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Synthesis and characterization of a new layered aluminophosphate templated with 1,3-diaminopropane: $[H_3N(CH_2)_3NH_3]_{0.5}[AlPO_4(OH)(OH_2)]\cdot H_2O$ †

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A new layered aluminophosphate has been synthesized hydrothermally in the presence of 1,3-diaminopropane and its structure solved from X-ray powder diffraction data. The compound with the composition $[C_3H_{12}N_2]_{0.5}[AlPO_4(OH)(H_2O)]\cdot H_2O$ crystallizes in the orthorhombic space group *Pnma* (No. 62) with $a = 6.91848(11)$, $b = 22.2989(4)$ and $c = 9.6074(2)$ Å. The layers contain only 6-co-ordinated aluminium forming [–Al–(OH)–Al–] chains, and these are connected to one another *via* phosphorus tetrahedra. The structure of the layers is closely related to that of the layered aluminium methylphosphonate AlMepO-ζ. This compound represents the third example of layered aluminophosphates with an atomic ratio P : Al = 1 : 1. Its thermal decomposition has been monitored by X-ray diffraction and solid state NMR.

Introduction

Interest in aluminophosphate synthesis over the past few years has been stimulated by a continuous increase in the number of newly discovered materials. These materials exist in a variety of structural architectures, from one-dimensional chains to three-dimensional open frameworks. Three-dimensional materials are probably the most interesting ones for applications as molecular sieves in catalysis,[1–3] provided that the templating molecules can be removed without damaging the inorganic framework. The family of two-dimensional layered compounds is also interesting because of their diversity in terms of structure and composition. This diversity is reflected in the atomic P : Al ratio of the anionic inorganic layers, which can vary from 1 to 2 : 1.[4–25] Most of these compounds are synthesized under hydrothermal or solvothermal conditions in the presence of mono- or di-amines which are protonated during crystallization and act as interlayer charge-compensating molecules in the crystalline solids. The structure-directing role of the organic molecules is still poorly understood. As for aluminosilicates, different structures can be templated by the same molecule depending on the gel composition and crystallization conditions. As an example, we have recently reported the formation of a three-dimensional open framework aluminophosphate in the presence of 1,4-diaminobutane at 200 °C whereas the same gel composition gave a lamellar compound when the crystallization temperature was below 170 °C.[26]

In the present paper we report on the synthesis and characterization of APDAP150, a new layered aluminophosphate prepared using 1,3-diaminopropane as template. This molecule was first reported to direct the crystallization of a three-dimensional open framework material.[27] Very recently, 1,3-diaminopropane was used by Kongshaug *et al.* to prepare a novel layered aluminophosphate under hydrothermal conditions.[21] This compound was one of the first examples of a layered aluminophosphate with P : Al = 1 : 1.

The novel structure reported here was obtained using different synthesis conditions, in particular a lower diamine concentration in the precursor gel. It is also characterized by a molar ratio P : Al = 1 : 1 and, therefore, represents the third example of such materials. The structure was determined and refined using X-ray powder diffraction data. The solid and its transformation as a function of temperature have been characterized by X-ray diffraction and solid state NMR.

Experimental

Synthesis

APDAP150 was obtained by hydrothermal crystallization of a gel containing pseudoboehmite (CATAPAL B, Vista, 74% Al_2O_3), phosphoric acid (85 wt%), 1,3-diaminopropane (DAP) and water. Typically, pseudoboehmite was dispersed in H_3PO_4 and water and the resulting mixture stirred until homogeneous. Then, the diamine was added dropwise and stirring maintained for 2 hours. The resulting gel, with the composition $Al_2O_3\cdot P_2O_5\cdot DAP\cdot 35H_2O$, was transferred to a Teflon lined stainless steel autoclave and heated at 150 °C for 2 days. The solid phase was recovered by centrifugation, washed with distilled water and air dried at 25 °C.

Characterization

The powder diffraction data of the sample were collected using strictly monochromatic Cu-Kα_1 radiation on a laboratory STOE STADP diffractometer equipped with a linear position-sensitive detector. The sample was loaded in a 0.3 mm glass capillary, which was rotated during the data collection. Further details of data collection and crystallographic data are given in Table 1.

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SEM pictures were obtained on a Hitachi S800 microscope.

Thermal analysis data were recorded on a Setaram TGDT A92 apparatus. The sample was heated in air from room temperature to 750 °C at a rate of 5 °C min^{-1}.

Solid state MAS NMR spectra were recorded on a Bruker DSX 400 spectrometer equipped with a double bearing 4 mm

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† Electronic supplementary information (ESI) available: fractional coordinates and isotropic displacement factors. See http://www.rsc.org/suppdata/dt/b0/b002187n/

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Table 1 Crystallographic data for APDAP150

	APDAP150
Chemical formula	$[C_3H_{12}N_2]_{0.5}[AlPO_4$-$(OH)(OH_2)]\cdot H_2O$
M	213.06
Space group	*Pnma* (no. 62)
Z	8
a/Å	6.91848(11)
b/Å	22.2989(4)
c/Å	9.6074(2)
λ/Å	1.54059
2θ range/°	6–97.6
Step size/°(2θ)	0.02
Peak range in FWHM	17
Number of observations	4573
Number of contributing reflections	750
Number of structural parameters	50
Number of profile parameters	7
Number of geometric restraints	51
Al–O(excluding O6) prescribed/Å	1.83(2)
Al–O6 prescribed/Å	2.00(4)
P–O prescribed/Å	1.52(1)
C–C prescribed/Å	1.54(1)
C–N prescribed/Å	1.48(1)
C–H prescribed/Å	0.97(1)
O–Al–O prescribed/°	90(2) or 180(4)
O–P–O prescribed/°	109.5(10)
Al–O–P prescribed/°	145(8)
C(H)–C–C(N,H) prescribed/°	109.5(10)
R(*F*)	0.065
R_{wp}	0.1024
R_{exp}	0.087

probe head. Samples were spun at the magic angle at a spinning speed of 14 kHz. The pulse lengths were 2 ($\pi/4$) and 0.7 µs ($\pi/6$) and the recycle delays were 30 and 1 s for ^{31}P and ^{27}Al nuclei, respectively. ^{27}Al and ^{31}P chemical shifts were referenced to $Al(H_2O)_6^{3+}$ and H_3PO_4 (85 wt%), respectively. ^1H–^{13}C CP MAS experiments were performed using a 7 mm probe head and a conventional CP MAS sequence. The contact time was 1 ms and the recycle delay 5 s.

Chemical analysis of the compound was obtained by atomic absorption after the aluminophosphate had been dissolved in HF–HCl solution.

Results and discussion

Synthesis

APDAP150 can be obtained within a relatively broad temperature range, typically from 120 to 175 °C. As can be seen in Fig. 1 the crystal morphology changes with the crystallization temperature. At 150 °C short prismatic crystals with dimensions of *ca.* 1.5 µm × 0.3 µm stick together to form round-shaped aggregates with a diameter of *ca.* 5 µm. At lower temperature, crystals are separated and adopt a needle-like morphology. Chemical analysis of the compound gave P : Al = 1 : 1 and carbon and nitrogen contents of 8.5 and 6.6 wt%, respectively.

Structure

Structure solution. The powder diffraction pattern of APDAP150 was indexed with an orthorhombic unit cell using the indexing program ITO[28] (Table 1). The systematic absences indicate that the space group was probably *Pnma* or $Pn2_1a$ (standard setting: $Pna2_1$). The integrated intensities were extracted from the pattern, assuming the centrosymmetric space group *Pnma*, using the XRS-82 package[29] after a manual background subtraction. These intensities were input into the structure solution program EXPO.[30] One aluminium, one phosphorus and four oxygen positions forming a layered structure were obtained from the set with the best figure of merit (CFOM = 0.946). A difference electron density map using the low angle data revealed the position of the missing framework oxygen, the template molecule and the non-framework oxygen. The hydrogen atoms could not be located so their positions for the methylene groups were generated geometrically and those for the amino and hydroxo groups simulated by increasing both the population parameters and the displacement parameters of the N and O atoms according to the number of protons. The population parameter (PP) for the N atom was set to 1.286 to simulate the NH_3^+ group and the PP of O atoms with hydrogen attached was set to 1.125 and 1.25 to simulate OH (or O^-) groups and water, respectively. Soft geometrical restraints for interatomic distances and angles (see Table 1) were applied to the framework and the template molecule throughout the

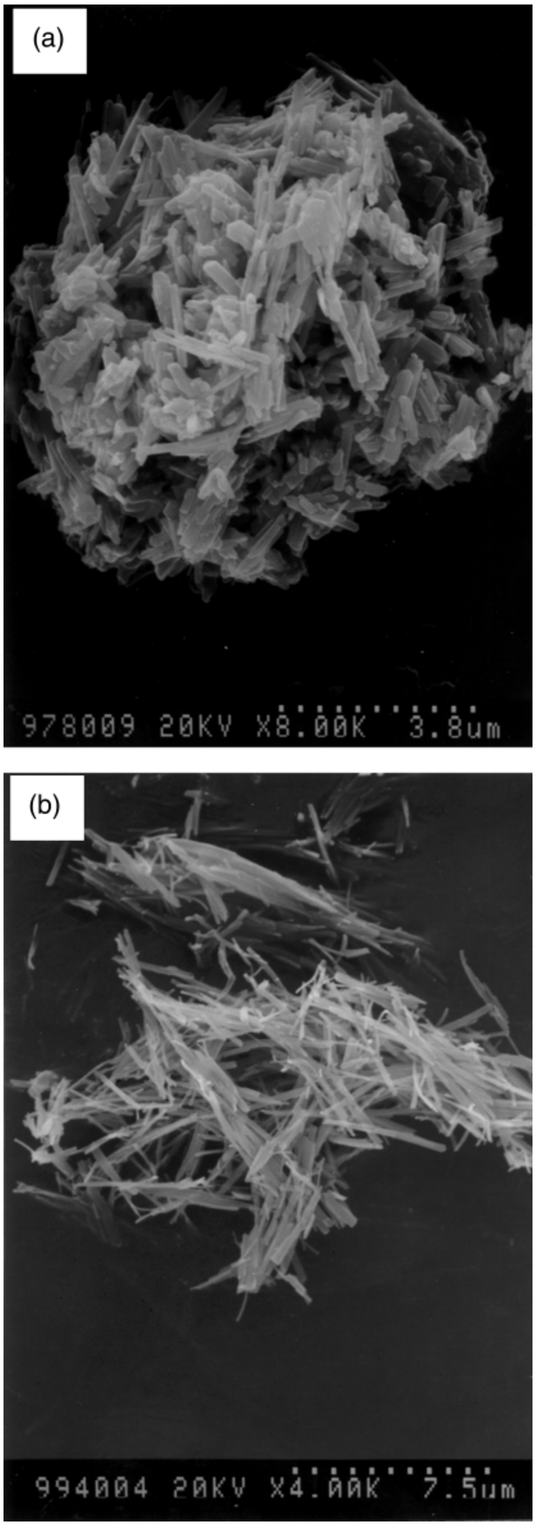

Fig. 1 SEM pictures of APDAP150 synthesized at 150 (a) and 120 °C (b).

Table 2 Bond lengths (Å) and angles (°) for APDAP150

P–O1	1.574(7)	O1–P–O2	110.8(5)	O4–Al–O5	88.5(4)
P–O2	1.561(7)	O1–P–O3	109.3(5)	O4–Al–O5#	90.2(4)
P–O3	1.567(8)	O1–P–O4	109.6(5)	O4–Al–O6	86.6(4)
P–O4	1.546(8)	O2–P–O3	108.3(4)	O5–Al–O5#	176.6(4)
Al–O2	1.898(8)	O2–P–O4	108.9(5)	O5–Al–O6	88.8(4)
Al–O3	1.910(8)	O3–P–O4	110.0(4)	O5#–Al–O6	88.4(4)
Al–O4	1.869(9)	O2–Al–O3	95.2(4)	P–O2–Al	139.3(5)
Al–O5	1.879(10)	O2–Al–O4	170.8(4)	P–O3–Al	127.4(5)
Al–O5#	1.899(10)	O2–Al–O5	93.1(4)	P–O4–Al	141.0(5)
Al–O6	2.085(9)	O2–Al–O5#	87.7(4)	Al–O5–Al	132.7(4)
N1–C2	1.484(11)	O2–Al–O6	84.4(3)	N1–C2–C1	108.6(8)
C1–C2	1.534(11)	O3–Al–O4	93.8(4)	C2–C1–C2	107.1(9)
O1 ··· O7	2.690(11)	O3–Al–O5	92.1(4)		
O6 ··· O7	2.837(11)	O3–Al–O5#	91.1(4)		
O7 ··· O7	2.662(11)	O3–Al–O6	179.4(4)		

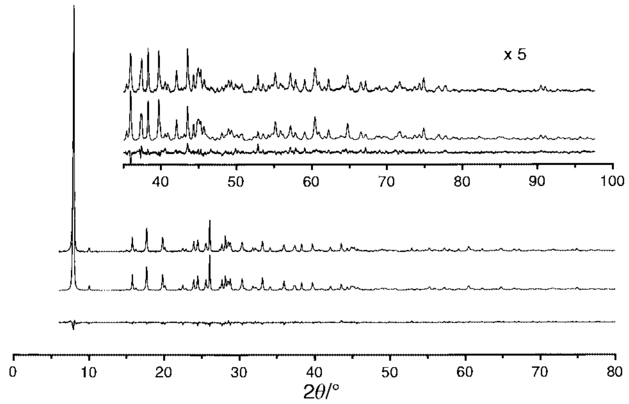

Fig. 2 Observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of APDAP150. The intensity scale at higher angles is enlarged by a factor of 5.

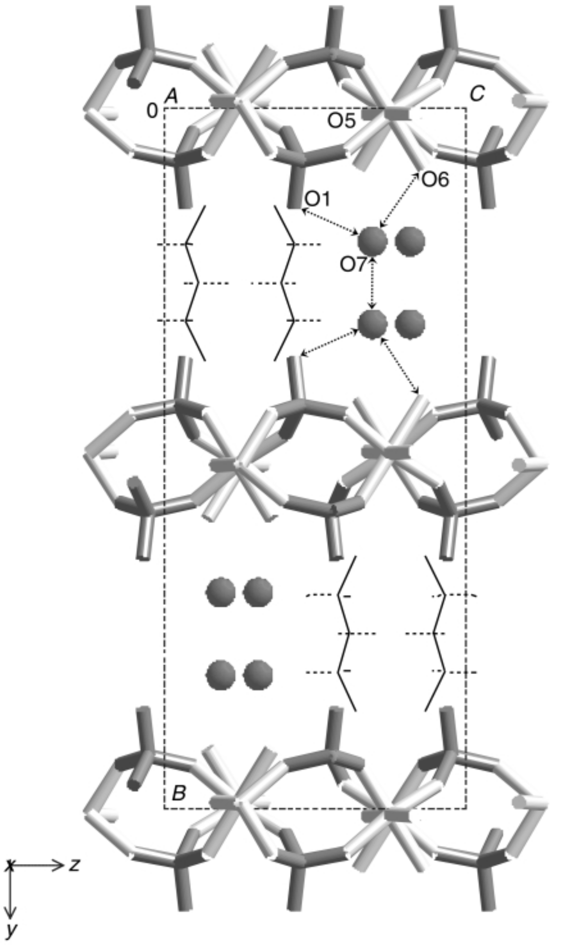

Fig. 3 Crystal structure of APDAP150 viewed along the *a* axis (dark gray: PO_4 tetrahedron). Template (thin lines) and non-framework water molecules (isolated balls) are located between the layers.

refinement. To reduce the number of parameters and stabilize the refinement, the displacement parameters for similar atoms (Al/P, O and C, respectively) were constrained to be the same. To reflect their different environment, the U_{iso} values for the OH (or O^-) groups and the water position associated with the framework were constrained to be two and three times the value refined for the other framework oxygen atoms, respectively. For the non-framework water oxygen (O7 in Fig. 3) the displacement parameter was fixed at 0.08 $Å^2$ to prevent divergence. All positional parameters were refined to convergence with progressively less weight on the restraints. The R_{wp} value finally converged to 0.1024 with a factor for the soft restraints of 3 and there was no further improvement when the symmetry was reduced to the non-centrosymmetric space group. The final Rietveld plot of APDAP150 and selected interatomic distances and angles are reported in Fig. 2 and Table 2, respectively.

Description of the structure. The crystal structure of APDAP150 is shown in Fig. 3. It is composed of two-dimensional sheets perpendicular to the *b* axis. Each sheet consists of one-dimensional zigzag chains of AlO_6 octahedra connected to one another *via* PO_4 tetrahedra (Fig. 4). Three of the oxygen atoms of the octahedrally co-ordinated Al are bonded to three different phosphate groups; two (O5) form the Al–O–Al bridges of the one-dimensional chain and the sixth (O6) is a water molecule. Only three oxygens of a tetrahedrally co-ordinated P are connected to different aluminium atoms, the fourth oxygen (O1) is not bonded and protrudes into the interlayer space. The template and non-framework water (O7) molecules are located between the sheets as shown in Fig. 3. According to ^{13}C MAS NMR, the template molecule is doubly protonated as a diammonium ion. Assuming that the framework contains no hydrogen atoms except the co-ordinated water, the framework would have a negative charge of 8 per unit cell. This could be compensated by the presence of a proton at a general crystallographic position. Elemental analysis data together with the structural analysis suggest the formula $[H_3N(CH_2)_3NH_3]_{0.5}[AlPO_4(OH)(OH_2)]\cdot H_2O$.

The two-dimensional sheet structure of APDAP150 is very similar to that of the layered aluminium methylphosphonate $[Al(O_3PCH_3)(OH)(OH_2)]$.[31,32] These structures are topologically the same, but the terminal oxygen (O1) in the former is replaced by a methyl group in the methylphosphonate structure and the configuration of the co-ordinated water is different. In the single crystal structure determination of the phosphonate structure[31] a proton was located at the bridging oxygen atom between the AlO_6 octahedra. For APDAP150 there are two possibilities for the proton position, namely near O1 or O5. It is more reasonable to attach the proton to O5 because aluminium hydroxide is generally less acidic than hydrogenphosphate and

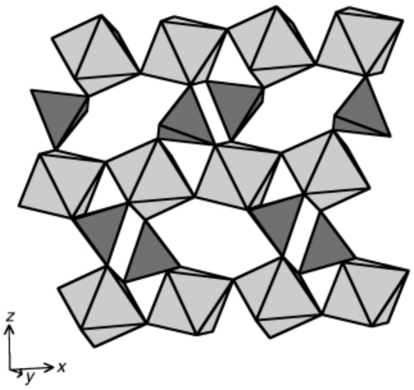

Fig. 4 Polyhedral drawing of the aluminophosphate layer of APDAP150 (dark gray, PO_4 tetrahedron; pale gray, AlO_6 octahedron).

because of the structural similarity to the phosphonate. There is a hydrogen bond network (O · · · O distance: 2.7–2.8 Å) between the non-framework oxygens (O7), the terminal oxygens (O1) and the co-ordinated water oxygens (O6) (Table 2). The AlO_6 octahedron is distorted since the Al–O6 distance is relatively long (2.09 Å) while the other Al–O distances are within the range of 1.86–1.91 Å. The PO_4 tetrahedron has no distortion (P–O: 1.55–1.57 Å). These distances are in good agreement with those of the phosphonate compound.

This compound represents the first example of a layered aluminophosphate with aluminium hydroxo chains [Al–(OH)–Al] within the sheets.

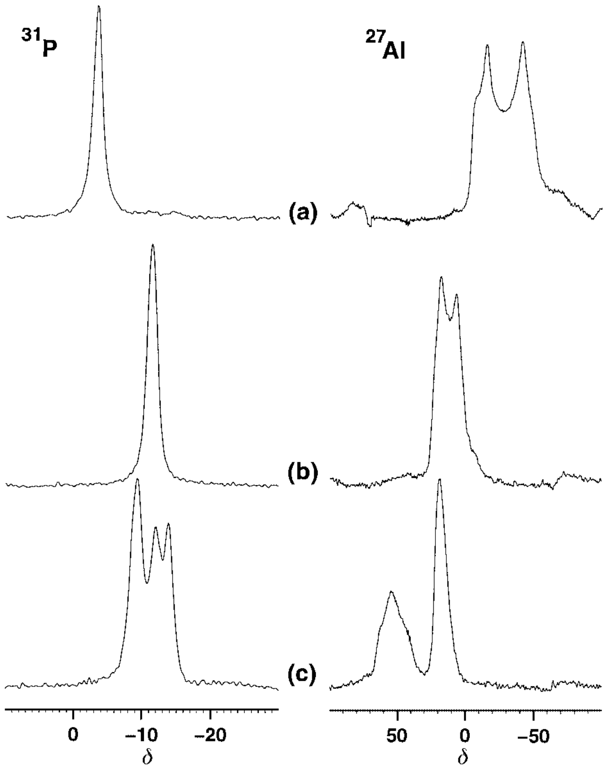

Fig. 5 ^{31}P and ^{27}Al MAS NMR spectra of APDAP150. As-synthesized (a), heated at 150 °C (b) and heated at 200 °C (c).

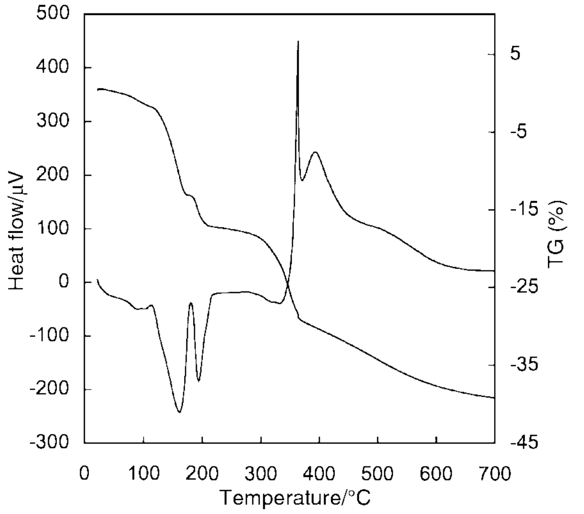

Fig. 6 TG and TDA curves for the decomposition of APDAP150.

Characterization

The ^{31}P MAS NMR spectrum of APDAP150 shows a single signal at δ −1.5 consistent with the unique crystallographic phosphorus site in the structure (Fig. 5a). The observed chemical shift is characteristic of O_3P–OH groups. The full width at half maximum (FWHM) of the signal is *ca.* 150 Hz, which is a direct consequence of the regularity of phosphorus tetrahedra (see Table 2). In contrast, the ^{27}Al NMR signal is quite broad and lies between δ 10 and −80 (Fig. 5a). The shape of the signal is typical of quadrupolar nuclei with a strong quadrupolar coupling constant (C_Q). Simulation of the line shape gives the approximate value C_Q = 15 MHz. The isotropic chemical shift is characteristic of octahedrally co-ordinated aluminium species. The strong C_Q value can be attributed to the distortion of AlO_6 octahedra, resulting from the presence of the long Al–O6 distance (Table 2). Both ^{31}P and ^{27}Al MAS NMR spectra are similar to those of the layered aluminium methylphosphonate AlMepO-ζ.[31] In the latter, the presence of O_3P–CH_3 groups shifts the ^{31}P NMR signal to δ 13.6. The displacement of NMR signals towards low fields upon substitution of oxygen with carbon is well known in organosiloxane compounds. Whilst the ^{29}Si NMR spectrum of [SiO_4] units is in the range of δ −90 to −110, that of O_3Si-C moieties appears in the region around δ −60.[33] For APDAP150 the ^{27}Al MAS NMR spectrum is approximately twice as broad as that of AlMepO-ζ. Moreover, the line shape is completely different, which suggests that the distortion of AlO_6 octahedra is different for the two materials.

The TG-DTA curve shows two endothermic peaks at *ca.* 170 and 200 °C and an intense exothermic peak at 400 °C (Fig. 6). The two endothermic peaks can be associated to the removal of water whereas the last peak around 400 °C corresponds to the decomposition of the organic molecules. X-Ray diffraction data show that the solid becomes amorphous at 400 °C. The thermal stability of APDAP150 was monitored by both X-ray diffraction and solid state NMR spectroscopy. The sample was first heated to 150 °C in air for 2 hours, as this corresponds to the temperature of the first weight loss in the TG curve. The XRD pattern of the corresponding solid remains practically unchanged except that reflections become broader and less intense, reflecting a significant loss in crystallinity (Fig. 7b). The ^{31}P MAS NMR spectrum of APDAP150 heated at 150 °C still shows a unique signal but with a chemical shift δ −11.3 (Fig. 5b). The shift is characteristic of the transformation of P–OH (or P–O^-) to P=O groups, indicating that non-framework water molecules have been expelled from the interlayer space. However, XRD does not show any evidence of a contraction along the *b* axis, so apparently the diammonium molecules continue to separate the layers by the same distance as in the as-synthesized compound. The ^{27}Al MAS NMR spectrum of APDAP150 is drastically modified upon heating to 150 °C (Fig. 5b). The signal is now observed in the region characteristic of 5-co-ordinated aluminium species. Thus, water molecules (O6) bonded to framework aluminium species have also been removed from the solid and trigonal bipyramidal [AlO_5] units have been formed. In the absence of these water molecules and assuming that the atomic positions have not been modified

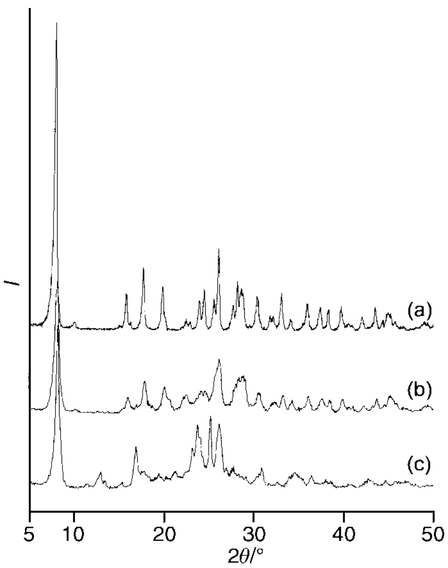

Fig. 7 X-Ray powder diffraction (XRD) patterns of APDAP150. As-synthesized (a), heated at 150 °C (b) and heated at 200 °C (c).

significantly by the thermal treatment, all Al–O bond lengths become comparable. The trigonal bipyramids are thus less distorted than the octahedra, and this explains why the ^{27}Al NMR linewidth and the quadrupolar coupling constant have been reduced by a factor of 2 between 25 and 150 °C.

From these data we can conclude that the first weight loss in the TG curve corresponds to the removal of all water molecules (framework and non-framework) from the solid. From the chemical formula of APDAP150, the theoretical weight loss value associated with dehydration is 14.3%, in good agreement with the observed value (approx. 14%).

APDAP150 was further heated to 200 °C, *i.e.* above the temperature corresponding to the second weight loss. At this temperature, a new XRD pattern is observed (Fig. 7c). The position of the basal reflection (020) did not change significantly with respect to the sample heated to 150 °C but its intensity increased. Some of the lines appear to be sharper, suggesting that a partial reordering of the structure has taken place. Unfortunately, the quality of the pattern was not good enough for indexing. The presence of both broad and narrow reflections indicates that the structure is not perfectly ordered in all directions. Nevertheless, the long-range disorder does not influence the NMR spectra, which remain well resolved. The ^{31}P MAS NMR spectrum consists of three peaks at *ca.* δ −9.3, −12.0 and −13.8 and indicates the presence of several crystallographically non-equivalent phosphorus sites in the structure (Fig. 5c). The ^{27}Al NMR spectrum shows a relatively symmetric signal around δ 20 along with a broad peak at δ 50, and these are assigned to 5- and 4-co-ordinated aluminium species, respectively; 4-co-ordinated species result from further dehydration of the compound, which probably proceeds by elimination of some of the bridging hydroxo groups. The calculated weight loss associated with dehydration from hydroxo groups (3.5%) is in excellent agreement with the observed value (3.6%). The two dehydration steps are non-reversible processes because the initial structure could not be recovered after contacting the heated solid with water vapor for several days.

Both dehydration temperatures are approximately 200 °C lower than those observed in the thermal decomposition of the aluminium methylphosphonate AlMepO-ζ.[31] Such a difference could be explained by the framework charge of APDAP150. The negative charge of the terminal oxygen (O1), which is more or less delocalized throughout the framework aluminium, makes the Al–O bonds less stable compared with the neutral framework of AlMepO-ζ. This is supported by the fact that the average Al–O distance in APDAP150 (1.9234 Å, Table 2) is slightly longer than in AlMepO-ζ (1.905 Å).[31] Moreover, the water position (O6) co-ordinated to aluminium participates in a hydrogen-bonding network with non-framework water molecules. The removal of non-framework water upon heating probably destabilizes the framework water molecule, which is then expelled simultaneously. Thus, the desorption of non-framework and framework water molecules occurs at similar temperatures, and this explains why only a single weight loss is observed in the TG-DTA curve.

Conclusion

The third example of layered aluminophosphate with an atomic ratio P : Al = 1 : 1 has been synthesized hydrothermally in the presence of 1,3-diaminopropane. The inorganic sheets of the compound contain [–Al–(OH)–Al–] chains crosslinked to one another *via* phosphorus tetrahedra. The structure is closely related to that observed in the layered aluminium methylphosphonate AlMepO-ζ. However, methyl groups are replaced by terminal oxygens and the configuration of the co-ordinated water molecule is different. The interlayer space is filled with doubly protonated organic molecules and water molecules, and these form a hydrogen-bonding network with the co-ordinated water molecules. Upon heating to 150 °C, both co-ordinated and non-co-ordinated water molecules are expelled simultaneously and the resulting sheets contain only 5-co-ordinated aluminium species. At higher temperature, dehydration of hydroxo bridges is observed and this leads to the formation of some 4-co-ordinated aluminium. The compound transforms into an amorphous material upon removal of the organic molecules at 400 °C.

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