Novel Pillared Aluminum Ethylene Diphosphonate Displaying Reversible Dehydration−Rehydration Behavior

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The novel aluminum ethylene diphosphonate $Al_2(OH)_2(H_2O)_2(O_3PCH_2CH_2PO_3)$ has been synthesized hydrothermally. It crystallizes in the triclinic space group ($P\bar{1}$; $a = 8.5977(10)$, $b = 7.0499(3)$, $c = 9.5290(4)$ Å; $\alpha = 89.997(21)$, $\beta = 104.321(8)$, $\gamma = 114.225(11)°$; $V = 506.98(8)$ Å^3) with aluminophosphonate layers similar to those found in $Al(OH)(H_2O)CH_3PO_3$ linked via ethylene (-CH_2CH_2-) groups. The solid loses water upon heating in two steps, the first at 100 °C and the second at 360 °C. The first water loss leaves a crystalline solid with a framework structure of $Al_2(OH)_2(O_3PCH_2CH_2PO_3)$, closely related to that of the parent (*C*2/*c*; $a = 15.3723(21)$, $b = 6.7613(8)$, $c = 9.7374(13)$ Å; $\beta = 102.392(9)°$; $V = 988.4438$ Å^3) whereas the second water loss results in major loss of crystallinity. X-ray powder diffraction has been used to determine and refine the structures of the parent and intermediate dehydrated phases. The main structural difference is the loss of one water molecule bound to aluminum, which changes the metal cation's coordination from octahedral to distorted square planar. The as-prepared and dehydrated samples have been simulated computationally. The transformation has been monitored by in-situ ^{27}Al MAS NMR spectroscopy; octahedral aluminum ($\delta_{iso} = -7.1$ ppm; asymmetry parameter, $\eta = 1.0$; quadrupolar coupling constant, QCC = 5.4 MHz) is converted to 5-fold coordinated aluminum ($\delta_{iso} = 20.7$ ppm; $\eta = 0$; QCC = 5.8 MHz) by heating at 130 °C for 1 h. The process is fully reversible.

Introduction

The recent intense interest in microporous hybrid organic−inorganic solids in general, and metal phosphonates in particular, is driven in part by their potential ability to incorporate organic functionality within a robust framework and to present both metal and organic species to guest molecules within the pores. In this way they are expected to possess unique properties as adsorbents and catalysts.[1−4] Diphosphonates of metals such as group 4 metals titanium and zirconium, rare earths, and transition metals are of particular interest.[5−13] Most of these possess a common structural motif—inorganic metallophosphonate layers linked by organic pillars—whereas a smaller number are better described as frameworks. Many of these metal diphosphonates possess interlayer space, the pore size of which is defined in one dimension by the length of the organic pillar.

The ethylene diphosphonate group has been used successfully in the hydrothermal synthesis of diphosphonates of such metals as vanadium, cobalt, copper, aluminum, and gallium.[14−19] Many of these structures are pillared layered structures that upon crystallization contain water coordinated to some of the metal cations or residing within channels in the structure, so that their dehydration behavior is diverse. The copper ethylene diphosphonate,[16] for example, loses water irreversibly from the metal's coordination sphere, result-

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ing in structural breakdown. The aluminum ethylene diphosphonate fluoride ($Al_2(H_2O)_2F_2[O_3PC_2H_4PO_3]\cdot H_2O$) and its isostructural gallium analogue lose water in two stages:[18,19] first from noncoordinating extra framework positions in the channel and subsequently from positions coordinated to aluminum, the latter dehydration leading to loss of crystallinity. The first stage of water loss is readily reversible in the gallium form, but rehydration is much slower in the aluminum form because of its slightly smaller pores. The mixed valence vanadium ethylene diphosphonate, MIL-3K,[14] also shows reversible dehydration, where loss of water results in the coordination of vanadium changing from square pyramidal to tetrahedral with retention of crystallinity and of the organic−inorganic framework. This indicates the possibility of creating low coordination metal sites that are accessible to adsorbed molecules and that may therefore have potential as adsorbents and catalysts.

As a continuation of our studies of aluminum phosphonates,[20−23] we have investigated the synthesis of such materials with alkyl diphosphonic acids of varying chain lengths. In the absence of fluoride, which has been shown to be a successful mineralizer in such systems,[18,19] the products of these hydrothermal syntheses are usually microcrystalline. We have been successful in preparing a novel aluminum ethylene diphosphonate hydroxide hydrate pure and in microcrystalline form. Here, we describe its synthesis and structure determination from high-resolution X-ray powder diffraction data. It is able to desorb water at low temperature from the coordination sphere of aluminum with retention of crystallinity, leaving a 5-fold coordinated site that is available for subsequent reversible re-adsorption of water.

Experimental Section

A series of experiments was performed in which the Al:P ratio of the reactant mixture was kept constant and the pH of the reaction solution was adjusted over the range of 2−7 by addition of sodium hydroxide. The title phase (AldiEPO-1) crystallized at pH 7. A specimen synthesis of AldiEPO-1, ($Al_2(OH)_2(H_2O)_2)[PO_3(CH_2)_2PO_3]$, was as follows: 0.03 g (0.37 mmol) of $Al(OH)_3\cdot xH_2O$ and 0.07 g (0.37 mmol) of ethylene bisphosphonic acid in 0.16 mL of H_2O were stirred, and the pH was adjusted to 7 by dropwise addition of sodium hydroxide solution. The mixture was heated at 160 °C for 2 d in a Teflon-lined steel autoclave. The product was filtered, washed, and dried to give a white crystalline solid.

Laboratory powder X-ray diffraction was performed on a STOE diffractometer with Ge monochromated Cu Kα1 radiation (λ = 1.54056 Å). The as-prepared solids were examined in transmission geometry, where the sample was supported between two thin Mylar films whereas the heat-treated samples were examined in Debye−Scherrer geometry in 0.7-mm quartz glass capillaries. For the as-prepared compound, high-resolution X-ray diffraction data was also collected in Debye−Scherrer geometry at station 9.1 at the Daresbury synchrotron facility, using monochromatic X-rays of wavelength 0.99559 Å. To collect reflections of lower *d* spacing, which have lower relative intensity, with better statistics, different 2θ ranges of the pattern were collected for different times. Data collection times were as follows: 2−20°, 1 s; 20−31.7°, 2 s; 31.7−41.9°, 3 s; 41.9−48.0°, 4 s; 48.0−52.7°, 6 s; 52.7−56.6°, 8 s; and 56.6−60°, 10 s. The diffraction intensities were normalized.

Chemical analysis was performed by laser ablation ICPMS, using an aluminophosphate of known composition ($AlPO_4$) as a reference, and the organic content was measured using a Carlo Erba elemental analyzer. The behavior of the sample upon heating was determined by thermogravimetric analysis at 5 °C/min under flowing nitrogen. For powder diffraction of dehydrated samples, the material was heated under vacuum in a 0.7-mm quartz glass capillary and sealed prior to examination.

^{31}P and ^{27}Al MAS NMR studies of the as-prepared material were performed on a Varian Infinityplus 500 MHz spectrometer, fitted with a T_3 Chemagnetics 4-mm probe, at resonance frequencies of 130.324 and 202.466 MHz for ^{27}Al and ^{31}P, respectively. A 1 M aqueous solution of $Al(NO_3)_3\cdot 9H_2O$ (0 ppm) and calcium hydrogen phosphate dihydrate (Brushite) (−1.2 ppm) were used as chemical shift standards. Samples were spun at the magic angle at a speed of 10 kHz. Pulse durations were 1.0 and 4.0 μs, and pulse delays were 0.2 and 1.0 s for ^{27}Al and ^{31}P, respectively. Variable temperature ^{27}Al MAS NMR from 21 to 130 °C was performed, and the dehydration behavior was studied for different durations at 130 °C. The end-cap of the rotor possessed a small channel sufficient to allow the escape of water released during the heating.

The structures of the as-prepared title compound (AldiEPO-1) and its dehydrated product (AldiEPO-1d) were modeled using a first principles approach involving no adjustable parameters based on Density Functional Theory (DFT). DFT[24] is a general theory that describes the total energy of a system in terms of the electron density. DFT-based calculations were performed using CASTEP (version 4.2)[25] implemented on an IBM/RS6000 parallel machine with 3 nodes, each with four 375 MHz power3 processors. Exchange and correlation energies were treated using the Generalized Gradient Approximation (GGA) based on the Perdew and Wang functional. Ultrasoft pseudopotentials were used with a kinetic energy cutoff of 260 eV for the planewave basis set, with a finite basis correction being applied during unit cell optimizations. Experimentally determined structures (without H positions) were used as starting models for the energy minimizations, and hydrogen atoms were placed on carbons and oxygens as predicted from chemical and bond valence sum calculations. Geometry optimizations were performed at constant pressure with variable unit cell parameters and full relaxation of the internal coordinates without symmetry constraints. Convergence criteria of 0.2×10^{-4} eV atom^{-1} for the total energy, 0.001Å for RMS displacement of atoms, 0.05 eV atom^{-1} for the RMS force on the atoms, and 0.1 GPa for the RMS stress tensor were imposed.

Results and Discussion

Synthesis and Structure of the As-Prepared Compound, $Al_2(OH)_2(H_2O)_2[O_3PC_2H_4PO_3]$ (AldiEPO-1). The X-ray powder diffraction pattern (Figure 1a) was initially indexed using Louer's algorithm (DICVOL)[26] in the monoclinic system with the cell parameters a = 15.80, b = 7.07, c = 9.474 Å and β = 106.6°; the compound was assumed to contain a single crystalline phase. Systematic absences suggested that the cell was C-centered. The similarity of the *b* and *c* cell parameters of the new compound with *b* and *a* of the previously

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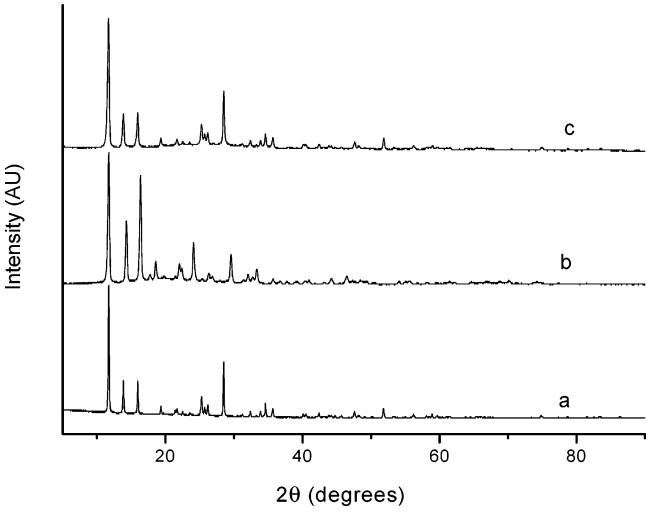

Figure 1. Powder X-ray diffraction patterns ($\lambda = 1.54056$ Å) of (a) as synthesized $Al_2(OH)_2(H_2O)_2(O_3PCH_2CH_2PO_3)$ (AldiEPO-1), (b) AldiEPO-1 dehydrated at 200 °C (AldiEPO-1d), and (c) AldiEPO-1d rehydrated by exposure to the atmosphere.

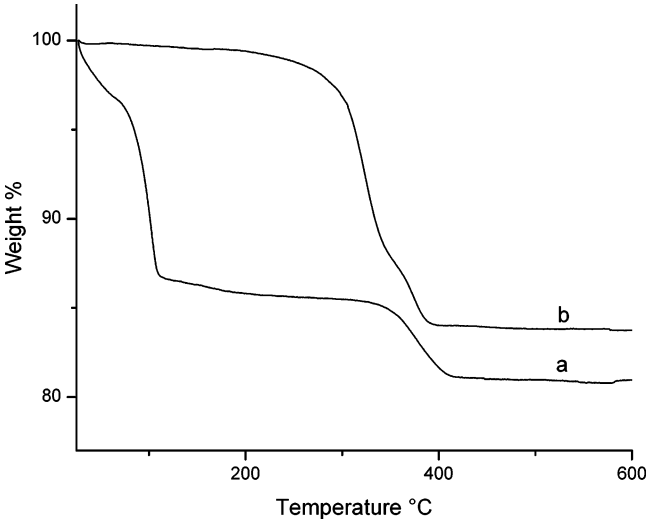

Figure 2. TG curves of (a) AldiEPO-1 and (b) $Al(OH)(H_2O)CH_3PO_3$ heated under N_2 atmosphere at 10 °C/min.

reported, layered aluminum methyl phosphonate, $Al(OH)CH_3PO_3 \cdot H_2O$ ($P2_1/a$; $a = 9.474$, $b = 7.07$, $c = 7.865$ Å; $\beta = 106.6°$)[20,27] and the doubling of the third axis suggest a closely related structure with the same aluminophosphonate layer motif, linked via $-CH_2CH_2-$ bridges in the case of the new compound, rather than stacked so that the methyl groups do not overlap. This was supported by additional chemical and structural data.

The chemical composition of the compound was determined from a combination of ICP, elemental analysis, and TGA studies. Analysis indicates that the Al/P ratio is 1:1. Thermogravimetric analysis (Figure 2a) exhibits two well-defined weight losses, centered at 100 and 360 °C, which are attributed to loss of coordinated water (obsd = 11.6%; calcd = 11.4%) and water from the decomposition of structural hydroxyls (as water; obsd = 5.2%; calcd = 5.7%), respectively, in the approximate molar ratio of 2:1. Working from elemental

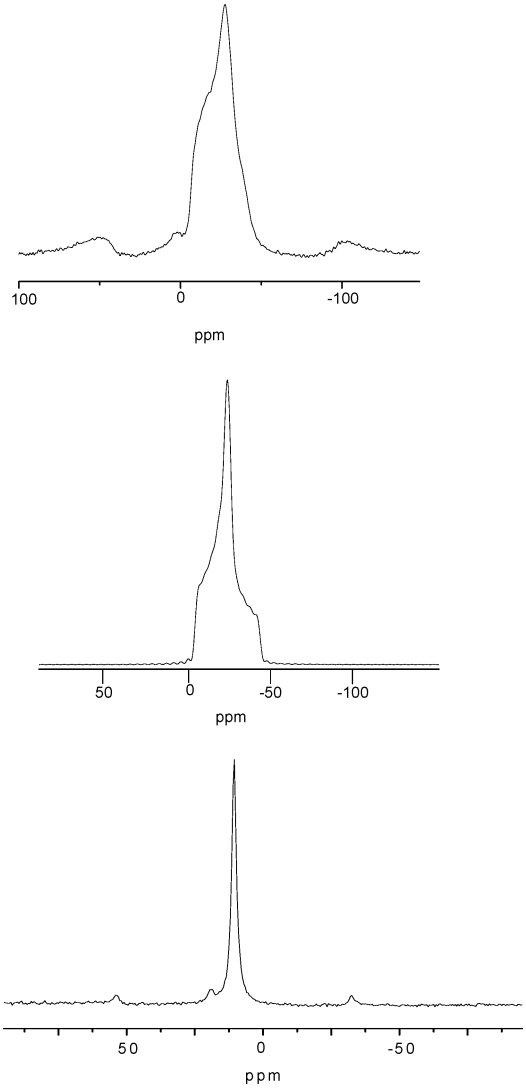

Figure 3. ^{27}Al MAS NMR of AldiEPO-1 observed (top) and simulated (middle) using $\delta_{iso} = -7.1$ ppm, asymmetry parameter, $\eta = 1.0$, quadrupolar coupling constant, QCC = 5.4×10^6. ^{31}P MAS NMR of AldiEPO-1 (bottom).

C and H contents suggests an empirical composition of $Al_2(OH)_2(H_2O)_2[PO_3(CH_2)_2PO_3]$ ($C_{obsd} = 6.59\%$, $C_{calcd} = 7.7\%$; $H_{obsd} = 3.06\%$, $H_{calcd} = 3.22\%$).

The ^{27}Al MAS NMR signal (Figure 3) possesses asymmetry and isotropic chemical shift values similar to those of the characteristic signal of $Al(OH)(H_2O)CH_3PO_3$ (AlMePO-1).[20] The spectrum could be simulated using the program SIMPSON[28] (Figure 3), and the isotropic chemical shift, asymmetry parameter, and quadrupolar coupling constant were calculated to be −7.1 ppm, 1.0, and 5.4 MHz, respectively. The difference between the observed and simulated spectra may be attributed to chemical shift anisotropy, dipolar interactions, and the presence of two crystallographically distinct aluminum sites. These are not accounted for in the simulation. Only one phosphorus site (12.3 ppm) was resolved by ^{31}P MAS NMR (Figure 3), indicating that all the phosphonate moieties are in chemically similar environments. Furthermore, the IR spectrum has broad peaks at 3482 and 3394 cm^{-1} corresponding

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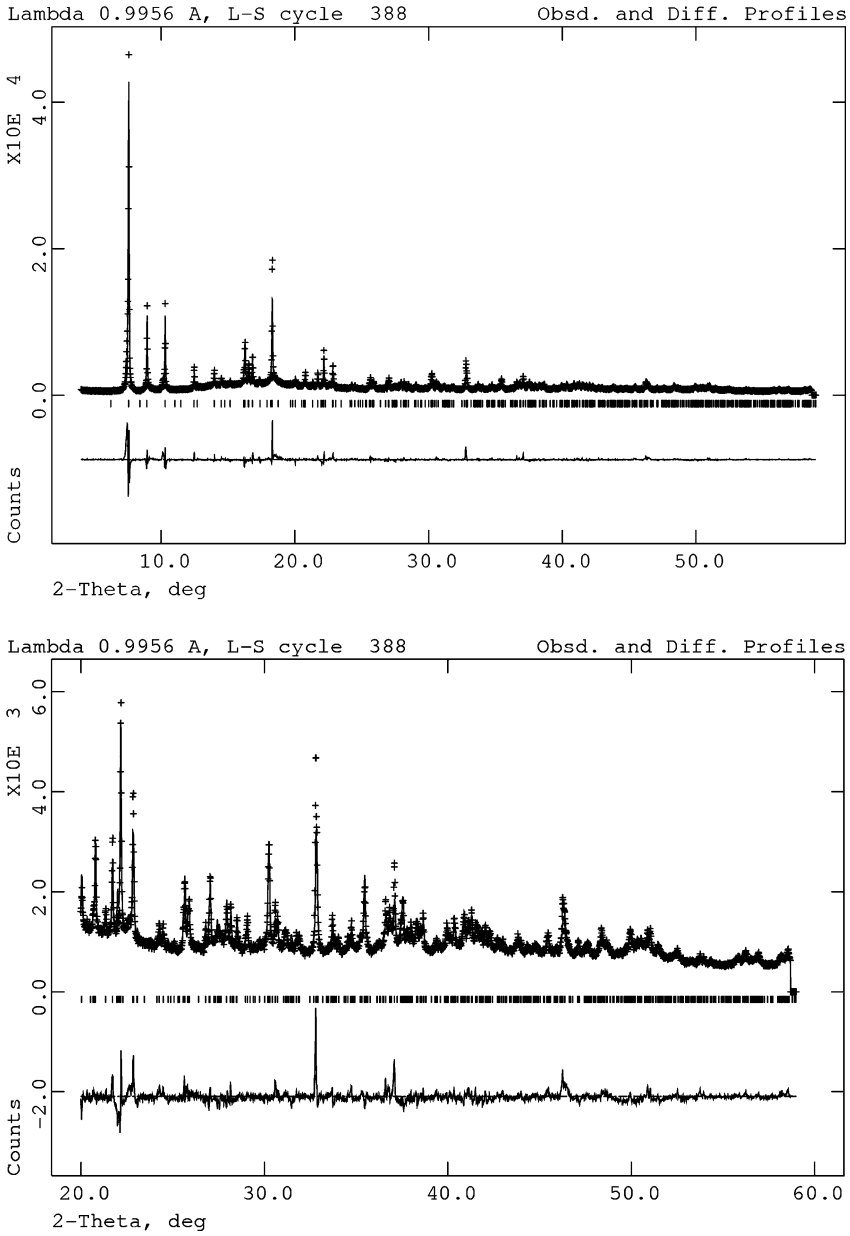

Figure 4. Observed (crosses), calculated (solid line), and difference X-ray diffraction patterns (λ = 0.99559 Å) of AldiEPO-1 (above). The higher angle range ($2\theta = 20-60°$) has been expanded for clarity (below). The structure has been refined against the experimental data (wR_p = 13.32% R_p = 8.26%).

to the stretching and a sharp peak at 1670 cm^{-1} corresponding to the bending vibration of hydrogen-bonded water molecules. A small peak at 2940 cm^{-1} is attributed to C−H stretching vibration.

The ethylene-pillared model, in space group *C*2/*c* as suggested by the systematic absences, was therefore used as a starting point for Rietveld refinement[29] of the laboratory data using the GSAS package.[30] However, the refinement did not proceed smoothly as the peak positions could not be accurately matched by the monoclinic cell. It became apparent that the true symmetry is triclinic, with a reduced unit cell of a = 8.594 Å, b = 7.054 Å, c = 9.538 Å, α = 89.97°, β = 104.34°, and γ = 114.11°. The space group was assumed to be $P\bar{1}$, and the positional parameters of the eight non-hydrogen atoms of the asymmetric unit of the monoclinic model were transformed to 16 positions in the new cell. Energy minimization calculations (see later) support the presence of centers of symmetry. Subsequent refinement of these positional parameters against laboratory X-ray data was performed within the GSAS suite of programs, keeping soft constraints on Al−O, P−O, P−C, and C−C bonds and constraining the AlO_6 and PCO_3 polyhedral geometries with constraints in the O−O and O−C distances. This led to a goodness of fit R_{wp} of 11.0% in the laboratory data. The same structural model was then refined against synchrotron X-ray powder diffraction data. The background was matched using linear interpolation between manually estimated values, and the peak-shape parameters were fitted using pseudo-voigtian peak shape parameters. Bond lengths and angles were constrained as for refinement of the laboratory X-ray data. The final fit to the synchrotron data

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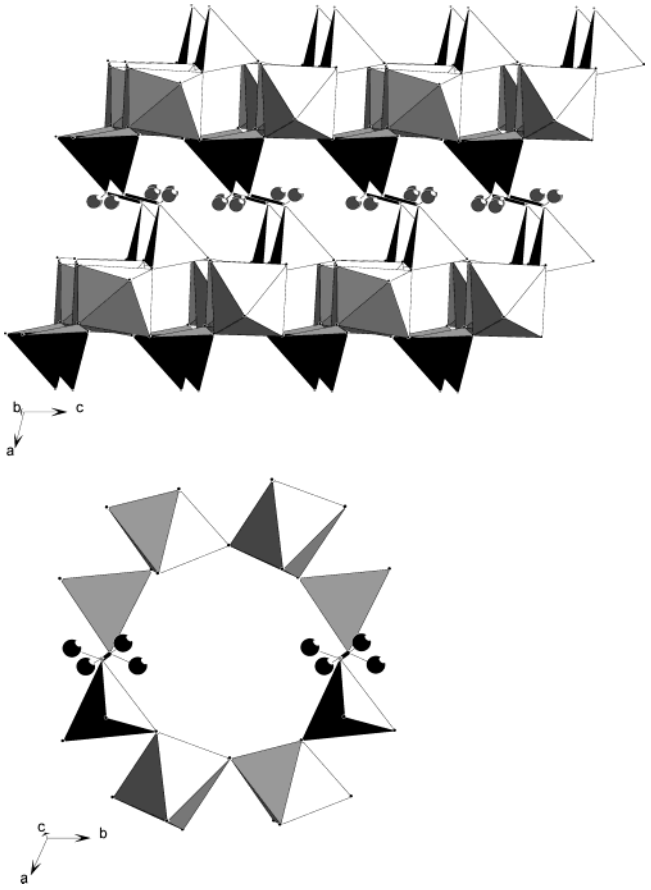

Figure 5. Structure of AldiEPO-1 using polyhedral representation of AlO_6 octahedra and O_3PC tetrahedral. The hydrogen atoms of the ethylene units are represented by small spheres. The full framework (above) is viewed along the *b*-axis. The narrowest portion of the channel system along the *c*-axis is shown below.

(Figure 4, Table 1) achieved a wR_p of 13.3%. The hydrogen positions for the ethylene groups were calculated and included, but the wR_p was not affected by the incorporation of these positions.

The title compound has a three-dimensional structure with the aluminophosphonate inorganic layers pillared by the ethylene (-CH_2CH_2-) group of the diphosphonic acid. The asymmetric unit consists of two crystallographically distinct aluminum and phosphorus atoms, although these are not resolved by the solid-state NMR. Aluminum exists in octahedral coordination, and each AlO_6 octahedron shares two of its trans corners with two other AlO_6 octahedra and three corners with three different PO_3C tetrahedra. The unshared corner is occupied by the oxygen of a water molecule [$AlO_3(OH_2)$-$(OH)_2$], Table 2. Bond valence sum calculations[31] gave values of 0.3 for these "water" oxygen atoms (O9, O10) and 1.0 for the shared oxygens in the AlO_6 chains that are predicted to be hydroxyl groups (O5, O6). The structure can be considered to be made up of one-dimensional chains of corner-sharing AlO_6 octahedra running along the *b*-axis (Figure 5a). These chains are linked together in the *ab* plane by the basal plane of PO_3C tetrahedra with the apical methylene group pointing alternatively up and down. This mode of linking of the phosphonate groups facilitates three-dimensional connectivity by pillaring each layer with adjacent layers on both sides. Similar types of inorganic layer are observed in other metal phosphonates.[32,33] The pillared structure possesses a zigzag channel system parallel to the *c*-axis, bounded at its narrowest point by a strongly corrugated ring made up of four AlO_6 octahedra, four O_3PC tetrahedra, and two C−C bonds

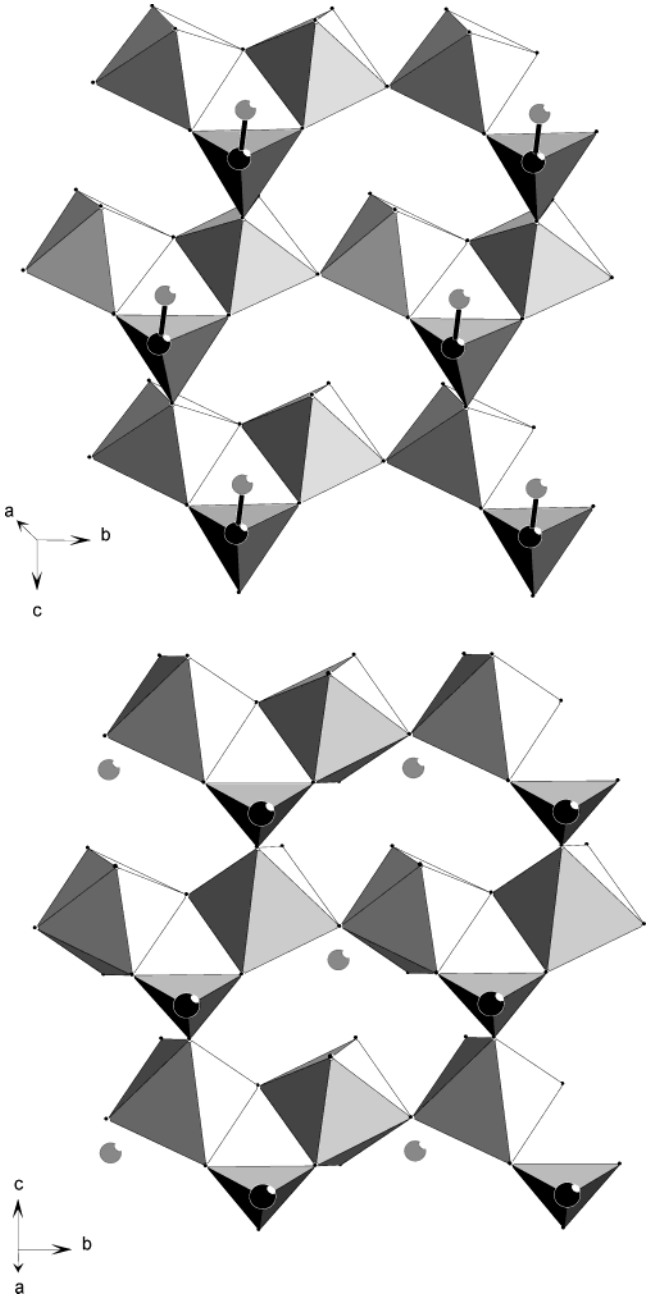

Figure 6. Views into the aluminophosphonate layers of Al-$(OH)(H_2O)CH_3PO_3$ (below) and AldiEPO-1 (above), showing the relation of methyl groups of adjacent layers (below) and of methylene groups attached to adjacent layers (above). For the former, the methyl groups from the inorganic layer (methyl carbon atoms, black spheres) are approximately equidistant from those of the layer above (gray spheres), whereas for the latter, the bound methylene groups carbon atoms (gray) are at very different distances from the three nearest carbon atoms of the inorganic layer (black).

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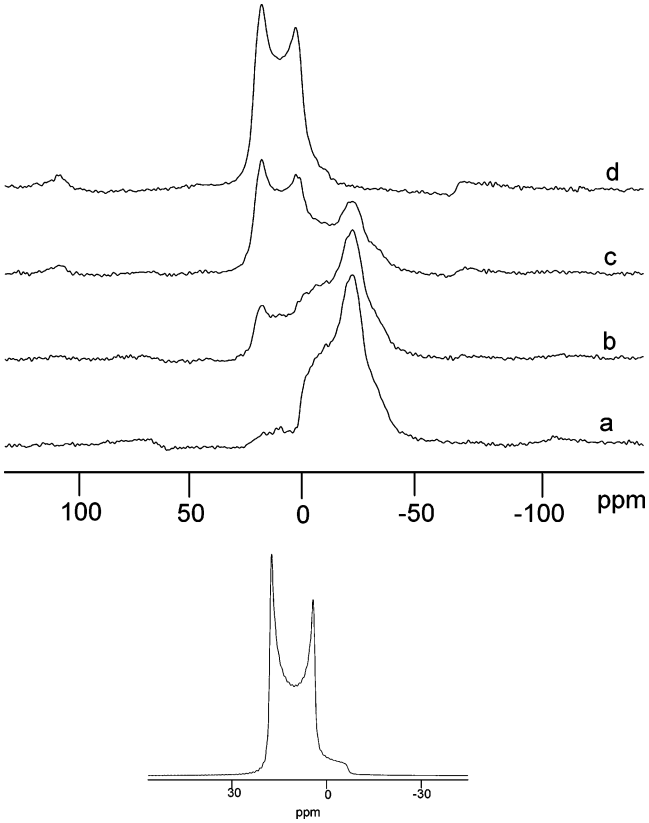

Figure 7. In-situ ^{27}Al MAS NMR of AldiEPO-1 being dehydrated (to AldiEPO-1d) by heating at 130 °C at durations of (a) 0, (b) 8, (c) 20, and (d) 65 min (above) and simulated spectrum for the completely dehydrated sample using $\delta_{iso} =$ 20.7 ppm, $\eta = 0$, QCC $= 5.8 \times 10^6$ (below).

Table 1. Structural and Instrumental Data for Rietveld Refinements of AldiEPO-1 and the Dehydrated Sample, AldiEPO-1d

compound	AldiEPO-1	AldiEPO-1d
formula	$Al_2C_2H_{10}O_{10}P_2$	$AlCH_3O_4P$
fw	309.96	135.98
λ (Å)	0.995559	1.54163
space group	$P\bar{1}$	$C2/c$
a (Å)	8.5977 (10)	15.3723(21)
b (Å)	7.04994 (32)	6.7613(8)
c (Å)	9.5290 (4)	9.7374(13)
α (°)	89.997 (18)	90
β (°)	104.321 (8)	102.392(9)
γ (°)	114.225 (11)	90
V (Å^3)	506.98(8)	988.449(23)
Z	2	8
2θ range (°)	2−59.99	5−89.98
reflns	1012	215
refined params	51	27
R_p	0.0820	0.0837
wR_p	0.1334	0.1116
wR_{exp}	0.0402	0.0527

(Figure 5b). The free diameter is reduced by hydrogen atoms attached to both the ethylene carbons and also the bridging oxygen atoms that run along the chains of AlO_6 octahedra. This gives a free diameter of ca. 3.5 Å, assuming a proton van der Waals radius of 1 Å.

The structures of AldiEPO-1 and $Al(OH)(H_2O)CH_3PO_3$ (AlMePO-1) can helpfully be compared (Figure 6). In each case the aluminophosphonate layer structure is identical, with an orthogonal in-layer repeat unit of 7.07 × 9.45Å. For the AlMePO, the next layer stacks on top of this, with the methyl groups of the second layer fitting into the recess between three methyl groups

Table 2. Selected Bond Distances (Å) for AldiEPO-1 and AldiEPO-1d[a]

AldiEPO-1		AldiEPO-1d	
Al(1)−O(1)	1.76(4)	Al(1)−O(1)	1.703(15)
Al(1)−O(3)	1.67(4)	Al(1)−O(2)	1.706(14)
Al(1)−O(5)$_{hy}$	1.88(5)	Al(1)−O(3)$_{hy}$	1.814(23)
Al(1)−O(6)$_{hy}$	1.90(5)	Al(1)−O(3′)$_{hy}$	1.196(22)
Al(1)−O(7)	1.78(4)	Al(1)−O(4)	1.810(18)
Al(1)−O(9)$_w$	2.09(4)	P(1)−C(1)	1.852(22)
A1(2)−O(2)	1.92(4)	P(1)−O(1)	1.600(21)
A1(2)−O(4)	1.84(4)	P(1)−O(2)	1.605(16)
A1(2)−O(5)$_{hy}$	1.85(5)	P(1)−O(4)	1.583(23)
A1(2)−O(6)$_{hy}$	1.98(5)	C(1)−C(1)	1.4586(2)
A1(2)−O(8)	1.89(4)		
A1(2)−O(10)$_w$	2.07(4)		
P(1)−C(1)	1.81(4)		
P(1)−O(2)	1.74(4)		
P(1)−O(4)	1.60(4)		
P(1)−O(7)	1.57(4)		
P(2)−C(2)	1.73(5)		
P(2)−O(1)	1.56(4)		
P(2)−O(3)	1.66(4)		
P(2)−O(8)	1.80(4)		
C(1)−C(2)	1.404(32)		

[a] The subscripts hy and w represent the hydroxyl and water oxygen atoms, respectively.

projecting from the first layer. The C−C distances of each methyl group to the C of the three methyl groups of the adjacent layer are closely similar (3.77−3.9 Å) and no pore structure is present. For the pillared structure, however, the carbons of adjacent layers are covalently bound so adjacent layers are arranged differently with respect to each other. Indeed the C−C bond vector lies in the *ac* plane and dictates the direction of stacking. Apart from the short covalent C−C bond distance (1.4 Å), the other C−C distances between a methylene C attached to one layer to carbons attached directly to the next layer are 3.88 Å and a much longer 6.3 Å. As a result, a channel system is created.

Dehydration Behavior of Parent Compound and Structure of Dehydrated Compound, $Al_2(OH)_2[O_3PC_2H_4PO_3]$(AldiEPO-1d). AldiEPO-1 shows interesting water desorption and re-adsorption behavior. TGA shows that water is lost in two steps. Dehydration could be achieved by evacuation, even at room temperature, to give AldiEPO-1d. XRD indicates that a high degree of crystallinity is retained after the first stage but that loss of water at the higher temperature of 400 °C results in a major loss of crystallinity. Furthermore, material heated to remove water in the first stage readsorbs water to regenerate the original structure (Figure 1c), whereas the solid prepared by the two-stage removal of water at 400 °C did not rehydrate to a crystalline material. This dehydration/rehydration behavior is quite different from that observed for AlMePO-1, for which almost exactly the same total weight loss occurs in a single, complex step centered at around 330 °C (Figure 2b).

^{27}Al NMR studies were also performed on the material. A sample was dehydrated in-situ in the NMR spectrometer at 130 °C to remove water in the first stage. As the sample is heated, the peak at −20 ppm reduces in size and is replaced by another, with characteristic quadrupolar shape, with horns at 14 and 2 ppm, until this dominates the spectrum (Figure 7). The spectrum of the dehydrated material was simulated assuming an asymmetry close to zero, a quadrupolar

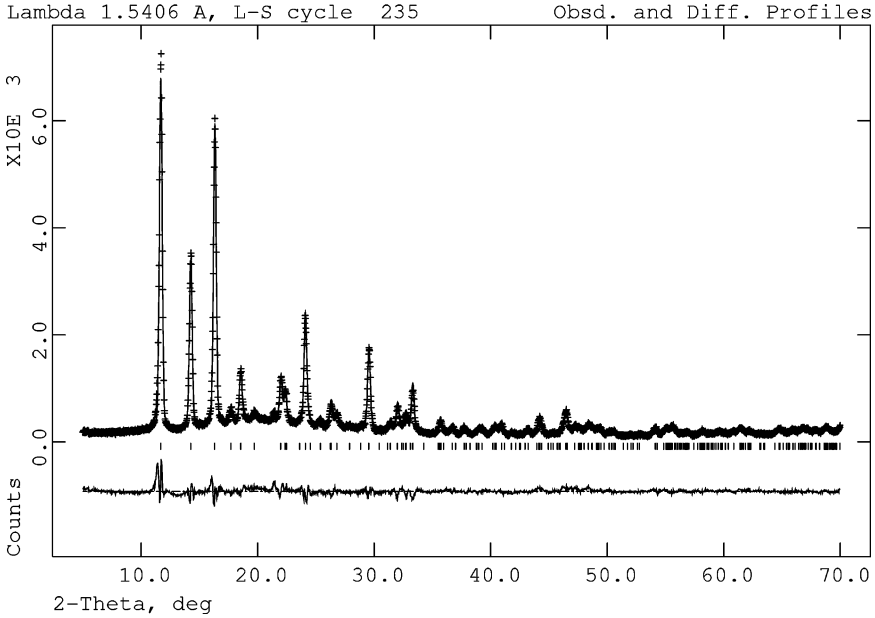

Figure 8. Observed (crosses), calculated (solid line), and difference X-ray diffraction patterns ($\lambda = 1.54056$ Å) of the dehydrated sample AldiEPO-1d ($wR_p = 11.17\%$ and $R_p = 8.36\%$).

coupling constant of 5.8 MHz, and an isotropic chemical shift of 20.7 ppm. This chemical shift is within the range expected for 5-fold coordinated aluminum.[34,35]

The dehydration behavior can be explained in terms of the parent structure. The first water to be removed is that coordinated to aluminum, leaving the dehydrated compound $Al_2(OH)_2[O_3PCH_2CH_2PO_3]$. The ^{27}Al NMR of this compound is that expected for a 5-fold coordinated species and confirms that the water is lost from a position next to the aluminum. The X-ray diffraction pattern of the dehydrated sample (Figure 1b) is satisfactorily indexed with a C-centered monoclinic unit cell ($a = 15.3719(21)$, $b = 6.7613(8)$, $c = 9.7372(13)$ Å; $\beta = 102.392(9)°$) closely related to that originally estimated for the hydrated material ($a = 15.9979$, $b = 7.0521$, $c = 9.5423$ Å; $\beta = 109.311°$). It is likely that this material is closely structurally related to the parent solid. One model consistent with the X-ray powder diffraction data has the same framework, but with the aluminum species having become 5-fold coordinated. Using this model as a starting point and refining it against the experimental data using the Rietveld method gives a good fit to the laboratory X-ray data (Figure 8).

Interestingly, a similar change in aluminum coordination is suggested by our results for the reversible dehydration of $Al(OH)(H_2O)[PO_3\text{-}CH_2C_6H_4Br]$,[36] which has the same aluminophosphonate layer structure as AldiEPO-1 and for which similar ^{27}Al MAS NMR spectra are reported upon dehydration.

The refined structure of AldiEPO-1d shows that the channels have been retained and the coordination geometry of the aluminum in the dehydrated solid is a distorted square pyramid (Figure 9). The polyhedron displays angles ranging from 82.6 to 99.8° in the basal plane. The apical oxygen, O(2) makes a short angle of

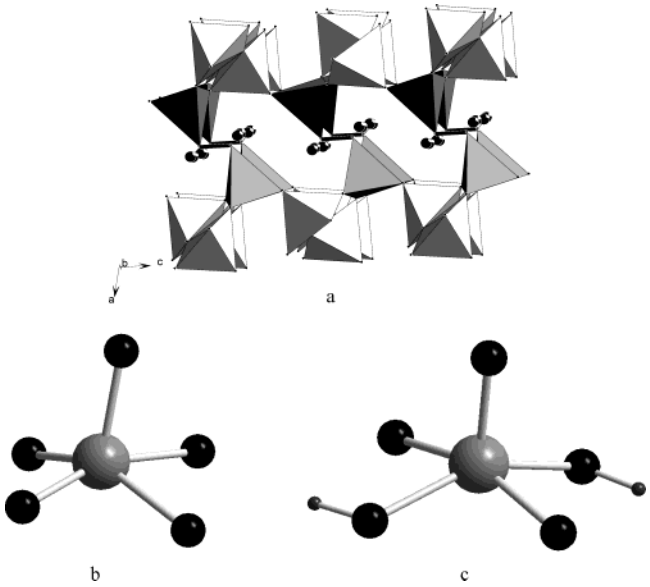

Figure 9. (a) Structure of AldiEPO-1d, with similar type of polyhedral representation as Figure 5. The aluminum adopts 5-fold coordination, with square pyramidal geometry (b) from XRD studies and (c) from energy minimization studies.

89.8 with the planar O(4) as compared to the other angles ranging from 102.5 to 106.9°. The bond valence sum for the hydroxyl oxygen was calculated to be 1.0. A similar geometry has been observed for AlO_5 in the aluminosilicate mineral vesuvianite.[34]

The facile loss of the first stage of water from AldiEPO-1, particularly when compared to the related AlMePO-1, can be attributed to the presence of convenient channels in the structure along the *c*-axis that occur as a result of the constrained stacking of the Al−P−O layers via the ethylene pillars (Figure 10). The distance that water molecules would have to travel along this channel from one aluminum site to another is only 5.1 Å. The AlMePO-1 has no such channels available, due to the different layer stacking, and so water loss only occurs as the entire structure breaks

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(36) Chaplais, G.; Le Bideau, J.; Leclercq, D.; Mutin, H.; Vioux, A. *J. Mater. Chem.* **2000**, *10*, 1593.

Table 3. Observed and Simulated Unit Cell Parameters for AldiEPO-1 and AldiEPO-1d[a]

sample	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	*β* (°)	*γ* (°)
AldiEPO-1 (experimental)	8.596(1)	7.0493(3)	9.528(1)	89.98(2)	104.33(1)	114.20(1)
AldiEPO-1 (simulated)	8.686	7.065	9.605	90.15	104.62	114.06
AldiEPO-1d (experimental)	8.392(1)	6.763(1)	9.738(1)	90.12(2)	101.26(1)	113.66(1)
AldiEPO-1d (simulated)	8.490	6.788	9.822	89.93	102.34	113.39

[a] The latter expressed in the primitive cell for comparison.

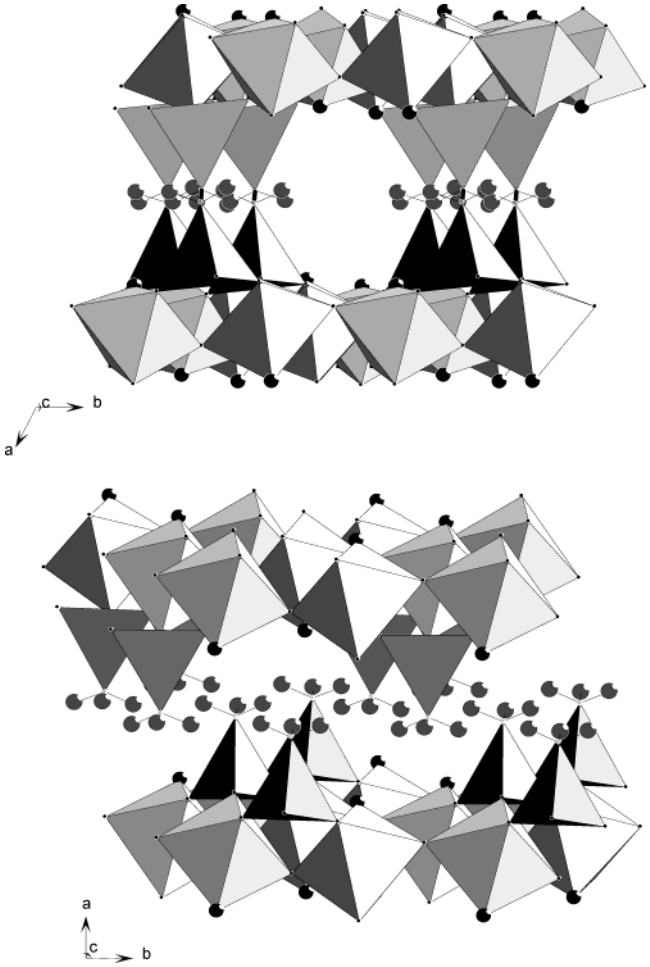

Figure 10. Comparison of the structures of AldiEPO-1 and $Al(OH)(H_2O)CH_3PO_3$, viewed along the related structural axis and showing the layer offset that results in blockage of the channels in the aluminum methyl phosphonate.

down. The second loss of water results from the thermal decomposition of the structural hydroxyls that form the bridges in the chains of AlO_6 octahedra in AldiEPO-1d, which leads to a major loss of structural order.

Computer simulations of the structures of AldiEPO-1 and AldiEPO-1d were performed using the DFT methods described in the Experimental Section. The unit cell parameters of the energy minimized structures are compared with experimental values in Table 3 and show good agreement.

The calculated structure of the as-prepared material is closely similar to that determined experimentally and retains the $P\bar{1}$ symmetry of the starting model. The predicted hydrogen positions attached to oxygens of the aluminophosphonate layer are closely similar to those reported from single-crystal measurements on the related layers of $Al(OH)(H_2O)CH_3PO_3$. The structure of the dehydrated material also retains the centers of symmetry upon minimization, and the square pyramidal AlO_5 geometry observed experimentally is reproduced (Figure 9c). It is likely that this geometry is adopted in preference to trigonal bipyramidal because of the constraints imposed by the rigid lattice. Computer simulation of the dehydrated material also indicates that the remaining proton on the Al−OH−Al bridging hydroxyl remains closely coplanar with the two aluminum atoms and the hydroxyl oxygen.

Summary

An aluminum ethylenediphosphonate framework solid is prepared phase pure by hydrothermal synthesis at neutral pH. The structure was solved from X-ray powder diffraction data and found to be made up of aluminum oxide hydroxide layers pillared by ethylene diphosphonate groups. The layers are themselves made up of apex-sharing chains of AlO_6 octahedra that are linked to each other by the phosphonate groups.

The solid loses water in two steps upon heating; the first water loss is reversible and crystallinity is retained, whereas the second loss is associated with partial structural breakdown. The first water loss is due to removal of water from the coordination sphere of aluminum, whereas the second loss results from the condensation of bridging hydroxyls. The first, reversible, step has been monitored by in-situ ^{27}Al MAS NMR, in which the signal changes from that due to distorted octahedrally coordinated aluminum to that of axially symmetric 5-fold coordinated aluminum. The structure of the dehydrated intermediate has been shown by Rietveld refinement of laboratory X-ray diffraction data to retain the framework connectivity of the parent solid, the main change being the loss of coordinated water to leave square pyramidal AlO_5. The ease of this dehydration is readily explained in terms of channels running through the structure.

The new solid is made up of aluminophosphonate layers with the same structure as those present in the layered AlMePO-1, but they are linked by the organic groups rather than each layer being covered on both sides by methyl groups and stacking closely with adjacent layers. This pillaring has the effect of creating a rigid framework and connected porosity. The observed ability of aluminum phosphonates to crystallize in a number of layered structures indicates the potential of this method to generate new porous structures.

This is a rare example of an organic−inorganic hybrid framework where a "defect" site with incomplete coordination can be created without loss of framework connectivity. Solids with such sites are expected to show shape-selective adsorption behavior for small polar molecules and maybe of use, for example, as drying agents. We are currently pursuing routes to prepare larger pore materials with similar metal cation sites.

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Supporting Information Available: (1) Atomic coordinates, thermal parameters, and full bond distances and bond angles for AldiEPO-1 and AldiEPO-1d; (2) IR spectrum of AldiEPO-1; (3) ^{27}Al MAS NMR spectrum of rehydrated AldiEPO-1d; (4) XRD pattern of AldiEPO-1 heated to 400 °C; (5) atomic coordinates from DFT calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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