

Synthesis and Structure of a Novel Large-pore Microporous Magnesium-containing Aluminophosphate (DAF-1)

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$Mg_{0.22}Al_{0.78}PO_4 \cdot 0.12(C_{16}H_{38}N_2) \cdot xH_2O$ crystallizes during hydrothermal synthesis into a unique extended three-dimensional (3-D) tetrahedrally-coordinated framework structure possessing two parallel channel systems with approximately circular aperture openings of *ca.* 6.1 and 7.5 Å respectively, the latter of which contains supercages 16.3 Å in diameter: these large pores are linked perpendicularly by two types of interconnecting apertures, the minimum diameter of one of which is *ca.* 3.9 and that of the other 5.4 Å

In addition to the many molecular sieve structures adopted by aluminium phosphate, when crystallized under mild conditions in the presence of an appropriate organic template,^{1,2} there is a growing number of others in which divalent ions of metals (M) such as Mg, Mn, Co, Ni and Zn are incorporated into the framework.^{3,4} Some of the structures taken up by the so-called MeAPOs or MAPOs (metal aluminium phosphates) are unique: they have so far defied synthesis in the absence of the framework-incorporated M^{2+} ion. Thus, MAPO-36 is readily prepared and has a unique structure,^{5,6} but the corresponding aluminium phosphate (ALPO-36) has so far not been synthesized. MAPOs are of considerable intrinsic interest for this and other reasons; but they are also of great potential value as powerful solid acid catalysts.⁷⁻¹⁰ MgAPO-36, for example, rivals the protonated form of faujasite (zeolite H-Y) in its activity as a superacid for the catalytic cracking of alkanes.^{4,11}

The title compound was synthesized under hydrothermal conditions starting from a gel of composition; 0.2 MgO: 0.4 HOAc: 0.9 Al_2O_3 : P_2O_5 : *ca.* 30 H_2O : 0.9 $R(OH)_2$, where

$R(OH)_2$ is decamethonium hydroxide and HOAc acetic acid. Typically, a mixture of phosphoric acid (Aldrich, 85 wt%) with water, hydrated aluminium oxide (Aldrich, 55 wt%) Al_2O_3 , 45 wt% H_2O) and magnesium acetate [Aldrich, $Mg(OAc)_2 \cdot 4H_2O$] was stirred until homogeneous and then a concentrated aqueous solution of decamethonium hydroxide was added (prepared by rotary evaporation of the filtrate of a mixture of decamethonium bromide (Aldrich) and an excess of Ag_2O). The gel was stirred again to homogeneity, sealed in a Teflon-lined stainless steel autoclave and heated at 190 °C for 2 days under autogeneous pressure. The resulting crystalline product consisted of roughly equi-dimensional hexagonal prisms of DAF-1 (Davy Faraday-1) up to *ca.* 125 μm in size and a second phase of much smaller particle size. Chemical analysis by ICPAE (inductively coupled plasma atomic emission) spectroscopy of separated DAF-1 crystals gave a 1:1 ratio of (Mg, Al):P. Analysis of the hydrocarbon content by combustion coupled to mass spectrometry was consistent with charge balancing of the anionic framework by divalent decamethonium cations [$\{-(CH_2)_5NMe_3\}_2\}^{2+}$. Combining the

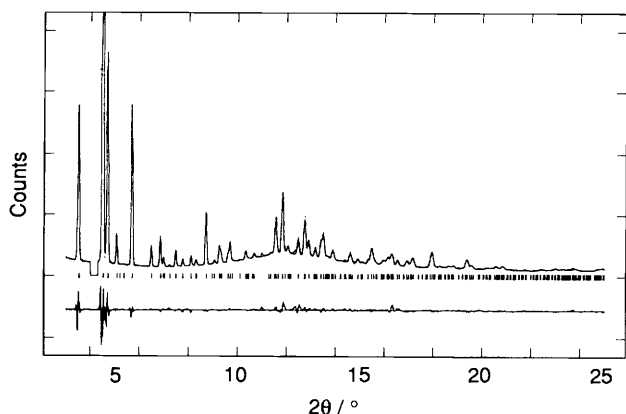


Fig. 1 Synchrotron X-ray powder diffraction data ($\lambda = 0.8566 \text{ \AA}$) of calcined DAF-1, with fitted pattern and difference profile as calculated using constrained refinement of the framework atoms and excluding an impurity peak between 4.0 and $4.3^\circ 2\theta$. The profile is plotted to 50% of full scale, and the broad diffuse X-ray scattering is from the silica glass capillary.

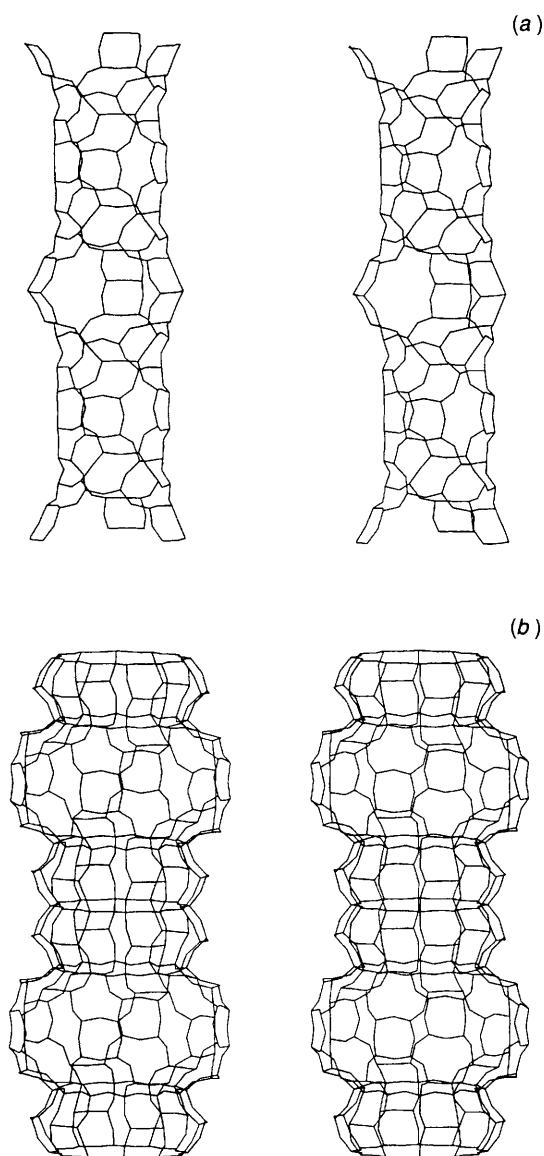


Fig. 2 Stereoplots of the inner surface of the channels of DAF-1: (a) narrow uniform channels (6.1 \AA) and (b) the wider channels (7.5 \AA), including supercages. Two unit cell lengths ($2c$ of the average cell) are represented. Bonds between the framework tetrahedral and oxygen atoms are represented by straight lines.

analyses, the measured composition $[\text{Mg}_{0.22}\text{Al}_{0.78}\text{PO}_4 \cdot 0.12(\text{N}_2\text{C}_{15}\text{H}_{42}) \cdot 0.61\text{H}_2\text{O}]$ was close to the idealised composition $[\text{Mg}_{0.22}\text{Al}_{0.78}\text{PO}_4 \cdot 0.12(\text{N}_2\text{C}_{16}\text{H}_{38}) \cdot 0.61\text{H}_2\text{O}]$ that assumes the template molecules have remained intact during synthesis. Solid-state ^{27}Al and ^{31}P MASNMR, both with proton decoupling, show the as-synthesized material possesses only tetrahedrally-coordinated aluminum (a single resonance at $\delta 39.7$ from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$) and tetrahedrally-coordinated phosphorus (a cluster of incompletely resolved peaks from $\delta -14$ to -28.5 from H_3PO_4), and the ^{31}P NMR confirms the presence of magnesium within the tetrahedral framework.

Variable temperature X-ray powder diffraction of the DAF-1, separated and ground fine, showed it to be a novel phase. It retains its crystallinity upon removal of the organic template and is stable in dry-air to temperatures in excess of 620°C . The calcined material loses crystallinity upon exposure to moisture unless an organic has been pre-adsorbed as the sample is cooled after calcination. If stabilised in this way it is able to reversibly adsorb organic molecules [e.g. 11.5 wt% of methylcyclohexane at 100°C under 40 Torr (1 Torr = 133.322 Pa) of methylcyclohexane in dry nitrogen].

The framework structure of as-prepared DAF-1 was readily determined from single crystal data.[†] Attempts to locate and refine the organic template molecules within the pore structure have proved difficult, probably due to their disorder, and only fragments have been found so far. In view of uncertainty in the true unit cell (strict alternation of the di- and tri-valent Mg and Al ions with the pentavalent phosphorus in adjacent tetrahedral sites must result in a doubling of the c -axis found in this work) no attempt was made to distinguish between magnesium, aluminium and phosphorus in the tetrahedral sites. Although the fit so far obtained for this single crystal data is relatively poor, much of the remaining difference is due to scattering from the organic template molecules. Indeed, comparison of the experimental synchrotron X-ray powder diffraction data of a calcined sample from which the template molecules had been removed with that simulated using the framework coordinates determined from the single crystal analysis and subsequently refined using the GSAS Rietveld refinement program^{14–16} shows close agreement (Fig. 1).[‡] The

[†] Crystal data for DAF-1: Hexagonal, space group $P6/mmm$ (Mg + Al/P ordering neglected, scattering factor of silicon used for all framework atoms).

As prepared (room temp.): $\text{Mg}_{0.22}\text{Al}_{0.78}\text{PO}_4 \cdot 0.12(\text{N}_2\text{C}_{16}\text{H}_{38}) \cdot 0.61\text{H}_2\text{O}$, $a = 22.351(2)$, $c = 21.639(2) \text{ \AA}$, $V = 9361.85 \text{ \AA}^3$, $Z = 66$, $D_c = 1.90 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 5.39 \text{ cm}^{-1}$, $\lambda = 0.71069 \text{ \AA}$. A single crystal was examined using Mo-K α radiation on an Enraf-Nonius 4-circle diffractometer equipped with a FAST area detector. A crystal-to-detector distance of 49.95(9) mm and a swing angle of 20° were used, ensuring that all reflections to $\theta_{\text{max}} = 22.35^\circ$ were collected. A total of 13822 reflections were collected and merged to give 1597 unique data of which 1319 were considered to be observed. The framework structure was solved by direct methods using the SHELX program.¹² Refinement gave $R = 0.121$ and $R_w = 0.215$. Analysis of the residuals for individual reflections showed that $F_o \ll F_c$ for $\langle 120 \rangle$ and $\langle 002 \rangle$. Removal of these two reflections led to current R -values of $R = 0.088$ and $R_w = 0.122$.

Calcined sample: $\text{Mg}_{0.22}\text{Al}_{0.78}\text{PO}_4$, $a = 22.164(1)$, $c = 21.241(1) \text{ \AA}$, $V = 9036.5 \text{ \AA}^3$, $Z = 66$, $D_c = 1.48 \text{ g cm}^{-3}$, $\lambda = 0.8566(1) \text{ \AA}$. Data were collected using monochromated X-radiation at station 9.1 of the Daresbury synchrotron.¹³ The powder profile over the 2θ -range 3 to 35.6° was matched using the GSAS Rietveld program of Larson and von Dreele,¹⁵ excluding the 2θ range 4.0 to 4.3° because it contained a reflection due to an impurity. Also, peak intensities above 35.6° were very low and were not included in the refinement. Atomic parameters were refined with the constraint that the T–O distances should be within 0.1 \AA of 1.64 \AA , the mean of Al–O and P–O distances. A final fit of $R_{\text{wp}} = 6.4\%$, $R_p = 4.0\%$ was obtained.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

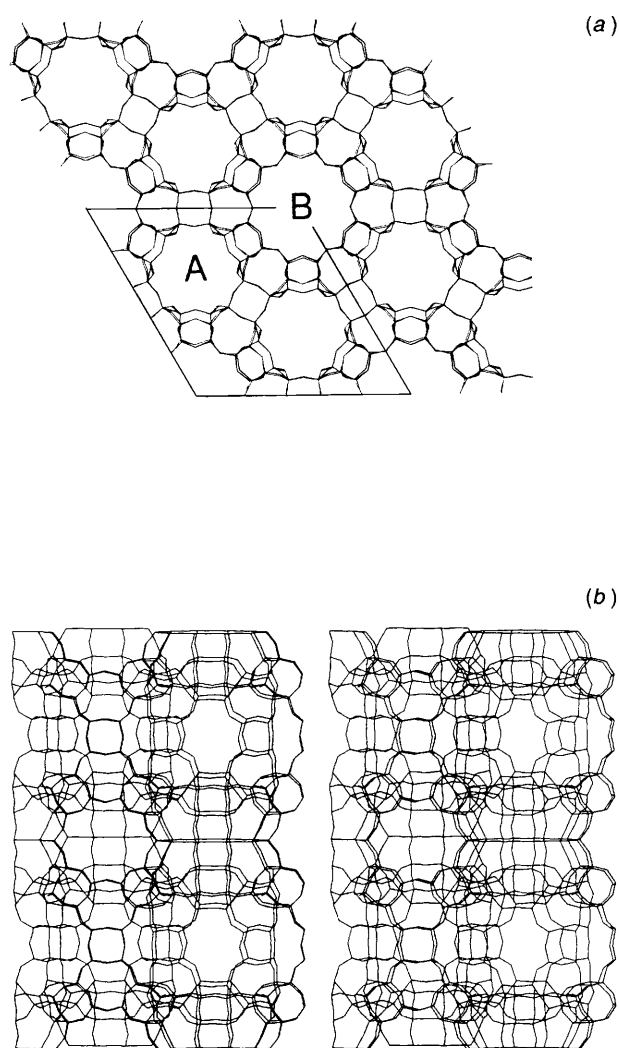


Fig. 3 (a) Projection of the structure down [001] showing the arrangement of the two types of large pore channels, and indicating the unit cell in the 001 projection and (b) a stereoplot of a portion of the structure, two unit cells (of the average structure) in z , showing the linkage of the channels *via* eight- and ten-ring apertures.

calcined sample was prepared by heating in dry oxygen at 615 °C for 1.5 h and stabilised by adsorption of methyl cyclohexane upon cooling from 150 °C to room temperature after calcination. It was loaded into a thin-walled silica glass capillary, and the methyl cyclohexane removed by heating under vacuum at 175 °C. The fractional atomic coordinates determined by Rietveld refinement are mostly within 0.01 and all within 0.02 of those determined from the single crystal study.

The solid, which has exceptionally large unit cell dimensions even without taking Al/P ordering into account, is novel for a variety of reasons, not least because it contains two types of wide (12-membered) channels, the internal surfaces of which are depicted in Fig. 2. One has a uniform diameter, with a minimum free axis of *ca.* 6.1 Å, while the other is limited by two types of 12-membered rings (the smaller having an opening 7.4 by 7.6 Å) and opens out to a supercage, the free diameter of which is 16.3 Å. The nature of this latter channel is not unlike, but quite distinct from that of mordenite, in which there are 'side pockets' off the main pores.

A projection down [001] [Fig. 3(a)] shows the spatial arrangement of these channels, with those of uniform cross section whose pore is described by puckered 12 rings being

labelled type A and those limited by planar 12-rings and containing supercages labelled type B. Per unit cell, there are two channels of type A and one of type B. A stereoplot of a part of the structure reveals their connectivity [Fig. 3(b)]. Each of the larger channels (type B) is linked to six smaller channels (type A) *via* oval eight-ring pores (minimum free diameter 3.9 Å). Each smaller channel (type A) is linked not only to three type B channels by eight-ring pores but also to three more channels of type A *via* ten-ring openings with centres $c/2$ above those of the eight-rings. These oval ten-ring pores have free dimensions 5.4 by 6.5 Å. For molecules small enough to pass through the eight-ring openings the entire pore space is interconnected. For larger molecules unable to pass through these eight-rings, the structure can be considered as two pore systems, the first (accessed by puckered 12-rings) 3-D extended, the other (accessed by planar 12-rings) 1-D.

We are at present evaluating the catalytic properties and refining the structural details of this interesting solid, the first AlPO_4 -based structure to possess 3-D connectivity *via* large 12-ring and medium ten-ring pores, and the first microporous solid reported to possess two parallel and distinctly different large pore channel systems.

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