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Crystal Structures of a Series of Novel Alkylammonium Phosphates and Their Formation in Aluminophosphate Synthesis Mixtures

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The crystal structures of several novel alkylammonium phosphate salts were determined by single-crystal X-ray methods: cyclopentylammonium monohydrogen phosphate (CMP) ($[C_5H_9NH_3^+]_2[HPO_4^{2-}]$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.197(3)$ Å, $b = 5.992(1)$ Å, $c = 16.580(3)$ Å, $\beta = 98.57(2)°$); octylammonium dihydrogen phosphate (ODP) ($[CH_3(CH_2)_7NH_3^+][H_2PO_4^-]$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 4.554(1)$ Å, $b = 34.652(3)$ Å, $c = 7.328(1)$ Å, $\beta = 90.66(1)°$); and decylammonium dihydrogen phosphate (DDP) ($[CH_3(CH_2)_9NH_3^+][H_2PO_4^-]$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.358(2)$ Å, $b = 39.749(12)$ Å, $c = 9.131(4)$ Å, $\beta = 90.45(2)°$). Each are composed of anionic layers of hydrogen-bonded phosphate molecules, separated by charge-balancing alkylammonium cations. The long-chain alkylammoniums in ODP and DDP are interdigitated, while the cyclopentylammoniums in CMP define a bilayer-like arrangement. Large crystals were grown by recrystallization, but the materials were also observed to form in the corresponding solvothermal aluminophosphate synthesis mixtures. We have isolated phosphate salt compounds in aluminophosphate synthesis mixtures containing a variety of different alkylamines and suggest they are initially present in such experiments whenever the alkylamine is primary or secondary.

Introduction

Alkylammonium phosphates are solid-state materials composed of hydrogen bonded networks of anionic $[H_xPO_4]^{x-3}$ phosphate centers ($x = 0-3$) and alkylammonium cationic molecules. Each N−H bond donates a hydrogen bond to an oxygen of a phosphate, creating a three-dimensional hydrogen bonded network. The alkylammonium phosphates readily form in, and may be recrystallized from, a number of solvents. Despite this, only seven crystal structures have been reported to date. The majority contain an alkylenediammonium cation, where the phosphates are hydrogen bonded approximately into anionic layers, separated by monolayers of alkylenediammonium molecules. For example, ethylenediammonium monohydrogen phosphate was reported independently by two groups.[1,2] The unit cell axes were defined differently for each report but the overall structure is the same. The isostructural ethylenediammonium monohydrogen arsenate was also reported.[2]

An example of a dihydrogen phosphate salt is that of ethylenediammonium,[3] also composed of phosphate layers separated by monolayers of ethylenediammonium. However, in this case, the phosphates each donate and accept two hydrogen bonds. The layout of the hydrogen bonds may be thought of as chains extending along the *a* axis, doubly hydrogen bonded to the next chain along the *b* axis to define a continuous layer in the *ab* plane. For all dihydrogen phosphate salts, there is a larger amount of intralayer hydrogen bonding due to the additional proton on each phosphate group. A dihydrogen phosphate pentahydrogen bisphosphate salt of ethylenediammonium also exists, where the two types of dihydrogen phosphates and one trihydrogen phosphate define a hydrogen-bonded three-dimensional framework, with the ethylenediammoniums occupying the voids.[4]

Other examples of alkylenediammonium phosphate salt compounds are 1,3-propanediammonium monohydrogen phosphate monohydrate,[5] 1,3-propanediammonium dihydrogen phosphate,[6] and 1,4-diammoniumbutane dihydrogen phosphate.[7] Further structural variation is displayed by the coexistence of sodium in the structure[8] or the use of an alkylamine derivative as cation, such as an amino acid.[9]

Aakeröy et al. have synthesized a number of dihydrogen phosphate salts containing cyclic amines.[10] They reported the crystal structures of only the piperidinium and benzylammonium salts, which were recrystallized from methanol and aqueous solution, respectively. The former contains secondary piperidiniums which interact with two adjacent phosphate layers, thereby cross linking them via two hydrogen bonds. This group also claims to have prepared 24 salts of various primary, secondary and tertiary amines. Riou et al. reported the crystal structure of piperazinium monohydrogen phosphate monohydrate.[11] It consists of a three-dimensional network of hydrogen bonds between piperaziniums and, notably, isolated phosphates. No hydrogen bonding exists between phosphate groups. Even

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

compound	$[C_5H_9NH_3^+]_2[HPO_4^{2-}]$, CMP	$[CH_3(CH_2)_7NH_3^+][H_2PO_4^-]$, ODP	$[CH_3(CH_2)_9NH_3^+][H_2PO_4^-]$, DDP
empirical formula	$C_{10}H_{25}N_2O_4P$	$C_8H_{22}NO_4P$	$C_{10}H_{26}NO_4P$
a, Å	4.197(3)	4.554(1)	7.358(2)
b, Å	5.992(1)	34.652(3)	39.749(12)
c, Å	16.580(3)	7.328(1)	9.131(4)
α, deg	90	90	90
β, deg	98.57(2)	90.66(1)	90.45(2)
γ, deg	90	90	90
V, Å^3	1394.7(5)	1156.3(2)	2671(2)
Z	4	4	4
fw	268.29	227.24	255.29
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
temperature, K	173(2)	173(2)	173(2)
λ, Å	0.710 73	0.710 73	0.710 73
ρ_{obsd}, g cm^{-3}	not measured	not measured	not measured
ρ_{calcd}, g cm^{-3}	1.278	1.305	1.270
μ(Mo Kα), cm^{-1}	2.04	2.30	2.07
$R\ (F_o)^a$	0.0610	0.0474	0.0679
$R_w\ (F_o^2)^a$	0.1559	0.1542	0.1861

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

more interesting is that they synthesized the crystals in a hydrothermal fluoroaluminophosphate experiment containing piperazine.

As previously mentioned, the alkylammonium phosphate salts form readily in most solvents. Therefore they would be expected to form in the reaction gels of aluminophosphate experiments, and even as coprecipitates in the products. Bibby and co-workers discussed a dipropylamine-related phosphate salt that forms initially in the reaction mixture, as evidenced by powder X-ray diffraction.[12] They postulate that it is the dihydrogen phosphate salt, but did not determine the structure. Riou et al. note that the phosphate salts may be present in the aluminophosphate products synthesized at lower temperatures.[11]

Other than these two reports, there has been little discussion in the aluminophosphate literature on the nature of the reaction mixtures prior to heating. Most reports describe the molar ratios and preparation of the reaction mixture and heat them for a required amount of time, studying in detail the final aluminophosphate product. Additionally, only limited amounts of characterization have been performed to date for any of the alkylammonium phosphate salts.

Here, we describe the crystal structures of three novel alkylammonium phosphates. The phosphates are arranged in layers and are separated by interdigitated or bilayers of organic amines. Evidence is shown for their formation in various solvothermal aluminophosphate reaction mixtures and in some cases the final product after heating. This phenomenon is also shown to occur using other alkylamines for which we have not yet obtained the crystal structure. On the basis of these results, we suggest that phosphate salts are present in other aluminophosphate and metal phosphate systems.

Experimental Section

Synthesis. The alkylammonium phosphate salts could be readily prepared in many solvents such as water, methanol, or tetraethylene glycol (TEG), simply by adding phosphoric acid (85 wt %, Aldrich) followed by an alkylamine (Aldrich). This was the case whether or not a source of aluminum oxide was added to the slurry. A powder of the material could be obtained by filtering this slurry and washing with acetone. ODP and DDP were recrystallized from deionized water, while CMP was recrystallized from a 50 vol % methanol (BDH assured) solution. The temperature of recrystallization was 50 °C for DDP and room temperature for ODP and CMP.

X-ray Diffraction Data. Powder (PXRD) patterns were collected on a Siemens D5000 diffractometer (Cu Kα radiation, $\lambda = 1.541\ 78$ Å). The step size used was 0.030°, step time 1.0 s, and scan range 1−50° (2θ). The detector in the instrument was a Kevex 2005-212 solid-state detector.

Single-crystal data for all 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.[13] The structures were solved using the SHELXTL\PC V5.0 package[14] and refined by full-matrix least-squares on F^2 using all data (negative intensities included). Nonaliphatic hydrogen atoms were refined with isotropic thermal parameters, while aliphatic hydrogen atoms were included in calculated positions and treated as riding atoms. A summary of selected crystallographic data are given in Table 1. The views of each structure were produced using the Cerius^2 program by Molecular Simulations, Inc. Shading scheme: phosphorus, black; oxygen, hydrogen and nitrogen, white; carbon, gray. The hydrogens of the alkylammonium molecules were omitted for clarity.

Results and Discussion

Cyclopentylammonium Monohydrogen Phosphate (CMP), $[C_5H_9NH_3^+]_2[HPO_4^{2-}]$. This phase was observed to form spontaneously in a predominantly non aqueous TEG starting synthesis mixture. The TEG−Al_2O_3−H_3PO_4−cyclopentylamine slurry was studied by PXRD and scanning electron microscopy (ca. 20 × 5 μm needles).[15] The mixture was an opaque slurry, and upon filtering, a white powder of CMP was obtained. No CMP was observed after heating the reaction mixture, as the product was one or more of the aluminophosphates phases UT-2, UT-3 or other as-yet unknown materials.[15,16]

CMP was subsequently recrystallized from a 50 vol % methanol solution. Thermal ellipsoids and atom labeling scheme of the resulting single-crystal X-ray study are given in Figure 1a. Fractional atomic coordinates are given in Table 2, while selected bond lengths and bond angles are given in Table 3. The structure of CMP consists of phosphate molecules arranged

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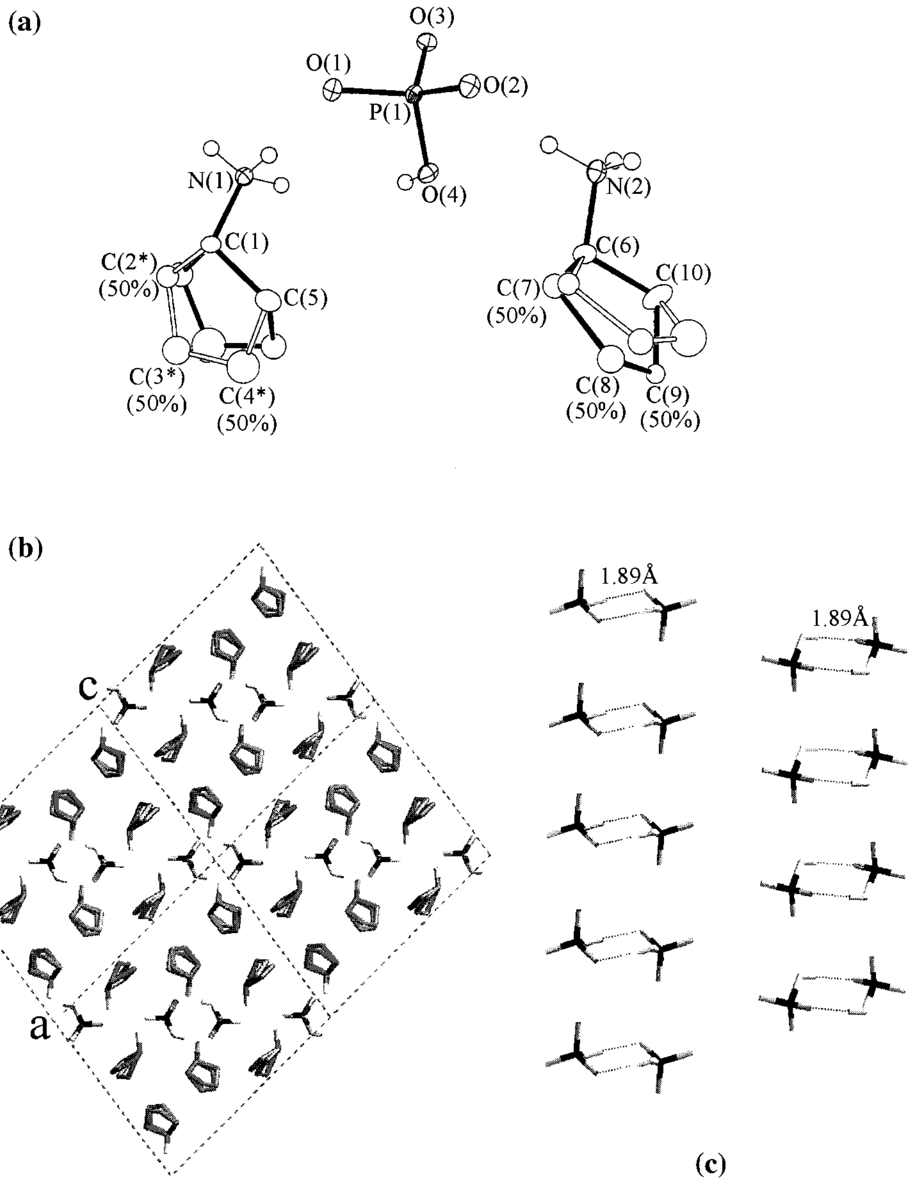

Figure 1. Cyclopentylammonium monohydrogen phosphate (CMP). (a) Thermal ellipsoids and naming scheme of the asymmetric unit. (b) *b* projection, showing the bilayer arrangement and partial disorder of the cyclopentylammonium carbon-rings. (c) View of one phosphate layer which contain hydrogen bonded phosphate dimers.

approximately into layers, where the cyclic amines define a bilayerlike interlayer region (Figure 1b), similar to their arrangement in UT-2 and UT-3.[15] For each of the two crystallographically distinct cyclopentylammonium molecules, the α carbon and one of the β carbons of the carbon five-rings are stationary, while the other three carbons are distributed equally between two sites. The phosphate layers themselves contain monohydrogen phosphate hydrogen bonded into dimers (Figure 1c). No further intralayer hydrogen bonding exists between adjacent phosphate pairs. However, an extensive hydrogen bonding network exists between the phosphates and the $R-NH_3^+$ groups of the cyclopentylammoniums.

Octylammonium Dihydrogen Phosphate (ODP), $[CH_3(CH_2)_7NH_3^+][H_2PO_4^-]$. The slurry of a TEG-$Al_2O_3-H_3PO_4$-octylamine synthesis mixture also contained a highly crystalline phosphate salt. The morphology and crystal size (ca. 10 μm) are nearly identical to those of the analogous hexylamine and decylamine systems, below. The PXRD pattern of this novel phase is shown in Figure 4c. Very large crystals (needles, several cm in length and several mm in width) may be recrystallized from water at room temperature.

The single-crystal XRD analysis showed the material to be octylammonium dihydrogen phosphate (ODP). Thermal ellipsoids and atom labeling scheme are shown in Figure 2a, fractional atomic coordinates are given in Table 4, and selected bond lengths and bond angles are given in Table 5. ODP is composed of dihydrogen phosphate arranged in layers (Figure 2b). One oxygen of the phosphate is static and protonated. The other three oxygens are disordered equally between two sites with occupancies 0.5. The second hydrogen could not be resolved but is presumably distributed statistically over the disordered oxygens. Each hydrogen of the ammonium headgroup could be located and donates a hydrogen bond to the terminal oxygens of the phosphates. The octylammonium molecules are interdigitated between the phosphate layers to define a hydrophobic interlayer region (Figure 2c). If no Al_2O_3 is added to the synthesis mixture, ODP is the only phase present in the product after heating. If Al_2O_3 is added, then a

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

	x	*y*	*z*	*U*(eq)^a
P(1)	1076(1)	621(2)	945(1)	21(1)
O(1)	879(2)	3134(4)	966(2)	27(1)
O(2)	1822(2)	−123(4)	1641(2)	30(1)
O(3)	1293(2)	−51(4)	104(1)	26(1)
O(4)	131(2)	−672(5)	1102(2)	29(1)
N(1)	−1032(2)	4336(6)	428(2)	26(1)
C(1)	−1670(3)	5061(7)	1010(2)	33(1)
C(2)	−2729(8)	5232(20)	452(7)	46(3)^b
C(3)	−3288(13)	3947(28)	984(10)	92(5)^b
C(4)	−2739(7)	2251(18)	1377(6)	47(3)^b
C(2*)	−2614(8)	5769(18)	656(6)	36(3)^b
C(3*)	−3332(9)	5014(22)	1109(8)	60(3)^b
C(4*)	−2917(10)	3186(25)	1608(9)	78(4)^b
C(5)	−1792(4)	3240(8)	1638(3)	47(1)
N(2)	1552(3)	−4230(6)	2275(2)	27(1)
C(6)	746(3)	−4347(7)	2742(2)	31(1)
C(7)	776(8)	−2787(19)	3409(6)	33(3)^b
C(8)	618(8)	−4173(17)	4156(6)	40(2)^b
C(9)	244(6)	−6372(12)	3850(4)	22(2)^b
C(7*)	989(8)	−2863(17)	3582(6)	26(3)^b
C(8*)	1014(7)	−4558(16)	4259(5)	35(2)^b
C(9*)	900(11)	−6574(22)	3939(7)	76(4)^b
C(10)	632(4)	−6715(7)	3069(3)	45(1)
H(4O)	−319(29)	−450(66)	785(23)	22(11)
H(11)	−1225(30)	2877(78)	200(24)	39(12)
H(12)	−415(29)	4064(62)	713(22)	23(10)
H(13)	−1058(29)	5341(72)	−10(26)	33(11)
H(21)	2022(33)	−4590(76)	2604(27)	41(13)
H(22)	1605(29)	−2710(77)	2068(24)	37(12)
H(23)	1467(28)	−5281(68)	1864(24)	27(11)

^{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. ^{b} These atoms are disordered and were therefore only refined isotropically.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for CMP

P(1)−O(2)	1.512(3)	P(1)−O(3)	1.527(3)
P(1)−O(1)	1.533(3)	P(1)−O(4)	1.603(3)
N(1)−C(1)	1.483(5)	C(1)−C(5)	1.535(6)
O(2)−P(1)−O(3)	113.9(2)	O(2)−P(1)−O(1)	112.5(2)
O(3)−P(1)−O(1)	110.0(2)	O(2)−P(1)−O(4)	104.0(2)
O(3)−P(1)−O(4)	107.9(2)	O(1)−P(1)−O(4)	108.1(2)
N(1)−C(1)−C(5)	112.0(3)	N(1)−C(1)−C(2)	104.4(5)

mesolamellar aluminophosphate is the product, with a trace amount of ODP.[17−19]

Decylammonium Dihydrogen Phosphate (DDP), $[CH_3(CH_2)_9NH_3^+][H_2PO_4^-]$. Similarly, the TEG−$Al_2O_3$−$H_3PO_4$−decylamine synthesis mixture contained pseudoboehmite and decylammonium dihydrogen phosphate (DDP). The mixture was observed to be the same after two months of aging at room temperature. In the absence of Al_2O_3, DDP was the only phase present in the final product after heating, for example, at 180 °C for 5 days. Depending on the conditions, varying ratios of a mesolamellar aluminophosphate (MLA) and DDP were formed in the product when Al_2O_3 was added.[17−19] For example, 180 and 200 °C produced a trace amount of DDP in a majority MLA product, while lower temperatures of 150 and 80 °C produced larger amounts of DDP. An ethylene glycol solvent produced little or no DDP and only the MLA phase, while various poly(ethylene glycol)s of average molecular weights 300, 400, and 1000 gave products similar to those of TEG. Interestingly, aqueous conditions gave DDP as the majority phase under similar conditions. The MLA phase became the dominant phase only as the molar ratio of water to poly(ethylene glycol) was decreased.

DDP was recrystallized from water at 50 °C, and its structure was solved by single-crystal XRD. Thermal ellipsoids and atom labeling scheme are shown in Figure 3a, fractional atomic coordinates are given in Table 6, and selected bond lengths and bond angles are given in Table 7. The PXRD pattern of DDP was published previously[17−19] and is identical to the projected powder pattern based on the single-crystal XRD structure. DDP is isostructural to ODP, above, but the phosphates in DDP are not disordered (Figure 3b). There are two crystallographically distinct phosphates and decylammoniums, as opposed to one phosphate and one octylammonium for ODP. Each dihydrogen phosphate donates two hydrogen bonds and accepts two hydrogen bonds to define a continuous, uninterrupted phosphate layer (P−O···H−OP distances 1.54−1.80 Å, Figure 3b). The primary ammonium headgroups each donate three hydrogen bonds (N−H···O−P distances 1.89−2.09 Å). The decylammonium chains are again interdigitated (Figure 3c, cf. Figure 2c).

Other Alkylammonium Phosphates. Many other novel alkylammonium phosphate salts were observed to form spontaneously in various aluminophosphate synthesis mixtures using different alkylamines. Some examples will be given here, and represent only a small number of the phosphate salts that should be possible to synthesize. The PXRD patterns will be given, which illustrate their characteristic high crystallinity.

***n*-Alkylammonium Phosphates.** Phosphate salts of all of the $C_nH_{2n+1}NH_2$ *n*-alkylamines may be prepared for $n = 1−18$. The crystal structures for $n = 8$ and 10 and $x = 2$ were shown above. Phosphate salts were also characterized for hexylammonium phosphate ($n = 6$), heptylammonium phosphate ($n = 7$), nonylammonium phosphate ($n = 9$), undecylammonium phosphate ($n = 11$), and tetradecylammonium phosphate ($n = 14$). The PXRD patterns are shown in Figure 4, with the exception of undecylammonium phosphate, which was previously published.[18,19] Judging by the similarity in the PXRD patterns to those of ODP (Figure 4) and DDP,[17−19] these are likely the dihydrogen phosphate salts. Note the shift of the 100% peak to lower angle (2θ) as the number of carbons in the alkyl chain is increased. It should also be possible to prepare another series of novel phases by crystallizing the monohydrogen phosphate salts of these alkylamines (see below).

Phosphate salts of $C_nH_{2n-1}NH_2$ cycloalkylamines were prepared for cyclopentylamine ($n = 5$, CMP, above), cycloheptylamine ($n = 7$) and cyclododecylamine ($n = 12$). The PXRD pattern of CMP was previously published,[15] while the latter two are shown in Figure 5a and b, respectively. It is likely these are also monohydrogen phosphate salts, and more phases should be possible by forming the dihydrogen phosphate salts.

These phosphate salts form in, for example, water or methanol, upon the addition of phosphoric acid and the respective alkylamine. They also form in the TEG−Al_2O_3−H_3PO_4−alkylamine synthesis mixtures. The phosphate salt was the only product after heating if no Al_2O_3 was added to the synthesis mixture, while a mesolamellar aluminophosphate material was formed in the presence of Al_2O_3.[16−19] A number of preliminary recrystallization attempts were made for some of the alkylamines. For hexylamine, very large crystals were recrystallized from water, but turned out to be stacked, multicrystalline plates and did not allow for single-crystal XRD data

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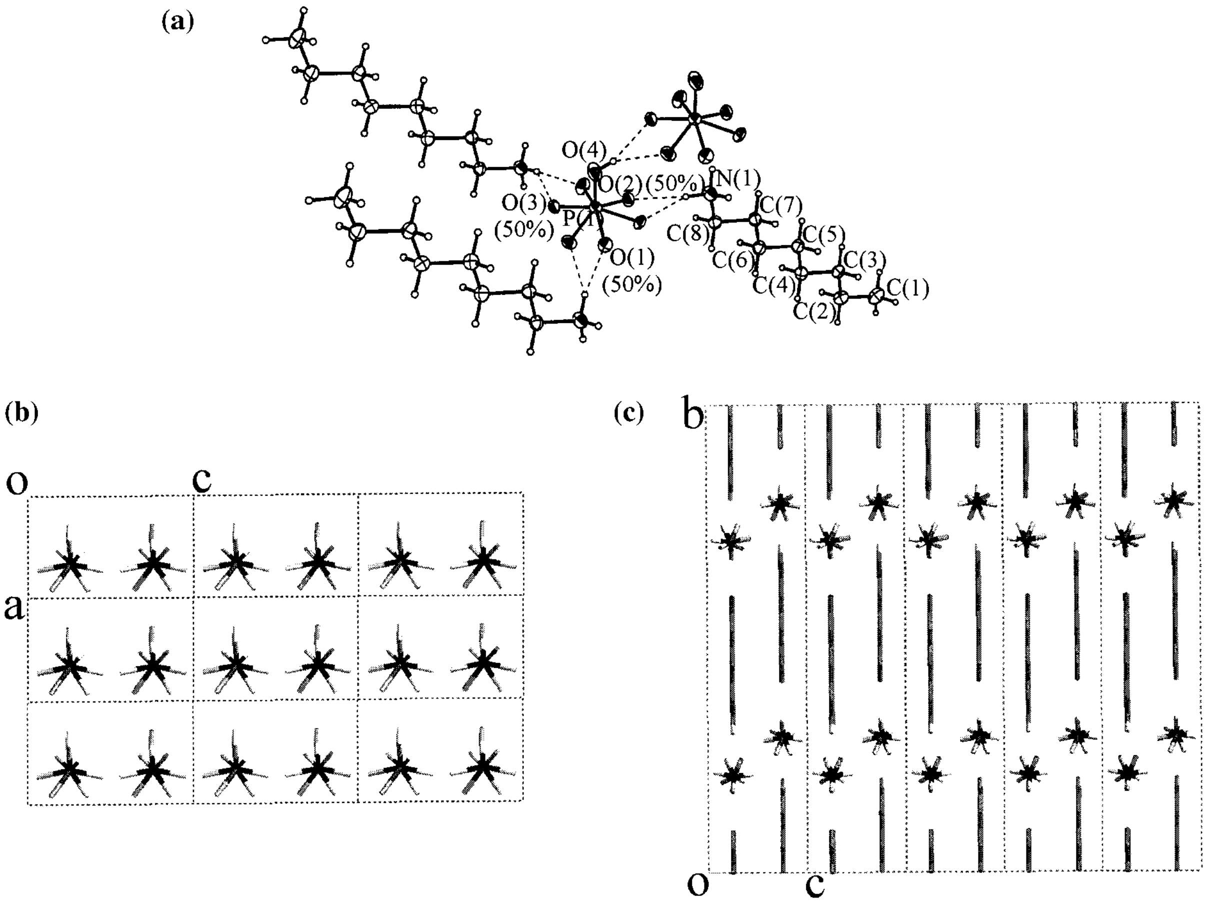

Figure 2. Octylammonium dihydrogen phosphate (ODP). (a) Thermal ellipsoids and naming scheme of the asymmetric unit. (b) *b* projection, showing one phosphate layer and the disorder of three of the four phosphate oxygens. (c) *a* projection, showing the interdigitated structure of ODP.

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

	x	*y*	*z*	*U*(eq)[a]
P(1)	3409(2)	7079(1)	2396(1)	16(1)
O(1)	2745(9)	7133(1)	460(5)	22(1)
O(1*)	775(9)	6967(1)	1319(6)	24(1)
O(2)	4685(9)	7459(1)	3198(5)	21(1)
O(2*)	4786(9)	7459(1)	1603(5)	19(1)
O(3)	812(8)	6946(1)	3593(5)	19(1)
O(3*)	2779(10)	7167(1)	4427(5)	26(1)
O(4)	5731(6)	6751(1)	2514(4)	32(1)
N(1)	9087(6)	7989(1)	2470(4)	27(1)
C(1)	9223(8)	10911(1)	2499(5)	33(1)
C(2)	7418(7)	10542(1)	2497(5)	26(1)
C(3)	9238(7)	10175(1)	2503(4)	21(1)
C(4)	7420(7)	9807(1)	2490(4)	22(1)
C(5)	9256(7)	9439(1)	2490(4)	22(1)
C(6)	7412(7)	9072(1)	2485(4)	23(1)
C(7)	9246(6)	8704(1)	2494(4)	21(1)
C(8)	7314(6)	8347(1)	2461(4)	20(1)
H(4O)	7223(89)	6802(12)	2489(54)	29(12)
H(1A)	7896(6)	7786(1)	2410(4)	29(2)
H(1B)	10155(6)	7977(1)	3494(4)	29(2)
H(1C)	10272(6)	7988(1)	1513(4)	29(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.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for ODP

P(1)−O(1)	1.459(4)	P(1)−O(1*)	1.480(4)
P(1)−O(3*)	1.549(4)	P(1)−O(2)	1.552(4)
P(1)−O(3)	1.551(4)	P(1)−O(4)	1.554(2)
P(1)−O(2*)	1.573(4)	N(1)−C(8)	1.481(4)
C(1)−C(2)	1.519(5)	C(2)−C(3)	1.519(4)
C(3)−C(4)	1.520(4)	C(4)−C(5)	1.523(4)
C(5)−C(6)	1.524(4)	C(6)−C(7)	1.524(4)
C(7)−C(8)	1.517(4)		

O(1*)−P(1)−O(3*)	113.9(2)	O(1)−P(1)−O(2)	109.3(2)
O(1)−P(1)−O(3)	115.9(2)	O(2)−P(1)−O(3)	108.8(2)
O(1)−P(1)−O(4)	106.4(2)	O(1*)−P(1)−O(4)	112.6(2)
O(3*)−P(1)−O(4)	103.0(2)	O(2)−P(1)−O(4)	110.3(2)
O(3)−P(1)−O(4)	105.9(2)	O(1*)−P(1)−O(2*)	110.3(2)
O(3*)−P(1)−O(2*)	105.6(2)	O(4)−P(1)−O(2*)	111.0(2)
H(4O)−O(4)−P(1)	118(3)	C(3)−C(2)−C(1)	114.2(3)
C(2)−C(3)−C(4)	113.9(3)	C(3)−C(4)−C(5)	113.7(3)
C(4)−C(5)−C(6)	113.3(3)	C(5)−C(6)−C(7)	113.4(2)
C(8)−C(7)−C(6)	111.3(2)	N(1)−C(8)−C(7)	111.5(2)

collection. For undecylamine and cyclododecylamine, use of water, methanol or a 50 vol % methanol solution gave only smaller crystals in experiments performed to date.

(1,8)-Diaminooctane ($H_2N(CH_2)_8NH_2$). As mentioned above, phosphate salts have been reported for alkylenediamines with two, three and four carbons in the chain.[1−7] The tendency to form phosphate salts also occurred with this longer eight carbon chain. The phosphate salt is present in the initial TEG−Al_2O_3−H_3PO_4-(1,8)-diaminooctane reaction mixture and can be recrystallized as a pure phase from water. The synthesis product after heating for 5 days in TEG gave a multiphasic product containing plates, some large enough for single crystal X-ray diffraction analysis. The analysis and a subsequently projected PXRD pattern showed that one phase (100% peak at 12.2 Å, Figure 5c) was due to a phosphate salt, 1,8-diammonium octane dihydrogen phosphate (DODP). However, the data set was not of sufficient quality since the crystals were very thin. The other phases present in the PXRD (strong peaks at 16.5 and 15.7 Å) are likely due to one or more unknown aluminophosphate

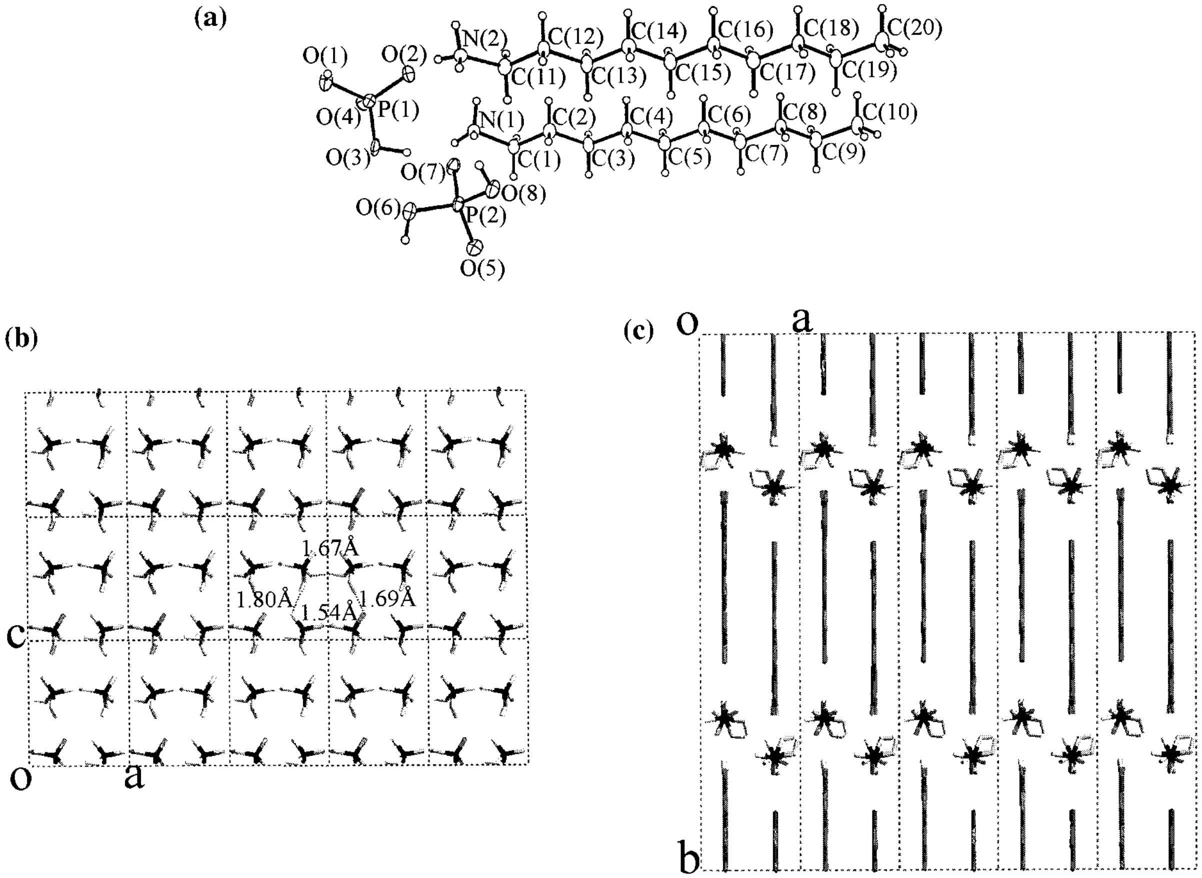

Figure 3. Decylammonium dihydrogen phosphate (DDP). (a) Thermal ellipsoids and naming scheme of the asymmetric unit. (b) *b* projection. The phosphates are not disordered in this case. Note the very strong intralayer hydrogen bonds. (c) *c* projection, showing the interdigitated nature of the decylammonium molecules.

structures, which could be the same as that synthesized by others in an aqueous system using 1,8-diaminooctane.[20]

A Second Decylammonium Phosphate Salt. Interestingly, entirely different results were obtained when decylamine was added before phosphoric acid into the solvent. Such a mixture in TEG became extremely viscous upon the addition of phosphoric acid. The slurry was filtered and the resultant powder displayed the PXRD pattern of Figure 5d. Note the very large *d* spacing of the first diffraction peak. One plausible explanation is that a bilayer is formed rather than an interdigitated arrangement, as this would be the approximate interlayer distance expected for a bilayer with the alkyl tails orthogonal to the layers.[21] It is reasonable to assume that the alkyl tails are orthogonal to the layers, since this is their conformation in ODP and DDP. It would also be expected that this phase is the monohydrogen phosphate salt, since the conditions were more basic due to the fact that the phosphoric acid was added last and in lower amounts to minimize viscosity.

Degree of Alkylamine. It is interesting to note that of all the alkylammonium phosphate salt crystal structures reported to date and described here, the amines are almost exclusively primary. Primary amines possess more hydrogens and can therefore donate a larger number of stronger hydrogen bonds, to create a more stable hydrogen bonded network. Secondary amines also form phosphate salts, but to date the only examples are piperidinium phosphate[10] and piperazinium phosphate.[11] Recently, we discovered the third such example, dimethylammonium dihydrogen phosphate.[22] The PXRD pattern of this phase is shown in Figure 5e.

Phosphate salts of tertiary amines are also possible, but should be less stable since they contain only one hydrogen. This would agree with the fact that only primary and secondary amines display extensive hydrogen bonding in solution.[23] Indeed, large crystals of triethylammonium phosphate were grown in a highly concentrated solution, but melted when exposed to air.[16] For the same reasons, phosphate salts containing quaternary ammoniums should be too unstable to form, and in fact none were ever observed (nor were those containing tertiary amines) during aluminophosphate synthetic work under typical conditions.[16]

Interdigitated versus Bilayer Packing Arrangement. The crystal structures described above possess either an interdigitated or a bilayer arrangement of alkylamines. Interdigitated versus bilayer arrangements have been discussed for other layered phases such as smectic mesophases,[24] hydrogen bonded alkylammonium sulfonates[25] or phospholipid membranes and vesicles.[26−29] An interdigitated arrangement represents a lower

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Table 6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for DDP

	x	*y*	*z*	*U*(eq)[a]
P(1)	2621(2)	2142(1)	783(1)	17(1)
O(1)	2691(5)	1849(1)	−358(4)	24(1)
O(2)	3365(4)	2465(1)	117(3)	22(1)
O(3)	552(5)	2202(1)	1117(4)	25(1)
O(4)	3649(4)	2031(1)	2118(3)	22(1)
N(1)	2724(6)	2924(1)	2925(5)	20(1)
C(1)	2542(7)	3238(1)	3823(5)	21(1)
C(2)	2562(7)	3549(1)	2870(5)	22(1)
C(3)	2521(7)	3870(1)	3787(5)	21(1)
C(4)	2515(7)	4192(1)	2874(5)	21(1)
C(5)	2508(7)	4513(1)	3786(5)	22(1)
C(6)	2511(7)	4834(1)	2874(5)	20(1)
C(7)	2506(7)	5155(1)	3792(5)	22(1)
C(8)	2522(7)	5476(1)	2880(5)	20(1)
C(9)	2513(7)	5797(1)	3789(5)	25(1)
C(10)	2521(7)	6118(1)	2886(6)	32(1)
P(2)	−2483(2)	2873(1)	811(1)	16(1)
O(5)	−3609(4)	2977(1)	2103(3)	21(1)
O(6)	−3230(5)	2535(1)	143(3)	23(1)
O(7)	−478(4)	2816(1)	1119(3)	22(1)
O(8)	−2710(5)	3154(1)	−390(4)	23(1)
N(2)	2315(6)	2925(1)	−2023(5)	20(1)
C(11)	2492(7)	3240(1)	−1152(5)	20(1)
C(12)	2450(7)	3548(1)	−2119(5)	21(1)
C(13)	2498(7)	3871(1)	−1215(5)	22(1)
C(14)	2483(7)	4190(1)	−2131(5)	21(1)
C(15)	2507(7)	4513(1)	−1219(5)	22(1)
C(16)	2495(7)	4834(1)	−2130(5)	20(1)
C(17)	2491(7)	5155(1)	−1216(5)	22(1)
C(18)	2476(7)	5476(1)	−2120(5)	21(1)
C(19)	2488(7)	5796(1)	−1208(5)	25(1)
C(20)	2471(8)	6117(1)	−2120(6)	32(1)
H(1A)	2629(64)	2753(13)	3595(55)	22(5)
H(1B)	3850(71)	2952(12)	2385(53)	22(5)
H(1C)	1887(69)	2943(12)	2217(56)	22(5)
H(2C)	2584(66)	2743(13)	−1540(54)	22(5)
H(2D)	3140(67)	2899(12)	−2776(57)	22(5)
H(2E)	1290(73)	2931(12)	−2507(55)	22(5)
H(1O)	2334(67)	1899(12)	−1149(58)	21(14)
H(3O)	244(96)	2453(20)	1091(76)	80(23)
H(6O)	−4387(103)	2511(20)	275(81)	85(28)
H(8O)	−2224(80)	3069(15)	−1232(67)	46(17)

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

density of packing of alkyl chains. For example, the above smectic mesophase contains an interdigitated structure due to the space introduced by large metal ions.[24]

Table 7. Selected Bond Lengths (Å) and Angles (deg) for DDP

P(1)−O(4)	1.497(3)	P(1)−O(2)	1.526(3)
P(1)−O(1)	1.563(3)	P(1)−O(3)	1.573(4)
O(1)−H(1O)	0.79(5)	N(1)−C(1)	1.500(6)
C(1)−C(2)	1.513(6)	C(2)−C(3)	1.524(6)
C(3)−C(4)	1.530(6)	C(4)−C(5)	1.524(6)
C(5)−C(6)	1.523(6)	C(6)−C(7)	1.528(6)
C(7)−C(8)	1.521(6)	C(8)−C(9)	1.524(6)
C(9)−C(10)	1.519(7)	P(2)−O(5)	1.504(3)
P(2)−O(7)	1.517(3)	P(2)−O(8)	1.572(3)
P(2)−O(6)	1.575(3)	O(6)−H(6O)	0.87(8)
C(11)−C(12)	1.510(6)	C(12)−C(13)	1.527(6)
C(13)−C(14)	1.518(6)	C(14)−C(15)	1.531(6)
C(15)−C(16)	1.523(6)	C(16)−C(17)	1.524(6)
C(17)−C(18)	1.518(6)	C(18)−C(19)	1.523(6)
C(19)−C(20)	1.523(7)		

O(4)−P(1)−O(2)	113.1(2)	O(4)−P(1)−O(1)	107.7(2)
O(2)−P(1)−O(1)	110.4(2)	O(4)−P(1)−O(3)	111.8(2)
O(2)−P(1)−O(3)	107.5(2)	O(1)−P(1)−O(3)	106.2(2)
N(1)−C(1)−C(2)	111.4(4)	C(1)−C(2)−C(3)	111.5(4)
C(2)−C(3)−C(4)	113.6(4)	C(5)−C(4)−C(3)	113.8(4)
C(6)−C(5)−C(4)	113.7(4)	C(5)−C(6)−C(7)	113.6(4)
C(8)−C(7)−C(6)	113.6(4)	C(7)−C(8)−C(9)	113.8(4)
C(10)−C(9)−C(8)	114.1(4)	O(5)−P(2)−O(7)	115.9(2)
O(5)−P(2)−O(8)	107.2(2)	O(7)−P(2)−O(8)	109.5(2)
O(5)−P(2)−O(6)	110.2(2)	O(7)−P(2)−O(6)	106.2(2)
O(8)−P(2)−O(6)	107.5(2)	N(2)−C(11)−C(12)	111.6(4)
C(11)−C(12)−C(13)	111.5(4)	C(14)−C(13)−C(12)	113.9(4)
C(13)−C(14)−C(15)	113.6(4)	C(16)−C(15)−C(14)	114.0(4)
C(15)−C(16)−C(17)	113.7(4)	C(18)−C(17)−C(16)	113.9(4)
C(17)−C(18)−C(19)	113.9(4)	C(18)−C(19)−C(20)	113.7(4)

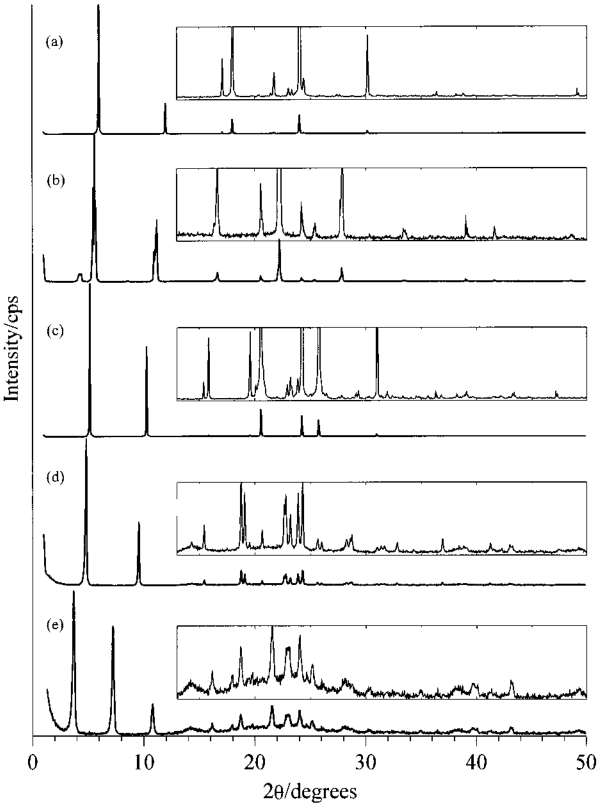

Figure 4. Some examples of PXRD patterns of phosphate salts of *n*-alkylamines (inset: expanded higher-angle region): (a) hexylammonium phosphate; (b) heptylammonium phosphate; (c) octylammonium dihydrogen phosphate (ODP); (d) nonylammonium phosphate; (e) tetradecylammonium phosphate.

The choice for the phosphate salts will depend on, first, the degree of protonation of the phosphate that is present in the system (e.g. $H_2PO_4^-$ or HPO_4^{2-}). This will depend on the pH of the reaction mixture, which is determined by the reagents that are used and their molar ratios, as well as the basicity of the alkylamine. The arrangement of alkyl chains in the final structure will then depend on several cooperative factors, such as size and shape of both the alkyl chain and ammonium headgroup of the alkylamine, and the distance and degree of hydrogen bonding in the phosphate layer (i.e. monomers, dimers, chains or a continuous sheet). For example, a more densely packed layer of divalent monohydrogen phosphates will require a larger amount of alkylamines per unit area, and therefore a bilayer arrangement would be expected (depending on the spacing of the phosphates). This would account for the larger *d* spacing, compared to that of the interdigitated DDP, in the PXRD for what is proposed to be decylammonium monohydrogen phosphate, Figure 5d.

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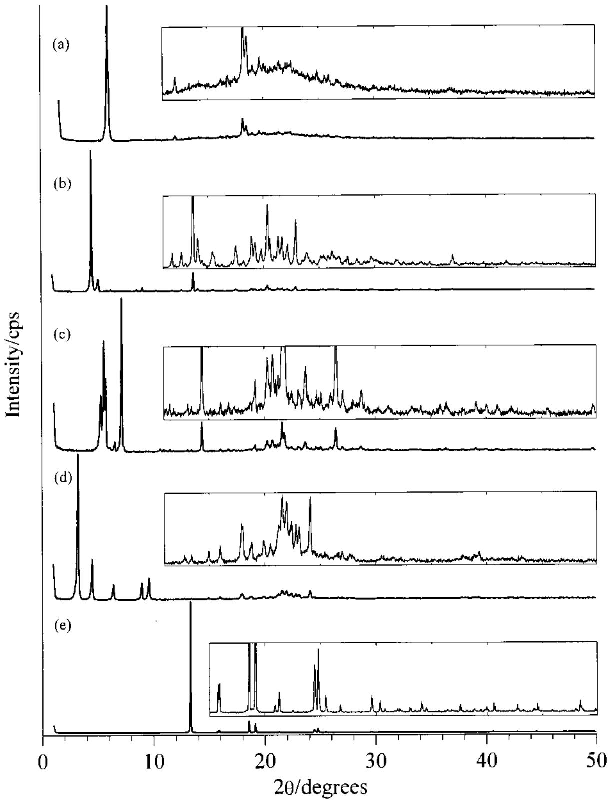

Figure 5. Further examples of PXRD patterns of alkylammonium phosphates (inset, expanded higher-angle region): (a) cycloheptylammonium phosphate; (b) cyclododecylammonium phosphate; (c) 1,8-diammoniumoctane phosphate; (d) decylammonium monohydrogen phosphate; (e) dimethylammonium dihydrogen phosphate.

Conclusions

A series of novel alkylammonium phosphates have been discovered during the investigation of initial solvothermal aluminophosphate reaction mixtures prior to heating. The materials may be recrystallized, allowing the determination of their structures. We suggest that characterization of starting aluminophosphate reaction mixtures should accompany the report of new aluminophosphate crystal structures to determine if an alkylammonium phosphate is present initially and/or in the final product. Furthermore, as the interlayer distance of alkylammonium phosphates is in the mesoscopic regime (>10 Å) and they are highly crystalline, care must be taken to avoid mislabeling such phases as layered or open framework aluminophosphates. While use of the term reaction “gel” certainly applies to silica systems, this is not entirely correct for many aluminophosphate systems. The present work furthers our understanding of the formation of extended aluminophosphates, for which we have recently published a new chain to layer to framework model.[30] It is possible these discoveries may also be relevant to the many other solvothermal metal phosphate systems which use organic amines, such as those of gallium phosphate or vanadium phosphate. Certainly, other novel alkylammonium phosphates and alkylammonium arsenates await discovery.

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Supporting Information Available: Listings of complete atomic coordinages, bond lengths and angles, anisotropic thermal parameters, and hydrogen atomic coordinates for all compounds are available on the Internet only. Access information is given on any current masthead page.

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