] The assembly of these materials is sometimes organic template specific. Interestingly, there exists only a single case of a 1-D chain aluminophosphate.[9,10] The majority of these low-dimensional aluminophosphates form under nonaqueous reaction conditions. Their isolation has been rationalized in terms of the solvating, hydrogen-bonding, viscosity and polarity properties of the nonaqueous solvent,[11] as well as the diminished rates of hydrolysis and mineralization of reaction intermediates in the synthesis.[12−14] In these nonaqueous synthesis systems water is viewed as a catalytic reagent.[15]

Herein we report the synthesis details, single-crystal X-ray diffraction (SC-XRD) structures, PXRD, SEM, and thermochemical analyses of new chain and layer aluminophosphates, denoted UT-2 and UT-3, respectively. They are formed in the same nonaqueous synthesis system, under slightly different reaction conditions, utilizing reagent amounts of water. The UT-2 chain structure is observed to thermally and irreversibly transform to the UT-3 layered phase in the solid state, and this strongly suggests that it behaves as a precursor to UT-3 in the synthesis. This structural interconversion is significant because the UT-2 chain has been viewed as a key player in the chain hydrolysis mechanism of $AlPO_4$-n formation.[12−14] The results of this study provide a new way of thinking about the templated-assembly of layer and open-framework aluminophosphates.

Experimental Section

Synthesis Procedures. Reagent amounts of water are dispersed into a tetraethylene glycol (TEG) solvent, followed by addition of pseudoboehmite (Dispal 23N4-80, Vista) with continuous stirring. Phosphoric acid (85 wt %) is then added dropwise, and the mixture stirred to ensure homogeneity. Cyclopentylamine (99%, Aldrich) is added dropwise.

[†] Present address: The Dow Chemical Co., Midland, Michigan 48674

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

compound	UT-2	UT-3
empirical formula	$C_{25}H_{61}Al_3N_5O_{20}P_5$	$C_{10}H_{25}Al_2N_2O_{12}P_3$
M_r	987.58	512.19
crystal size, mm	0.40 × 0.35 × 0.08	0.32 × 0.30 × 0.11
crystal class	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
temp, K	293	293
a, Å	10.063(2)	9.120(3)
b, Å	15.447(2)	28.289(6)
c, Å	15.736(2)	9.010(3)
α, deg	71.72(1)	90
β, deg	80.07(1)	111.82(1)
γ, deg	79.57(1)	90
V, Å^3	2266.6(6)	2158.0(11)
Z	2	4
D_{calc}, g cm^{-3}	1.447	1.576
μ(Mo Kα), cm^{-1}	3.36	4.17
F(000)	1040	1064
ω scan width, deg	0.43	0.54
range θ collected, deg	2.07 to 30.02	3.07 to 30.00
absorption correction	ΔF method[16]	ΔF method[16]
min and max transmission	0.3970, 0.9775	0.1682, 0.9655
no. reflns collected	13680	6642
independent reflns	12992	6288
R_{int}	0.0309	0.0622
no. obsd data [$I > 2\sigma(I)$]	8573	3628
R_1 [$I > 2\sigma(I)$]	0.0646	0.0622
wR_2 (all data)	0.1871	0.2016
weighting a, b	0.0851, 2.41	0.1161, 0.00
goodness of fit	1.026	1.001
parameters refined	532	270
max density in ΔF map, e/A^3	1.021	0.689

[a] Definitions of R indexes: $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2)]]^{1/2}$.

This causes gelation of the colorless slurry to a viscous, opaque, and pale-yellow mixture. The final molar ratio of the gel is

$$14TEG{:}xH_2O{:}0.9\ Al_2O_3{\cdot}nH_2O{:}3.6H_3PO_4{:}5.0\ C_5H_9NH_2$$

where $x = 0-500$. After stirring for at least 15 min, the gels are loaded into Teflon-lined stainless steel autoclaves and treated at 100−220 °C for 1−10 days. The resultant products are filtered, using copious amounts of deionized water and acetone. Drying in ambient air results in large, colourless crystals of the desired phase. The products are subsequently analyzed by SC-XRD, VT-PXRD, TGA, MS, and SEM.

X-ray Structural Characterization. A summary of selected crystallographic data is given in Table 1. Data for both compounds were collected on a Siemens P4 diffractometer using graphite-monochromatized 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.[16]

The structures were solved using the SHELXTL\PC V5.0 package[17] and refined by full-matrix least-squares 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 both structures, the H atoms of the P−OH group were refined with isotropic thermal parameters. The template cyclopentylamine molecules, in both structures, appear to have rather large anisotropic displacement parameters suggesting that these molecules are disordered. Attempts to model the cyclopentylamine molecules as disordered rigid groups did not give as satisfactory a refinement as allowing all atoms of the molecules to refine freely with anisotropic thermal parameters. Positional and isotropic thermal parameters, bond lengths and bond angles of UT-2 and UT-3 are given in Tables 2 and 3, respectively.

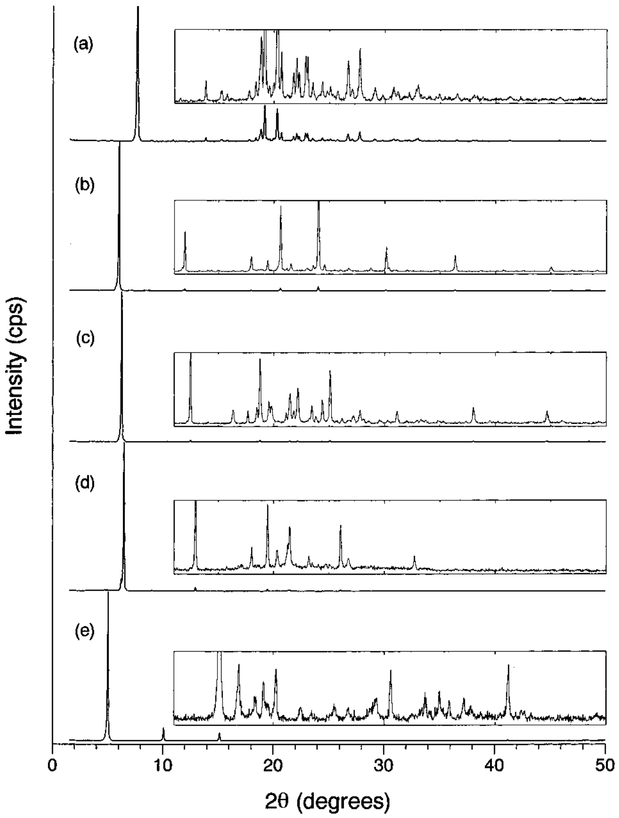

Figure 1. PXRD patterns of the pure-phase solids obtained from the synthesis system. (a) Cyclopentylammonium phosphate phase present in the initial reaction mixture; (b) UT-2 chain structure; (c) UT-3 layer structure; (d) 13.5 Å fibrous unknown phase; (e) 17.5Å unkown phase obtained in the fully aqueous system.

Results and Discussion

Initial Formation of an Alkylammonium Phosphate Phase. Representative examples of the synthesis conditions are summarized in Table 4. PXRD, TGA, MS, and SEM analyses of the initial mixtures shows that gelation occurs upon addition of the amine due to the formation of a cyclopentylammonium phosphate. The PXRD of this material is shown in Figure 1a. Optical and electron micrographs display the needlelike morphology of the crystals (Figure 2a). Large single crystals of this material were grown at room temperature by recrystallization from a 50% (by volume) methanol solution. SC-XRD analysis of this material showed it to have a bilayer arrangement of cyclopentylammonium cations, hydrogen-bonded to "layers" of phosphate molecules. The phosphate layers are, in fact, comprised of isolated dimers of hydrogen-bonded $[HPO_4]^{2-}$ molecules, where each donates one hydrogen bond to and accepts one hydrogen bond from the other. This structure likely templates the assembly of the aluminophosphate structures described below.

PXRD shows that the alumina source material coexists with the cyclopentylammonium phosphate in the synthesis mixture at room temperature. The known alumina-based mineralizing action of phosphates is blocked by the presence of the organic amine.[19] This is likely due to the incorporation of the phosphate into the alkylammonium phosphate phase.

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Table 2

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

	x	y	z	*U*(eq)[a]		x	y	z	*U*(eq)[a]
Al(1)	−127(1)	−2974(1)	676(1)	25(1)	C(11)	−7221(5)	−3983(3)	2662(3)	55(1)
Al(2)	−1426(1)	342(1)	929(1)	25(1)	C(12)	−6187(7)	−4856(3)	2785(4)	79(2)
Al(3)	−3472(1)	−1203(1)	−89(1)	23(1)	C(13)	−5633(11)	−4949(9)	3635(6)	175(5)
P(1)	−4337(1)	−42(1)	1351(1)	23(1)	C(14)	−6368(13)	−4259(13)	4023(8)	212(8)
P(2)	−596(1)	−1550(1)	−1117(1)	24(1)	C(15)	−7351(12)	−3728(5)	3531(5)	129(4)
P(3)	703(1)	−1326(1)	1155(1)	24(1)	C(21)	5272(5)	−7381(4)	1479(3)	60(1)
P(4)	−3204(1)	−3190(1)	1120(1)	27(1)	N(2)	4679(3)	−6644(2)	754(2)	38(1)
P(5)	2136(1)	−4552(1)	563(1)	30(1)	C(22)	6259(7)	−7136(6)	1890(4)	126(4)
O(1)	−1798(2)	−1087(2)	−592(2)	33(1)	C(23)	6154(13)	−7741(10)	2841(6)	243(9)
O(2)	−3685(2)	−2358(2)	313(2)	32(1)	C(24)	4958(12)	−8180(9)	3033(5)	186(6)
O(3)	−4083(2)	−3112(2)	1980(2)	37(1)	C(25)	4195(6)	−7777(5)	2255(4)	84(2)
O(4)	−3237(3)	−4052(2)	896(2)	46(1)	N(3)	92(4)	−6369(2)	1701(2)	47(1)
O(5)	−3799(3)	−703(2)	777(2)	35(1)	C(31)	−674(7)	−6387(5)	2608(4)	78(2)
O(6)	−4890(3)	−542(2)	2284(2)	35(1)	C(32)	−1383(11)	−5512(7)	2665(5)	155(5)
O(7)	−5426(2)	698(2)	891(2)	36(1)	C(33)	−1345(22)	−5491(13)	3560(10)	331(15)
O(8)	−979(3)	−1661(2)	−1948(2)	38(1)	C(34)	−310(17)	−6100(13)	3905(10)	240(8)
O(9)	−87(3)	−2494(2)	−485(2)	35(1)	C(35)	298(9)	−6669(8)	3311(5)	146(4)
O(10)	758(3)	−4064(2)	893(2)	37(1)	N(4)	−2859(4)	−2051(2)	2591(2)	43(1)
O(11)	3234(3)	−3982(2)	482(2)	47(1)	C(41)	−2140(8)	−2550(5)	3389(4)	86(2)
O(12)	1930(3)	−4585(2)	−393(2)	45(1)	C(42)	−3067(13)	−2973(8)	4131(6)	167(6)
O(13)	2357(3)	−5517(2)	1190(2)	40(1)	C(43)	−3179(20)	−2454(17)	4711(12)	313(14)
O(14)	−544(2)	945(2)	1357(2)	35(1)	C(44)	−2396(26)	−1729(12)	4387(11)	304(14)
O(15)	−1757(2)	−3039(2)	1210(2)	40(1)	C(45)	−1482(11)	−1936(9)	3708(5)	169(6)
O(16)	1535(3)	−1422(2)	1882(2)	37(1)	N(5)	−7709(3)	−218(2)	2629(2)	37(1)
O(17)	−760(2)	−826(2)	1313(2)	33(1)	C(51)	−8297(6)	−446(4)	3593(3)	62(1)
O(18)	−3131(2)	432(2)	1377(2)	31(1)	C(52)	−7850(11)	−1415(5)	4085(4)	121(3)
O(19)	564(3)	−2290(2)	1129(2)	36(1)	C(53)	−7263(21)	−1401(9)	4809(12)	293(12)
O(20)	1332(2)	−781(2)	229(2)	35(1)	C(54)	−7028(17)	−465(9)	4711(10)	245(9)
H(1O)	2264(53)	−4983(36)	−490(35)	56(16)	C(55)	−7813(10)	132(6)	4080(4)	111(3)
N(1)	−6706(3)	−3242(2)	1880(2)	42(1)					

(b) Selected Bond Lengths (Å) and Angles (deg) for UT-2

Al(1)-O(15)	1.714(3)	Al(1)-O(10)	1.716(2)	N(1)-C(11)	1.485(5)	C(11)-C(15)	1.514(9)
Al(1)−O(19)	1.736(3)	Al(1)−O(9)	1.740(3)	C(11)−C(12)	1.529(7)	C(12)−C(13)	1.493(11)
Al(2)−O(20)	1.726(3)	Al(2)−O(14)	1.734(2)	C(13)−C(14)	1.42(2)	C(14)−C(15)	1.350(13)
Al(2)−O(18)	1.738(2)	Al(2)−O(17)	1.757(2)	C(21)−C(22)	1.435(8)	C(21)−N(2)	1.459(5)
P(1)−O(6)	1.492(2)	P(1)−O(7)	1.528(2)	C(21)−C(25)	1.535(7)	C(22)−C(23)	1.492(9)
P(1)−O(5)	1.536(2)	P(1)−O(18)	1.539(2)	C(23)−C(24)	1.429(11)	C(24)−C(25)	1.466(10)
P(2)−O(8)	1.491(2)	P(2)−O(14)	1.534(2)	N(3)−C(31)	1.496(6)	C(31)−C(32)	1.431(9)
P(2)−O(1)	1.539(2)	P(2)−O(9)	1.540(2)	C(31)−C(35)	1.512(9)	C(32)−C(33)	1.426(14)
P(3)−O(16)	1.487(2)	P(3)−O(20)	1.528(2)	C(33)−C(34)	1.34(2)	C(34)−C(35)	1.464(14)
P(3)−O(19)	1.535(2)	P(3)−O(17)	1.552(2)				

O(15)−Al(1)−O(10)	108.69(14)	O(15)−Al(1)−O(19)	105.98(13)	P(2)−O(1)−Al(3)	141.6(2)	P(4)−O(2)−Al(3)	135.0(2)
O(10)−Al(1)−O(19)	111.09(13)	O(15)−Al(1)−O(9)	112.07(13)	P(1)−O(5)−Al(3)	163.3(2)	P(1)−O(7)−Al(3)	154.6(2)
O(10)−Al(1)−O(9)	108.79(13)	O(19)−Al(1)−O(9)	110.21(13)	P(2)−O(9)−Al(1)	135.4(2)	P(5)−O(10)−Al(1)	138.3(2)
O(20)−Al(2)−O(14)	110.45(13)	O(20)−Al(2)−O(18)	108.29(13)	N(1)−C(11)−C(15)	110.9(5)	N(1)−C(11)−C(12)	109.7(4)
O(14)−Al(2)−O(18)	110.19(12)	O(20)−Al(2)−O(17)	114.39(12)	C(15)−C(11)−C(12)	105.2(5)	C(13)−C(12)−C(11)	104.0(6)
O(14)−Al(2)−O(17)	106.96(13)	O(18)−Al(2)−O(17)	106.47(12)	C(14)−C(13)−C(12)	108.8(7)	C(15)−C(14)−C(13)	112.1(8)
O(6)−P(1)−O(7)	110.6(2)	O(6)−P(1)−O(5)	111.49(14)	C(14)−C(15)−C(11)	108.8(8)	C(22)−C(21)−N(2)	115.5(5)
O(7)−P(1)−O(5)	109.46(14)	O(6)−P(1)−O(18)	110.21(14)	C(22)−C(21)−C(25)	105.6(5)	N(2)−C(21)−C(25)	112.5(4)
O(7)−P(1)−O(18)	108.02(14)	O(5)−P(1)−O(18)	106.90(13)	C(21)−C(22)−C(23)	105.4(6)	C(24)−C(23)−C(22)	109.4(7)
O(8)−P(2)−O(14)	110.6(2)	O(8)−P(2)−O(1)	112.2(2)	C(23)−C(24)−C(25)	107.4(7)	C(24)−C(25)−C(21)	103.9(5)
O(14)−P(2)−O(1)	106.92(13)	O(8)−P(2)−O(9)	110.37(14)	C(32)−C(31)−N(3)	114.1(6)	C(32)−C(31)−C(35)	104.9(7)
O(14)−P(2)−O(9)	108.2(2)	O(1)−P(2)−O(9)	108.33(14)	N(3)−C(31)−C(35)	110.3(5)	C(33)−C(32)−C(31)	106.3(8)
O(16)−P(3)−O(20)	112.4(2)	O(16)−P(3)−O(19)	108.68(14)	C(34)−C(33)−C(32)	109.0(11)	C(33)−C(34)−C(35)	111.0(10)
O(20)−P(3)−O(19)	109.3(2)	O(16)−P(3)−O(17)	112.81(14)	C(34)−C(35)−C(31)	102.4(7)	C(42)−C(41)−N(4)	110.6(7)
O(20)−P(3)−O(17)	106.45(13)	O(19)−P(3)−O(17)	107.05(14)	C(42)−C(41)−C(45)	106.2(7)		

[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.

UT-2, a Novel One-Dimensional Chain Structure. In the predominantly nonaqueous synthesis system, where no water is added ($x = 0$), large crystals (SEM, Figure 2b) form at 150−180 °C (Table 4). The empirical formula of the material is $[Al_3P_5O_{20}H]^{5-}\cdot 5[C_5H_9NH_3^+]$, which we designate UT-2 (University of Toronto, structure no. 2). The PXRD pattern (Figure 1b) shows it to be highly crystalline. The SC-XRD structure of this material reveals the existence of aluminophosphate 1-D chains arranged into 2-D layers, (Figure 3). A projection of the theoretical PXRD pattern from the SC-XRD data accounts for all of the observed PXRD reflections. The crystallographic asymmetric unit contains five distinct cyclopentylammoniums, three aluminum atoms and five phosphorus atoms **(**Figure 3a). Crystallographic data, atomic coordinates, and thermal parameters are summarized in Table 2.

This is only the second reported case of a 1-D aluminophosphate chain structure. Two previous reports describe another aluminophosphate chain structure.[9,10]

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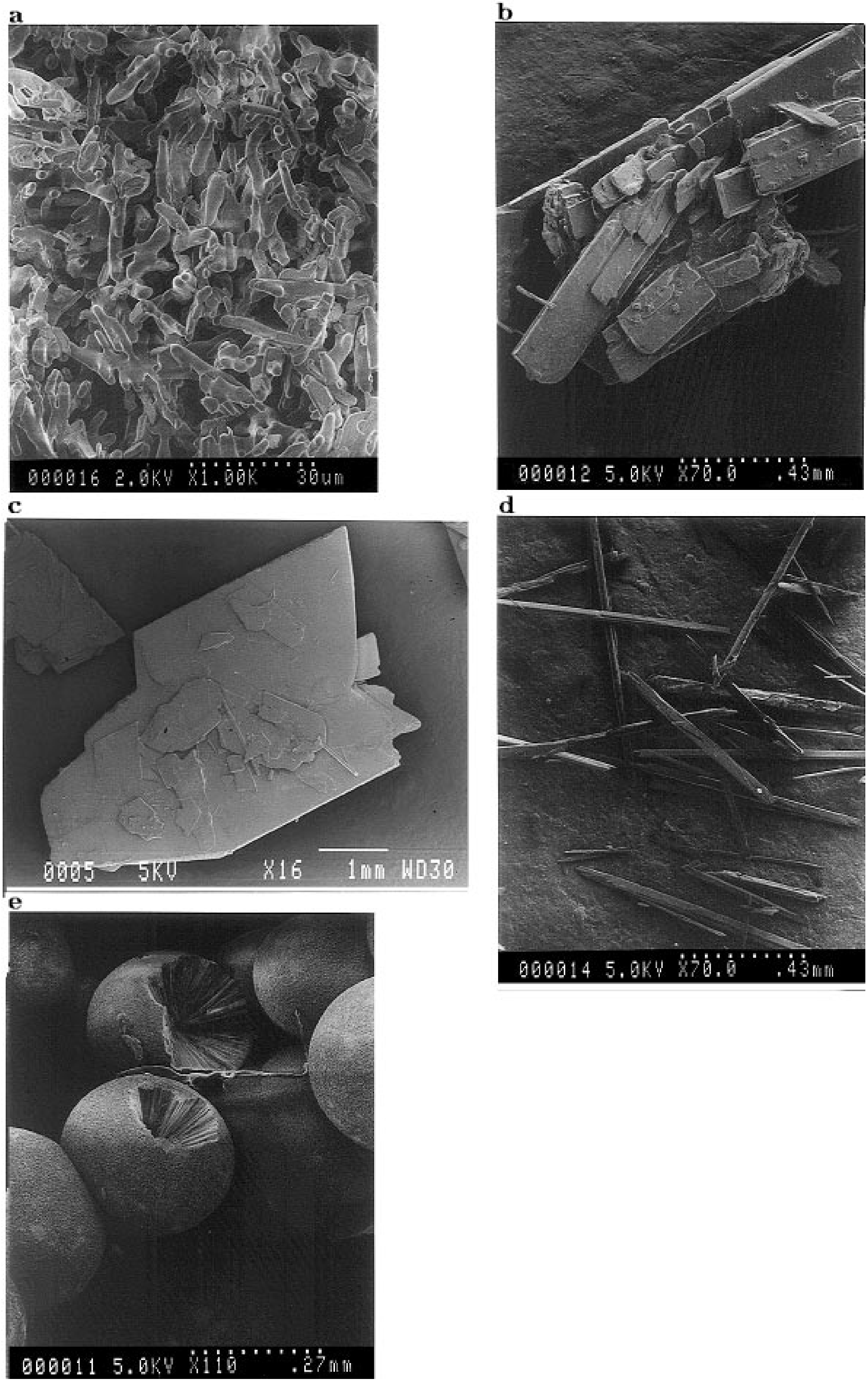

Figure 2. SEM of the solids. (a) Small needles of the self-assembling cyclopentylammonium phosphate phase present in the initial reaction mixture; (b) the large, thick crystals of UT-2; (c) UT-3 crystals, which are mostly observed to be twinned; (d) 13.5 Å fibrous needles; (e) 17.5 Å spherical aggregates.

Table 3

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

	x	*y*	*z*	*U*(eq)[a]
Al(1)	2872(1)	7725(1)	3044(1)	39(1)
Al(2)	8369(1)	7750(1)	3271(1)	41(1)
P(1)	1264(1)	7051(1)	4454(1)	40(1)
P(2)	744(1)	8535(1)	3373(1)	44(1)
P(3)	6339(1)	7856(1)	5363(1)	43(1)
O(1)	−230(3)	7328(1)	4178(3)	58(1)
O(2)	952(3)	6535(1)	4400(3)	53(1)
O(3)	2500(3)	7200(1)	6040(3)	51(1)
O(4)	893(4)	8830(1)	4772(3)	58(1)
O(5)	694(4)	8856(1)	1960(4)	57(1)
O(6)	−744(3)	8237(1)	2776(3)	55(1)
O(7)	2158(3)	8202(1)	3767(3)	51(1)
O(8)	1939(3)	7198(1)	3183(3)	48(1)
O(9)	4854(3)	7662(1)	4060(3)	51(1)
O(10)	6077(3)	8298(1)	6084(4)	61(1)
O(11)	6932(3)	7458(1)	6569(3)	61(1)
O(12)	7563(3)	7943(1)	4617(3)	55(1)
H(5O)	606(57)	8689(19)	1136(58)	70(15)
N(1)	3819(4)	8568(1)	7222(4)	57(1)
C(11)	4732(6)	8933(2)	8373(6)	74(1)
C(12)	3767(7)	9226(2)	9054(7)	94(2)
C(13)	4724(12)	9258(4)	10788(9)	167(4)
C(14)	5830(14)	8878(5)	11141(10)	222(7)
C(15)	5985(8)	8697(3)	9778(7)	114(3)
N(2)	−1077(4)	6155(1)	1546(4)	58(1)
C(21)	−1394(12)	5672(3)	1755(9)	144(4)
C(22)	−2558(13)	5431(3)	358(11)	185(5)
C(23)	−2674(22)	4971(4)	877(21)	301(11)
C(24)	−1859(26)	4999(5)	2626(21)	314(10)
C(25)	−1011(18)	5432(3)	3059(13)	239(8)

(b) Selected Bond Lengths (Å) and Angles (deg) for UT-3

Al(1)−O(9)	1.705(3)	Al(1)−O(3)#1	1.721(3)
Al(1)−O(7)	1.726(3)	Al(1)−O(8)	1.745(3)
P(1)−O(2)	1.483(3)	P(1)−O(1)	1.511(3)
P(1)−O(3)	1.515(3)	P(1)−O(8)	1.545(3)
P(2)−O(4)	1.476(3)	P(2)−O(6)	1.517(3)
P(2)−O(7)	1.529(3)	P(2)−O(5)	1.551(3)
N(1)−C(11)	1.481(6)	C(11)−C(12)	1.497(7)
C(11)−C(15)	1.509(7)	C(12)−C(13)	1.482(8)
C(13)−C(14)	1.427(10)	C(14)−C(15)	1.384(9)
O(9)−Al(1)−O(3)#1	109.44(13)	O(9)−Al(1)−O(7)	110.62(14)
O(3)#1−Al(1)−O(7)	110.22(14)	O(9)−Al(1)−O(8)	108.68(14)
O(3)#1−Al(1)−O(8)	105.60(13)	O(7)−Al(1)−O(8)	112.13(14)
O(2)−P(1)−O(1)	110.8(2)	O(2)−P(1)−O(3)	111.8(2)
O(1)−P(1)−O(3)	108.6(2)	O(2)−P(1)−O(8)	111.5(2)
O(1)−P(1)−O(8)	108.7(2)	O(3)−P(1)−O(8)	105.2(2)
O(4)−P(2)−O(6)	113.8(2)	O(4)−P(2)−O(7)	110.4(2)
O(6)−P(2)−O(7)	107.8(2)	O(4)−P(2)−O(5)	109.5(2)
O(6)−P(2)−O(5)	106.6(2)	O(7)−P(2)−O(5)	108.5(2)
P(1)−O(1)−Al(2)#3	154.8(2)	P(1)−O(3)−Al(1)#4	144.3(2)
P(2)−O(6)−Al(2)#3	142.2(2)	P(2)−O(7)−Al(1)	142.9(2)
N(1)−C(11)−C(12)	114.2(4)	N(1)−C(11)−C(15)	109.5(5)
C(12)−C(11)−C(15)	106.1(5)	C(13)−C(12)−C(11)	105.1(5)
C(14)−C(13)−C(12)	106.2(6)	C(15)−C(14)−C(13)	112.1(7)
C(14)−C(15)−C(11)	106.7(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.

The UT-2 chain contains three types of $P(O-Al)_nO_{4-n}$ units, where $n = 1, 2, 3$. Significantly, it contains a phosphate group with only one bridging oxygen to an aluminum and three terminal oxygens (P−OH 1.572(3) Å, $P-O_{bridging}$ 1.543(2) Å, $P{=}O_{terminal}$ 1.499(3) and 1.509(3) Å). This type of phosphate group would not be expected to survive in an aqueous synthesis, being easily cleaved at the sole bridging site as found for condensed phosphates.[20] Thus UT-2 can be viewed as a kinetically stabilized intermediate in the assembly of higher dimensionality aluminophosphates (see below). The P−OH group of the terminal phosphate hydrogen-bonds to a P=O group of an adjacent chain (P−OH···O−P distance, 1.855 Å). These hydrogen-bonded chains define the overall layer architecture of UT-2. Extensive hydrogen-bonding ($P-O\cdots H-N_{av}$ 2.08 Å) and ion-pairing exists between these anionic sheets and the interlamellar cyclopentylammonium cations.

UT-2 is also unique in several other respects. It is the first aluminophosphate chain structure to contain (i) triply bridging phosphate groups, (ii) six-rings of oxygen-bridged T atoms (T = Al, P), and (iii) edge-sharing four-rings. The repeat unit of the UT-2 chain structure (Figure 3), can be visualized as three corner-sharing four-rings (where the apexes are occupied by aluminum atoms) connected to three edge-sharing four-rings. This defines sections of five edge-sharing four-rings in a double-crankshaft conformation.

In a preliminary report, we had proposed just such an aluminophosphate chain structure as a reaction intermediate in the templated assembly of aluminophosphate open frameworks.[12−14] The details of this model will be reported in an accompanying paper.[13]

UT-3, a Novel Two-Dimensional Layered Structure. When an identical synthesis mixture used to prepare UT-2 is subjected to a slightly higher reaction temperature (Table 4), the product is an aluminophosphate 2-D layer rather than a 1-D chain structure. The empirical formula is $[Al_2P_3O_{12}H]^{2-}\cdot 2[C_5H_9NH_3^+]$ and we designate the structure UT-3. Large, thin single-crystal plates are typically obtained. By using reagent amounts of water and slightly higher temperatures ($x = 10$, $T = 200$ °C, Table 4), it was possible to obtain crystals thick enough for a SC-XRD structure analysis (SEM, Figure 2c). Crystallographic data, atomic coordinates, and thermal parameters for UT-3 are summarized in Table 3. A projection of the theoretical PXRD pattern of UT-3 from the SC-XRD data accounts for all of the observed the PXRD reflections (Figure 1c).

The labeling scheme of the crystallographic asymmetric unit is shown in Figure 4a. The UT-3 structure consists of alternating tetrahedral phosphorus and aluminum centers connected by bridging oxygens, arranged into a three-connected two-dimensional net of edge-sharing six-rings (Figure 4b). The phosphorus tetrahedra all contain a terminal phosphonyl group ($P{=}O_{av}$ 1.477(3) Å). The four-coordination of aluminum is satisfied by the oxygen of an out-of-plane phosphate group that connects two aluminums of the six-rings. Only one-half of the six-rings contain this doubly bridging phosphate group, in alternate rows of six-rings connected along the *c*-axis (Figure 4b). The phosphate groups reside above and below the layer plane along each row and possess two terminal oxygens, one of which is protonated (P=O 1.476(3) Å, P−OH 1.551(3) Å). The P−OH group participates in intralayer hydrogen-bonding to a phosphonyl group belonging to the two-dimensional net (P−OH···O−P, 1.821 Å). UT-3, like UT-2, also contains cyclopentylammonium bilayers interdisposed between, and interacting with, the anionic aluminophosphate layers. This arrangement creates an extensive network of hydrogen-bonds with the phosphate groups ($P\text{-}O\cdots H-N_{av}$ 1.99 Å).

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(20) Westman, A. E. R. *Top. Phosphorus Chem.* **1981**, *9*, 231.

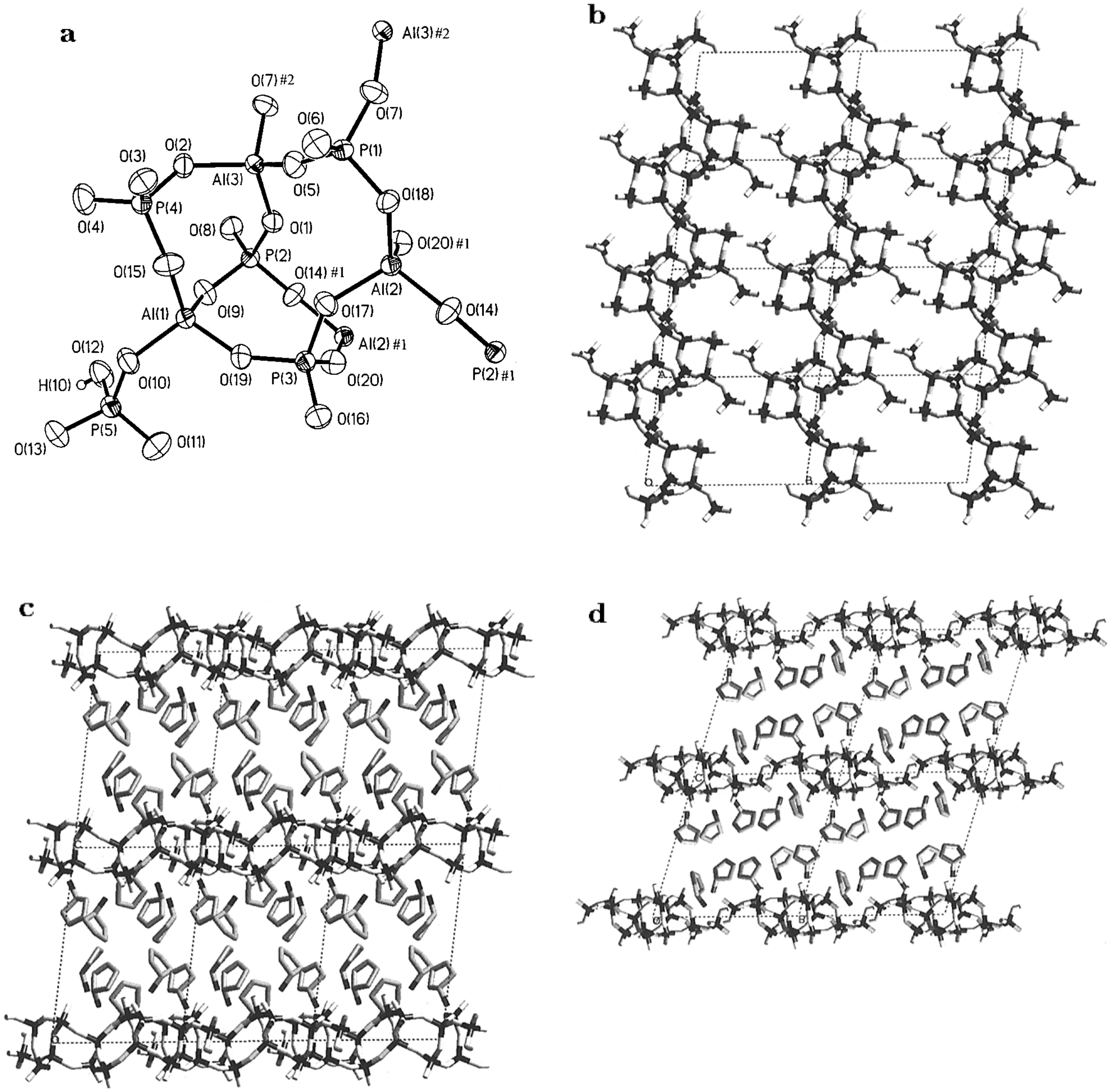

Figure 3. Cerius crystal graphics of the UT-2 chain structure, $[Al_3P_5O_{20}H]^{5-}\cdot 5[C_5H_9NH_3^+]$. (a) Thermal vibration ellipsoids and atom labeling scheme; (b) [001] projection of one layer of chains running down the *x* axis. Note the connection of the chains through hydrogen-bonded phosphate groups on adjacent chains; (c) [010] projection, showing the bilayer arrangement of the templating cyclopentylammoniums; (d) [001]-projection. In this view, the chains are seen end-on and their connection to form layers may be observed.

Table 4. Summary of Synthesis Conditions and Products

no.	value of *x* used	synthesis time (days)	synthesis temp (°C)	major phase(s) observed by PXRD
1	0	0	prior to thermal treatment	cyclopentylammonium monohydrogen phosphate, pseudoboehmite
2	0	3	180	UT-2
3	0	150	180	UT-3
4	0	3	220	UT-3, trace 13.5 Å phase
5	3.6	3	150	UT-2
6	3.6	3	190−220	UT-3
7	10	1 to 3	200	13.5 Å phase, trace UT-3
8	10	7	200	thicker crystals of UT-3, used for SC-XRD analysis
9	10	3 to 7	220	UT-3
10	50	25	200	11.7 Å phase, 11.4 Å phase
11	134	4 to 6	150	17.5 Å phase, trace 11.7 Å phase
12	134	6	180	11.4 Å phase, trace 17.5 Å phase
13	134	6	200−220	11.4 Å phase
14	134, 0 TEG	1 to 4	150 and above	17.5 Å spherical growths

UT-3 represents the first layered aluminophosphate to be synthesized in a predesigned mixed aqueous/nonaqueous system. Although the layer architecture is novel, it is structurally similar and stoichiometrically

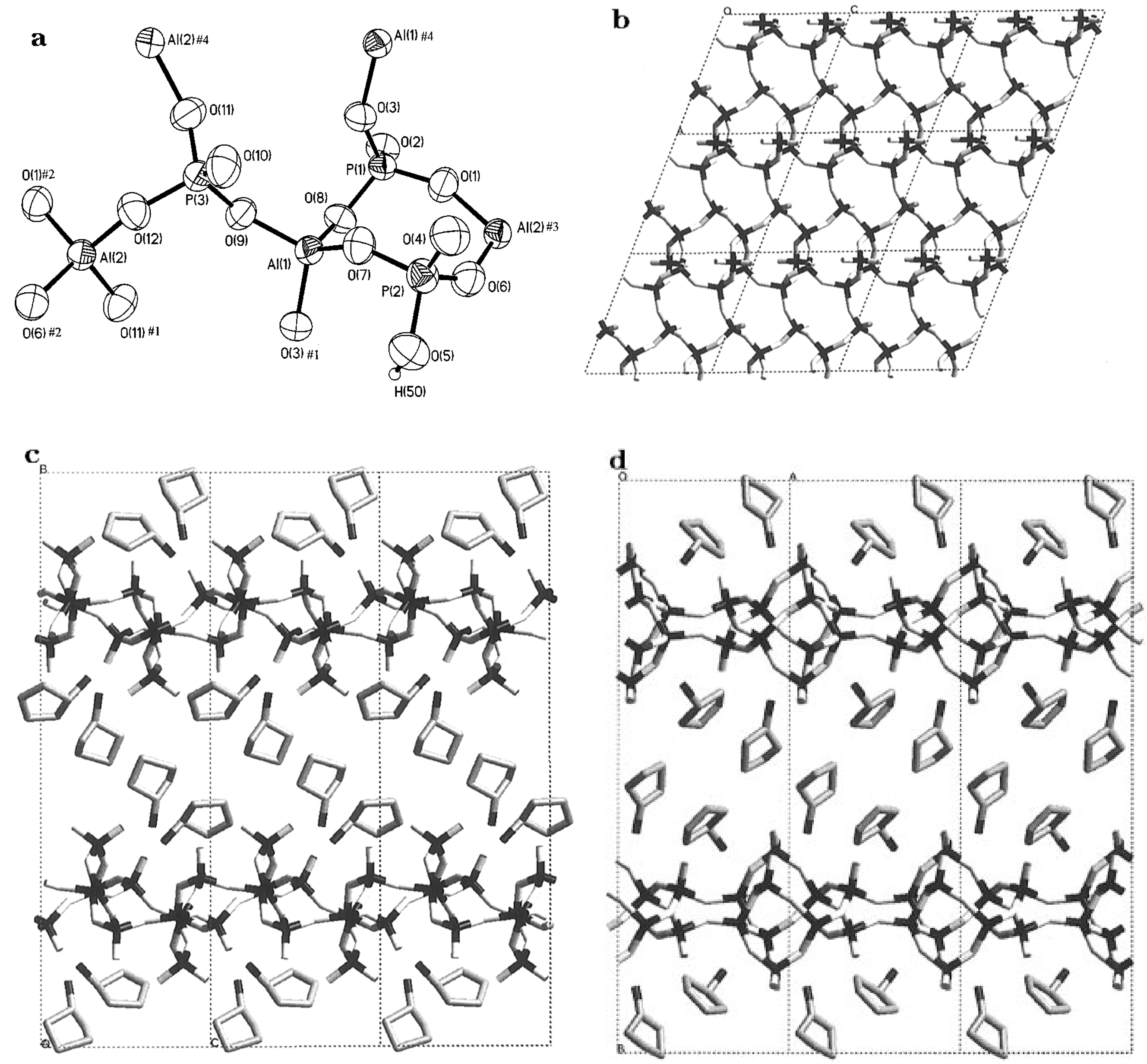

Figure 4. Cerius crystal graphics of the UT-3 layered structure, $[Al_2P_3O_{12}H]^{2-}\cdot 2[C_5H_9NH_3^+]$. (a) Thermal vibration ellipsoids and atom labeling scheme; (b) [010] projection of one aluminophosphate layer; (c) [100] projection, showing the layered nature of the compound and its template; (d) [001] projection.

equivalent to other layers that we have synthesized in corresponding TEG−cycloalkylamine systems,[21] as well as to a previously reported layered structure.[4]

Inspection of the $[Al_2P_3O_{12}H_x]^{x-3}\cdot(x-3)[R^+]$ (where x = 0, 1) structures show the arrangement of six-rings and doubly bridging phosphate groups to be unique for each case. Noteworthy, UT-5, another layered compound that we recently discovered in the TEG-cyclohexylamine system,[21] is isostructural with UT-3.

Multiple Phases through Similar Recipes. The use of more extensive hydrolitic conditions, achieved by the addition of water (i.e., increasing x) and/or use of higher temperature, results in the formation of several new phases (Table 4). For example, a phase with the majority PXRD reflection located at 13.5 Å (Figure 1d) can be obtained. The solid has a fibrous texture and is comprised of long needles with a high aspect ratio (SEM, Figure 2d). The crystals appear slightly fragmented and damaged, which is likely due to a synthetic overrun. The sample contains some UT-3 plates, which is seen in the PXRD pattern (Figure 1d).

A further increase of the water content of the TEG synthesis system results in a mixture of other new, high-crystallinity phases (100% peaks 11.7 and 11.4 Å, Table 4). Proceeding to entirely aqueous conditions yields an extraordinary morphology based on spherical agglomerates of needles (SEM, Figure 2e). The PXRD shows this material to have a highly open structure (Figure 1e). Finally, under higher temperature conditions and/or longer reaction time, the dense-phase $AlPO_4$−tridymite becomes the majority product.

Chain-to-Layer Transformation of UT-2 to UT-3. The UT-2 and UT-3 phases are obtained under very similar reaction conditions and sometimes they coprecipitate. TGA and PXRD studies reveal a remarkable

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(21) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A., *J. Chem. Soc., Chem. Commun.*, in press.

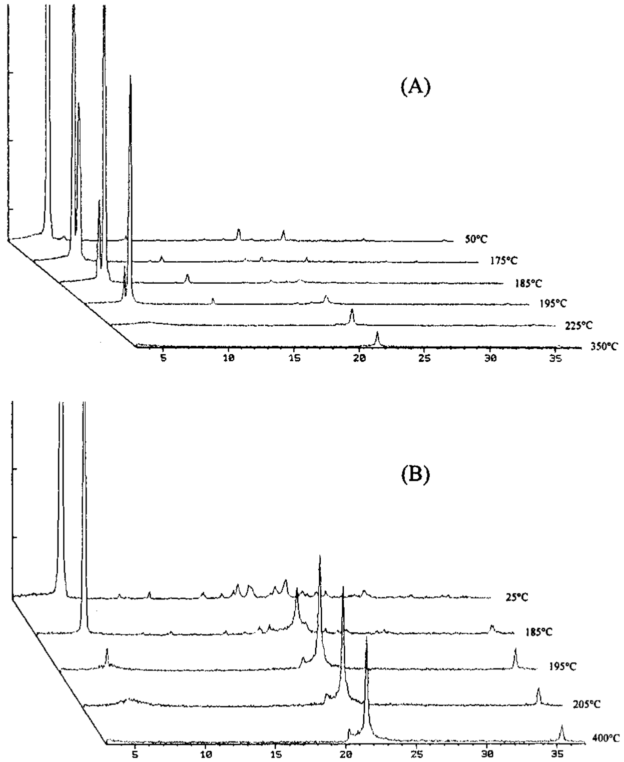

Figure 5. VT-PXRD patterns, with temperatures at which the patterns were collected displayed on the right: (a) UT-2; (b) UT-3.

solid-state transformation. By heating UT-2 for several hours in air at 200 °C, it smoothly and cleanly transforms to UT-3. These structural data strongly suggests that the UT-2 to UT-3 chain-to-layer transformation can be induced in the synthesis by the addition of reagent amounts of water, higher temperatures, and/or longer reaction time (Table 4). It is clear that the UT-3 layer is the more thermodynamically stable structure, while the UT-2 chain is the metastable precursor phase.

Thermal treatment of UT-3, either presynthesized or obtained by thermal treatment of UT-2, first transforms it to an amorphous low density material (broad PXRD reflection, *ca.* 14 Å). This is followed by collapse to the $AlPO_4$-tridymite dense phase at approximately 350 °C (VT-PXRD, Figure 5a,b). These transformations can be observed in the TGA (Figure 6).

In an accompanying paper, the details of the conversion of 1-D chain to 2-D layer to 3-D open-framework aluminophosphates will be presented. The cumulative information is used as the basis for proposing a new paradigm to explain the mode of formation of aluminophosphate molecular sieve frameworks.[13]

Conclusions

The newfound knowledge of the transformation of the aluminophosphate 1-D chain to the 2-D layer provides a new way of thinking about the templated assembly of $AlPO_4$-n materials. It suggests that this is the way in which UT-3 and other layered aluminophosphates are formed. This proposal receives support from the similarity of the structure of UT-3 to other 2-D aluminophosphates layers.[4,21] The UT-2 chain structure is stabilized only with the correct choice of template and reaction conditions. In this context, we have obtained an isostructural chain, UT-7, in the TEG−cycloheptylamine system.[22]

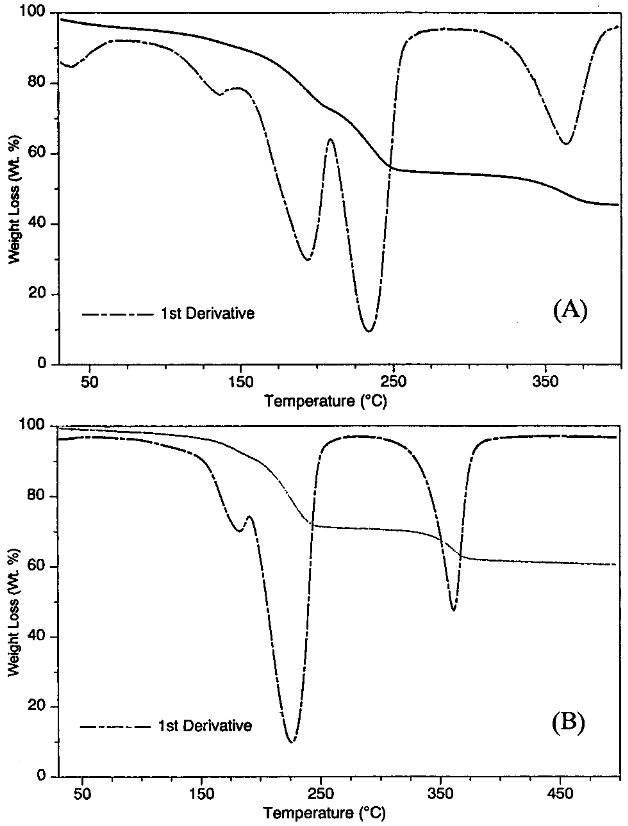

Figure 6. TGA data, whose peaks correspond to the observed VT-PXRD transformations: (a) UT-2; (b) UT-3.

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Supporting Information Available: Crystallographic details (6 pages); structure factor tables (44 pages). Ordering information is given on any current masthead page.

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(22) Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *Inorg. Chem.*, in press.