

Synthesis and characterization of two aluminophosphates templated by *N*-methyl-1,3-diaminopropane

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Abstract

Two crystalline aluminophosphates have been synthesized under hydrothermal conditions using *N*-methyl-1,3-diaminopropane (MeDAP) as structure-directing molecule. The first one, denoted MDAP-1 is observed as an intermediate phase during the crystallization of the final product MDAP-2. The structure of MDAP-1, a 2D-layered compound with the empirical formula $(C_4H_{14}N_2)_{1.5}[Al_3P_4O_{16}]$ was refined using powder X-ray diffraction data. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 14.080(10)$ Å, $b = 8.4763(1)$ Å, $c = 18.9954(1)$ Å, $\beta = 100.95(5)^\circ$ and $Z = 4$. Inorganic sheets contain a novel 4×6 net, constructed from capped 6-membered rings. The sheets are held together by partially disordered, doubly protonated MeDAP molecules. Single crystal analysis showed that MDAP-2 is isostructural with $AlPO_4-21$ and crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 8.488(6)$ Å, $b = 17.72(2)$ Å, $c = 9.024(6)$ Å, $\beta = 106.96(5)^\circ$ and $Z = 4$. MDAP-2 differs from $AlPO_4-21$ by the presence of an octahedrally coordinated aluminum in the framework.

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1. Introduction

The discovery of aluminophosphate molecular sieves $AlPO_4-n$ by researches at Union Carbide Corp. [1] in the early 1980s initiated an intense activity in the synthesis of inorganic materials with particular compositions and framework architectures. Many new crystalline compounds with chains (one-dimensional) [2–7], layered (two-dimensional) [8–46] or open-framework (three-dimensional) [47–57] structures have been synthesized and characterized over the last decade. In contrast to the originally 3D materials reported by Wilson et al., the P/Al ratio in layered materials is not necessarily equal to unity but can vary between 1 and 2. Moreover, aluminum atoms can be four-, five- or six-coordinated and Al–O–Al pairs as well as chains of aluminum

polyhedra have been commonly observed [33,37,39,56]. The flexibility in composition and aluminum coordination makes the family of $AlPO$ materials particularly rich compared to zeolites. Crystalline aluminophosphates are generally synthesized under hydrothermal or solvothermal conditions, at temperatures between 25 and 200 °C, in the presence of organic molecules. These molecules, mainly amines or diamines, play a structure-directing role and act as space fillers and charge compensators. The structure-directing role of the amine is complex and not yet fully understood. Indeed, one molecule can lead to different inorganic structures depending on synthesis parameters like the composition of the gel, the nature of the solvent, the crystallization time or the crystallization temperature. On the other hand, a given structure can be obtained in the presence of different amines, as it is the case for $AlPO_4-17$ for which many structure-directing agents have been reported [58–60].

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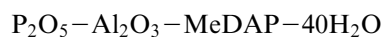
Primary diaminoalkanes with linear chains in C₂–C₈ have been extensively studied [4,8,10,11,16,33,37,39,46,47,51,55–57]. Although they lead principally to the formation of 2D-layered compounds, examples of 3D open frameworks have also been reported [51,55–57]. The molecule is generally doubly protonated and interacts with the inorganic framework via hydrogen bonding. In the particular case of layered materials, the doubly protonated diamines form a network of hydrogen bonds to adjacent layers and thereby keep the layers together. Compared to primary diamines, reports on the use of secondary or tertiary diamines for the preparation of crystalline aluminophosphates are scarce [45]. The substitution of one or several protons for alkyl groups modifies the geometry of the molecule, its basicity and the geometry of the hydrogen bonding scheme between N atoms and the inorganic framework. As a consequence, such molecules lead to structures that cannot be obtained using the corresponding primary diamines. Although 1,3-diaminopropane is known to direct the crystallization of aluminophosphates with 2D or 3D frameworks [32,37,56], the use of MeDAP as templating molecules has never been reported.

In the present work, we report the synthesis, characterization and structure determination of two aluminophosphates templated by *N*-methyl-1,3-diaminopropane (MeDAP).

2. Experimental

2.1. Synthesis

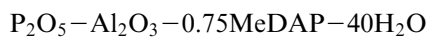
The various materials were prepared by hydrothermal crystallization of a gel containing pseudo-boehmite (CATAPAL B, Vista, 74 wt% Al₂O₃), phosphoric acid (85 wt% in water), *N*-methyl-1,3-diaminopropane (Aldrich) and water. Typically, 5 g pseudo-boehmite were dispersed in a solution containing 4.85 mL H₃PO₄ in 26 mL H₂O, and the mixture was stirred for 2 h until it was homogeneous. Then, 3.78 mL MeDAP were added dropwise, and stirring was maintained for two additional hours. The resulting gel, with the following composition:



was transferred to a Teflon-lined stainless-steel autoclave and heated at 200 °C under autogenous pressure for various periods.

Preliminary results indicated the formation of a crystalline phase after 2 h. The material, further denoted MDAP-1, was not stable and it rapidly disappeared, as evidenced by X-ray diffraction. Simultaneously, a new crystalline solid, denoted MDAP-2, was formed and could be obtained as a pure phase after 24 h. The intermediate solid MDAP-1 was in the form of small

aggregated hexagonal crystals, generally contaminated with amorphous phase. In order to isolate large crystals, both the crystallization temperature and the MeDAP concentration in the gel have been decreased. Heating a gel with the composition



at 175 °C for 12 h yielded large single crystals with a hexagonal habit with traces of a second phase. X-ray powder diffraction confirmed that the large crystals effectively corresponded to MDAP-1, the intermediate phase obtained after 2 h at 200 °C.

For comparison, AlPO₄-21 was synthesized using the gel composition



where TMEDA represents *N,N,N',N'*-tetramethylethylenediamine. The gel was heated at 200 °C for 24 h and the purity of the obtained solid was confirmed by X-ray diffraction.

2.2. X-ray data collection and structure determination

MDAP-1: a single crystal data set was collected at room temperature with a Picker 4-circle diffractometer with CuK α radiation. The structure was solved using SHELX-86 [61]. However, the quality of the crystal and its diffraction data did not allow a satisfactory refinement of the structure. Therefore, high-resolution synchrotron powder data were collected on the powder diffractometer of the Swiss-Norwegian Beam-Line (SNBL) at ESRF, Grenoble, France. The sample, loaded in a 1.0 mm glass capillary, was rotated during the measurement. The structure was then refined using the program XRS82 [62]. Unfortunately, the sample contained an unidentified impurity. The non-overlapping peaks resulting from the impurity phase were excluded from the refinement; however, this still left regions of the pattern that were contaminated. A plot of the low angle part of the pattern showing the excluded peaks is provided in the Supplementary Material. Soft geometrical restraints for interatomic distances and angles were applied to the AlPO₄-layer and the template molecule throughout the refinement. The distortion of the intensity due to the impurity did not allow to remove the geometric restraints and also resulted in a less than perfect fit as can be seen in the Rietveld plot shown in Fig. 1. None-the-less, the result of the refinement looks satisfactory. Further details on the data collection and the crystallographic data are given in Table 1. Atomic coordinates and a selection of interatomic distances and bond angles for the aluminophosphate layer in MDAP-1 are listed in Tables 2 and 3.

There are two crystallographically different template molecules present, one in general position (atoms C1, N2, C3–C5, N6) and one on the center of symmetry. The

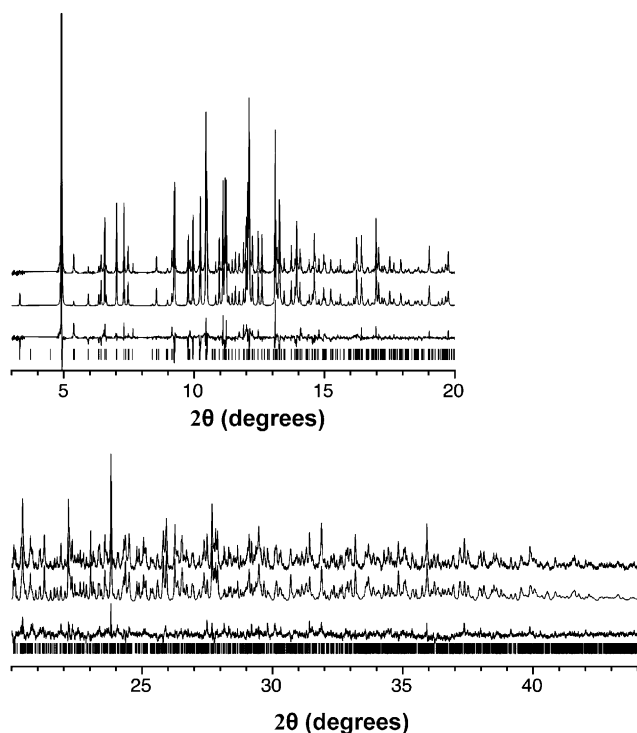


Fig. 1. Observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of MDAP-1. The tick marks indicate the position of the reflections. To show more details, the peak at 5° is truncated at about 1/3 of its height and the intensity scale at higher angles is enlarged by a factor of 6.

Table 1
Crystallographic data for MDAP-1

Chemical formula	(C ₄ H ₁₄ N ₂) _{1.5} [Al ₃ P ₄ O ₁₆]
Space group	P2 ₁ /c (No. 14)
Z	4
a (Å)	14.080(1)
b (Å)	8.476(1)
c (Å)	18.995(1)
β/°	100.96(5)
λ/Å	0.79960
2θ range/°(2θ)	3–44
Step size/°(2θ)	0.003
Peak range in FWHM	20
Number of observations (N)	12933
Number of contributing reflections	1925
Number of structural parameters (P ₁)	97
Number of profile parameters (P ₂)	8
Number of geometric restraints	96
R _F = $\sum F(\text{obs}) - F(\text{calc}) / \sum F(\text{obs})$	0.090
R _p = $[\sum [y(\text{obs}) - y(\text{calc})]^2 / \sum y^2(\text{obs})]^{1/2}$	0.20
R _{wp} = $[\sum w[y(\text{obs}) - y(\text{calc})]^2 / \sum wy^2(\text{obs})]^{1/2}$	0.21
R _{exp} = $[(N - P_1 - P_2) / \sum wy^2(\text{obs})]^{1/2}$	0.13

latter is disordered, as the molecule itself does not have a center of symmetry. Several attempts were made to refine two differently oriented molecules (with a site occupancy of 0.25) on this position, but all these

Table 2
Atomic coordinates and isotropic displacement parameters (Å²) in MDAP-1

Atom	x ^a	y	z	U _{iso}	pp
Al1	0.9000(5)	0.8593(8)	0.7359(4)	0.0251(4) ^b	1.0
Al2	0.5956(5)	0.8464(8)	0.7432(4)	0.0251 ^b	1.0
Al3	0.7551(5)	0.2673(8)	0.7943(4)	0.0251 ^b	1.0
P1	0.9663(4)	0.1433(8)	0.8390(3)	0.0251 ^b	1.0
P2	0.7718(4)	0.6372(8)	0.8159(3)	0.0251 ^b	1.0
P3	0.4291(4)	0.6425(9)	0.6614(3)	0.0251 ^b	1.0
P4	0.7201(5)	0.0461(7)	0.6649(3)	0.0251 ^b	1.0
O1	0.9577(9)	0.994(1)	0.7936(7)	0.0397(9) ^c	1.0
O2	0.6394(8)	0.952(1)	0.6822(7)	0.0397 ^c	1.0
O3	0.7503(9)	0.472(1)	0.7904(7)	0.0397 ^c	1.0
O4	0.8169(8)	0.949(1)	0.6771(6)	0.0397 ^c	1.0
O5	0.8611(8)	0.186(1)	0.8372(6)	0.0397 ^c	1.0
O6	0.4999(8)	0.751(1)	0.7030(7)	0.0397 ^c	1.0
O7	0.8454(8)	0.717(1)	0.7796(6)	0.0397 ^c	1.0
O8	0.4490(8)	0.627(1)	0.5877(6)	0.0397 ^c	1.0
O9	0.7386(9)	0.195(1)	0.7104(6)	0.0397 ^c	1.0
O10	0.4471(9)	0.483(1)	0.6982(7)	0.0397 ^c	1.0
O11	0.0230(9)	0.107(1)	0.9182(6)	0.0397 ^c	1.0
O12	0.3244(8)	0.706(1)	0.6571(6)	0.0397 ^c	1.0
O13	0.0131(9)	0.268(1)	0.8022(7)	0.0397 ^c	1.0
O14	0.7979(9)	0.644(1)	0.8919(5)	0.0397 ^c	1.0
O15	0.6771(8)	0.725(1)	0.7908(6)	0.0397 ^c	1.0
O16	0.6943(9)	0.076(1)	0.5870(5)	0.0397 ^c	1.0
C1	0.5660(8)	0.933(1)	0.4165(7)	0.05 ^d	1.0
C3	0.6327(8)	0.724(1)	0.4968(8)	0.05 ^d	1.0
C4	0.7223(7)	0.653(1)	0.5441(8)	0.05 ^d	1.0
C5	0.691(1)	0.527(2)	0.5927(5)	0.05 ^d	1.0
C11	0.083(1)	0.775(2)	0.4256(7)	0.08 ^d	1.0
C12	−0.0099(9)	0.794(1)	0.4528(9)	0.08 ^d	1.0
C13	0.006(1)	0.9140(4)	0.5118(5)	0.08 ^d	1.0
N2	0.6493(8)	0.883(1)	0.4709(7)	0.05 ^d	1.0
N6	0.6498(9)	0.398(1)	0.5453(7)	0.05 ^d	1.0

^a Estimated standard deviations of the last significant digit are given in parentheses

^{b,c} U_{iso} with the same superscript were constrained to be equal.

^d U_{iso} of the atoms of the organic template were fixed to these values.

attempts failed. Therefore, the molecule was finally modeled as a hexane molecule (C-atoms C11–C13) located on the symmetry center.

MDAP-2: a single crystal data set was collected at room temperature with a Picker 4-circle diffractometer with CuKα radiation. The structure was solved using SHELX-86 [61] and refined with SHELX-93 [63]. Owing to the difficulty to find large MDAP-2 crystals suitable for single crystal analysis, a very small crystal was finally selected but the scattering powder was not sufficient for anisotropic refinement. Since the quality of the single crystal data was not very good and due to the disorder of the non-centrosymmetric template molecule around a centrosymmetric special position in the crystal, the final R-factors remained quite high. Further details of the data collection and the crystallographic data are given in Table 4. Atomic coordinates and selected interatomic distances are reported in Tables 5 and 6.

Table 3

(a) Interatomic distances (\AA) and bond angles (deg) of the aluminophosphate layer in MDAP-1

P(1)–O(5)	1.52(1)	O(9)–P(4)–O(16)	114.3(7)
P(1)–O(11)	1.59(1)	O(9)–P(4)–O(2)	112.1(8)
P(1)–O(13)	1.49(1)	O(9)–P(4)–O(4)	107.5(7)
P(1)–O(1)	1.53(1)	O(16)–P(4)–O(2)	105.2(7)
P(2)–O(3)	1.49(1)	O(16)–P(4)–O(4)	106.2(8)
P(2)–O(7)	1.51(1)	O(2)–P(4)–O(4)	111.4(7)
P(2)–O(14)	1.42(1)	O(1)–Al(1)–O(4)	109.0(7)
P(2)–O(15)	1.52(1)	O(1)–Al(1)–O(7)	111.4(7)
P(3)–O(6)	1.47(1)	O(1)–Al(1)–O(13)	106.6(7)
P(3)–O(8)	1.48(1)	O(4)–Al(1)–O(7)	108.9(7)
P(3)–O(10)	1.52(1)	O(4)–Al(1)–O(13)	113.1(7)
P(3)–O(12)	1.56(1)	O(7)–Al(1)–O(13)	107.8(7)
P(4)–O(9)	1.52(1)	O(2)–Al(2)–O(6)	108.8(7)
P(4)–O(16)	1.48(1)	O(2)–Al(2)–O(15)	113.4(7)
P(4)–O(2)	1.48(1)	O(2)–Al(2)–O(10)	107.2(7)
P(4)–O(4)	1.57(1)	O(6)–Al(2)–O(15)	111.7(7)
Al(1)–O(1)	1.68(1)	O(6)–Al(2)–O(10)	105.5(7)
Al(1)–O(4)	1.64(1)	O(15)–Al(2)–O(10)	109.9(7)
Al(1)–O(7)	1.72(1)	O(3)–Al(3)–O(5)	116.5(7)
Al(1)–O(13)	1.72(1)	O(3)–Al(3)–O(9)	109.1(7)
Al(2)–O(2)	1.67(1)	O(3)–Al(3)–O(12)	108.0(7)
Al(2)–O(6)	1.63(1)	O(5)–Al(3)–O(9)	104.9(7)
Al(2)–O(15)	1.67(1)	O(5)–Al(3)–O(12)	103.3(7)
Al(2)–O(10)	1.79(1)	O(9)–Al(3)–O(12)	115.3(7)
Al(3)–O(3)	1.74(1)	P(1)–O(1)–A(11)	155.4(9)
Al(3)–O(5)	1.70(1)	P(4)–O(2)–A(12)	147.7(8)
Al(3)–O(9)	1.68(1)	P(4)–O(4)–A(11)	145.9(9)
Al(3)–O(12)	1.66(1)	P(2)–O(3)–A(13)	156.7(9)
O(5)–P(1)–O(11)	112.3(8)	P(1)–O(5)–A(13)	150.3(9)
O(5)–P(1)–O(13)	109.6(8)	P(3)–O(6)–A(12)	167.4(10)
O(5)–P(1)–O(1)	102.3(7)	P(2)–O(7)–A(11)	160.2(9)
O(11)–P(1)–O(13)	113.2(7)	P(4)–O(9)–A(13)	144.8(8)
O(11)–P(1)–O(1)	110.1(7)	P(3)–O(10)–A(12)	144.7(9)
O(13)–P(1)–O(1)	108.6(8)	P(3)–O(12)–A(13)	143.9(8)
O(3)–P(2)–O(7)	112.8(8)	P(1)–O(13)–A(11)	158.7(9)
O(3)–P(2)–O(14)	111.3(8)	P(2)–O(15)–A(12)	160.0(9)
O(3)–P(2)–O(15)	104.2(7)		
O(7)–P(2)–O(14)	112.2(8)		
O(7)–P(2)–O(15)	105.8(7)		
O(14)–P(2)–O(15)	109.9(8)		
O(6)–P(3)–O(8)	109.3(8)		
O(6)–P(3)–O(10)	105.8(7)		
O(6)–P(3)–O(12)	110.4(8)		
O(8)–P(3)–O(10)	108.2(8)		
O(8)–P(3)–O(12)	109.0(7)		
O(10)–P(3)–O(12)	114.0(8)		

(b) Interatomic distances (\AA) of hydrogen bonds in MDAP-1

N(2)...O(16)	2.72(2)
N(2)...O(14)	2.81(2)
N(6)...O(16)	2.88(2)
N(6)...O(8)	2.65(1)
C(11)...O(11)	3.34(2)
C(11)...O(16)	3.43(2)
C(12)...O(11)	2.95(2)
C(12)...O(14)	2.78(2)

The crystallographic data (excluding structure factors) for these two structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary

Table 4

Crystal data and structure refinement for MDAP-2

Empirical formula	(C ₄ H ₁₄ N ₂) _{0.5} [Al ₃ P ₃ O ₁₂ OH] 0.5 H ₂ O
Formula weight	873.90
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>Z</i>	4
<i>a</i> (\AA)	8.488(6)
<i>b</i> (\AA)	17.72(2)
<i>c</i> (\AA)	9.024(6)
Beta (deg)	106.96(5)
λ (\AA)	1.54178
Crystal size (mm)	.06 × .04 × .03
θ Range (deg)	4.99–50.00
Index ranges	−8 < = <i>h</i> < = 8, 0 < = <i>k</i> < = 17, 0 < = <i>l</i> < = 8
No. of reflections (>2 σ (<i>I</i>))	1164
No. of reflections	1333
Absorption correction	Numerical
Min. and max. transmission	0.78, 0.84
Rsig	0.025
No. of structural parameters	119
No. of restraints	7
<i>R</i> (<i>F</i> ²) for observed/all reflections	0.0685/0.0763
<i>R</i> _w (<i>F</i> ²) for observed/all reflections	0.1829/0.1901
Goodness of fit	1.164
Weighting scheme	1/[$\sigma^2(\text{Fo}^2) + (0.1P)^2 + 9.7P$] where $P = (\text{Fo}^2 + 2\text{Fc}^2)/3$
Refinement method	Full-matrix least-squares on <i>F</i> ²
Largest peak and hole on difference map	0.889, −0.607

mentary publication nos. CCDC 235848 and 235849. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

2.3. Characterization

P and Al contents were obtained by atomic absorption after dissolution of as-made materials in HF:HCl solution.

SEM pictures were taken with a Hitachi S800 microscope.

The amount of water and organic molecules in as-made compounds was estimated from thermal analysis data, recorded on a Setaram TGDT A92 apparatus. In a typical experiment, approximately 25 mg of the sample were heated in air from 25 to 750 °C at a heating rate of 5 °C/min.

Solid-state NMR spectra were recorded on a Bruker DSX 400 spectrometer equipped with a standard 4 mm probe head. Samples were spun at the magic angle in zirconia rotors at a spinning speed of approximately 14 kHz. The pulse lengths were 2 μs ($\pi/4$) and 0.7 μs ($\pi/6$) and the recycle delay were 30 and 1 s for ³¹P and ²⁷Al

Table 5
Atomic coordinates and isotropic displacement parameters (\AA^2) for MDAP-2

Atom	x	y	z	$U(\text{iso})^a$	pp
Al1	−0.0168(2)	0.17660(10)	−0.1922(2)	0.0159(4)	1
Al2	−0.5722(2)	0.20548(10)	−0.2928(2)	0.0120(4)	1
Al3	−0.1288(2)	0.10750(10)	−0.6706(2)	0.0146(4)	1
P1	0.20442(19)	0.28989(9)	0.02455(17)	0.0130(4)	1
P2	−0.26627(19)	0.16923(9)	0.00018(17)	0.0140(4)	1
P3	0.15764(17)	0.07140(8)	−0.36246(18)	0.0113(4)	1
O11	0.1627(5)	0.2234(2)	−0.0887(5)	0.0190(10)	1
O12	0.2383(5)	0.3592(2)	−0.0571(4)	0.0150(10)	1
O13	0.0596(5)	0.3064(2)	0.0841(5)	0.0187(10)	1
O14	0.3575(5)	0.2686(2)	0.1573(5)	0.0175(10)	1
O21	−0.1262(5)	0.1474(3)	−0.0684(5)	0.0243(11)	1
O22	−0.4307(5)	0.1588(2)	−0.1205(5)	0.0191(10)	1
O23	−0.2562(5)	0.1141(2)	0.1320(5)	0.0231(11)	1
O24	−0.2465(5)	0.2501(2)	0.0563(4)	0.0134(9)	1
O31	0.0436(5)	0.0943(2)	−0.2637(5)	0.0222(11)	1
O32	0.0654(5)	0.0838(2)	−0.5315(5)	0.0183(10)	1
O33	0.3126(5)	0.1187(3)	−0.3174(5)	0.0254(11)	1
O34	0.2087(4)	−0.0092(2)	−0.3295(4)	0.0123(9)	1
O1H	−0.0350(5)	0.2035(2)	−0.6906(5)	0.0185(10)	1
O1W	0.0212(14)	0.0597(7)	−0.8094(14)	0.056(3)	0.50
N1	0.4532(13)	0.0100(7)	−0.9670(14)	0.044(4)	0.50
C2	0.3243(18)	0.0529(9)	−0.9196(6)	0.070(6)	0.50
C3	0.364(3)	0.0665(3)	−0.7465(6)	0.095(8)	0.50
C4	0.3919(19)	−0.0036(4)	−0.6451(11)	0.049(3)	0.50
N5	0.5150(17)	0.0298(6)	−0.5059(13)	0.054(4)	0.50
C6	0.577(2)	−0.0258(9)	−0.3816(17)	0.049(3)	0.50

^a $U(\text{eq})$ for P atoms.

nuclei, respectively. ³¹P and ²⁷Al chemical shifts were referenced to H₃PO₄ (85 wt%) and Al(H₂O)₆³⁺, respectively. ¹H–¹³C CP/MAS spectra were obtained at 10 kHz using a conventional cross-polarization sequence with a contact time of 1.5 ms and a recycle delay of 5 s. ¹³C chemical shifts were referenced to tetramethylsilane (TMS).

3. Results and discussion

Synthesis. MDAP-1 is an intermediate phase formed during the crystallization of MDAP-2. Intermediate solids, generally low-dimensional solids, have been commonly observed during the crystallization of aluminophosphates. They are not always easy to isolate as pure compounds, particularly when syntheses are performed at high temperatures. Under such conditions, phases can appear and disappear very rapidly, typically within less than 30 min. As an example, we have observed the formation of an intermediate solid during the crystallization of AlPO₄-12 with ethylenediamine [62]. This compound forms after 45 min at 200 °C, is fully crystallized after 60 min but has completely

Table 6
Interatomic distances (\AA) and bond angles (deg) of the aluminophosphate layer in MDAP-2

P(1)–O(12)	1.502(5)	O(21)–Al(1)–O(31)	105.2(2)
P(1)–O(13)	1.507(5)	O(21)–Al(1)–O(11)	110.2(2)
P(1)–O(14)	1.535(4)	O(31)–Al(1)–O(11)	107.0(2)
P(1)–O(11)	1.532(4)	O(21)–Al(1)–O(14)	110.2(2)
P(2)–O(22)	1.510(4)	O(31)–Al(1)–O(14)	110.9(2)
P(2)–O(24)	1.512(5)	O(11)–Al(1)–O(14)	113.0(2)
P(2)–O(23)	1.523(5)	O(33)–Al(2)–O(13)	103.7(2)
P(2)–O(21)	1.541(5)	O(33)–Al(2)–O(1H)	144.9(2)
P(3)–O(34)	1.497(4)	O(13)–Al(2)–O(1H)	111.4(2)
P(3)–O(32)	1.512(4)	O(33)–Al(2)–O(22)	85.3(2)
P(3)–O(33)	1.514(5)	O(13)–Al(2)–O(22)	95.6(2)
P(3)–O(31)	1.549(5)	O(1H)–Al(2)–O(22)	89.8(2)
Al(1)–O(21)	1.727(5)	O(33)–Al(2)–O(24)	89.1(2)
Al(1)–O(31)	1.731(5)	O(13)–Al(2)–O(24)	95.8(2)
Al(1)–O(11)	1.746(4)	O(1H)–Al(2)–O(24)	88.8(2)
Al(1)–O(14)	1.755(4)	O(22)–Al(2)–O(24)	168.2(2)
Al(2)–O(33)	1.801(5)	O(23)–Al(3)–O(32)	150.1(2)
Al(2)–O(13)	1.805(5)	O(23)–Al(3)–O(12)	104.1(2)
Al(2)–O(1H)	1.840(5)	O(32)–Al(3)–O(12)	105.8(2)
Al(2)–O(22)	1.859(4)	O(23)–Al(3)–O(34)	87.0(2)
Al(2)–O(24)	1.867(4)	O(32)–Al(3)–O(34)	92.4(2)
Al(3)–O(23)	1.798(5)	O(12)–Al(3)–O(34)	91.0(2)
Al(3)–O(32)	1.806(4)	O(23)–Al(3)–O(1H)	89.8(2)
Al(3)–O(12)	1.829(5)	O(32)–Al(3)–O(1H)	87.2(2)
Al(3)–O(34)	1.869(5)	O(12)–Al(3)–O(1H)	96.2(2)
Al(3)–O(1H)	1.908(5)	O(34)–Al(3)–O(1H)	172.7(2)
Al(3)–O(1W)	2.199(7)	O(32)–Al(3)–O(1W)	75.0(3)
O(12)–P(1)–O(13)	108.0(2)	O(23)–Al(3)–O(1W)	75.2(2)
O(12)–P(1)–O(14)	109.9(2)	O(12)–Al(3)–O(1W)	175.9(2)
O(13)–P(1)–O(14)	111.1(2)	O(34)–Al(3)–O(1W)	84.9(3)
O(12)–P(1)–O(11)	109.8(2)	O(1H)–Al(3)–O(1W)	87.9(3)
O(13)–P(1)–O(11)	109.5(2)	P(1)–O(11)–Al(1)	135.9(3)
O(14)–P(1)–O(11)	108.1(2)	P(1)–O(12)–Al(3)	140.9(3)
O(22)–P(2)–O(24)	110.3(2)	P(1)–O(13)–Al(2)	56.0(3)
O(22)–P(2)–O(23)	108.3(2)	P(1)–O(14)–Al(1)	130.8(3)
O(24)–P(2)–O(23)	111.7(2)	P(2)–O(21)–Al(1)	143.9(3)
O(22)–P(2)–O(21)	109.7(2)	P(2)–O(22)–Al(2)	141.6(3)
O(24)–P(2)–O(21)	110.4(2)	P(2)–O(23)–Al(3)	134.1(3)
O(23)–P(2)–O(21)	106.3(2)	P(2)–O(24)–Al(2)	129.1(3)
O(34)–P(3)–O(32)	111.9(2)	P(3)–O(31)–Al(1)	137.5(3)
O(34)–P(3)–O(33)	107.2(2)	P(3)–O(32)–Al(3)	146.4(3)
O(32)–P(3)–O(33)	110.1(2)	P(3)–O(33)–Al(2)	154.8(3)
O(34)–P(3)–O(31)	109.2(2)	P(3)–O(34)–Al(3)	143.6(2)
O(32)–P(3)–O(31)	108.4(2)	Al(2)–O(1H)–Al(3)	144.4(2)
O(33)–P(3)–O(31)	110.0(2)		

disappeared after 75 min. However, intermediate structures have sometimes been isolated, characterized, and their structure was solved to get insights on the crystallization mechanism of the final solid [3]. Lower temperatures usually decrease the kinetics of crystallization and increase the period of stability of intermediate phases. However, temperature greatly influences the crystallization of the gel and the temperature range within which a given structure can be prepared is generally limited. In the case of MDAP-1, lowering the temperature and the amine concentration in the gel allowed us to stabilize the structure for several

hours and to obtain larger crystals suitable for a structure determination. X-ray powder patterns and SEM pictures of solids recovered at different periods during the crystallization at 200 °C indicate that MDAP-1 and -2 simultaneously exist in the batch. MDAP-2 particles do not form at the surface of MDAP-1 crystals; they do not result from a solid transformation of the intermediate phase but grow from species in solution. SEM pictures clearly show that large MDAP-1 plate-like crystals gradually dissolve in the reaction medium, thus providing the necessary species for the crystallization of MDAP-2. After 24 h, crystals typical of MDAP-1 have completely disappeared and a new phase is obtained, as evidenced by X-ray diffraction. The X-ray powder pattern of MDAP-2 shows strong similarities with the pattern of $\text{AlPO}_4\text{-21}$ (AWO framework type), suggesting that the structure of MDAP-2 could be closely related to that of $\text{AlPO}_4\text{-21}$.

The P/Al ratio in the synthesis gel is also critical for the formation of MDAP-2. For $\text{P/Al} > 1.5$, MDAP-2 is never obtained pure and is always contaminated by unknown phases. These phases have not yet been clearly identified and additional syntheses are necessary to isolate pure compounds for structure analysis.

Characterization and structure description of MDAP-1: chemical analysis of MDAP-1 gives 14 wt% aluminum and 21 wt% phosphorus, which corresponds to a molar ratio $\text{Al/P} = 0.76$, in excellent agreement with the value obtained from structure determination (Table 1). The ^1H – ^{13}C CP/MAS NMR spectrum (not shown) shows 3 distinct signals at 25, 35 and 47 ppm, along with shoulders at 23 and 38 ppm. Comparing this spectrum with that of *N*-methyl-1,3-propanediamine in acidic solution allows us to conclude that the molecule is incorporated intact in the structure and certainly doubly protonated. A thermogravimetric experiment shows that organic molecules decompose around 400 °C, with a unique weight loss corresponding to approximately 22 wt% (theoretical value 22.6 wt%). The organic-free material is totally amorphous, as evidenced by X-ray diffraction.

The structure of MDAP-1 consists of aluminophosphate layers separated by and connected to doubly protonated MDAP molecules. The unit cell contains 3 crystallographically non-equivalent Al sites. All aluminum atoms are tetrahedrally coordinated to 4 oxygen atoms, linking adjacent P atoms in the layers. This was confirmed by Solid-State NMR: the ^{27}Al spectrum of MDAP-1 consists in a unique signal at ca. 40 ppm, characteristic of Al atoms in a tetrahedral environment (not shown). Al–O bond lengths and O–Al–O bond angles are in the range of 1.63(1)–1.79(1) Å and 103.3(7)–116.5(7)°, respectively, which are typical of 4-coordinate Al atoms in crystalline aluminophosphates (Table 3). The four crystallographically distinct P atoms share three oxygens with adjacent Al atoms and possess

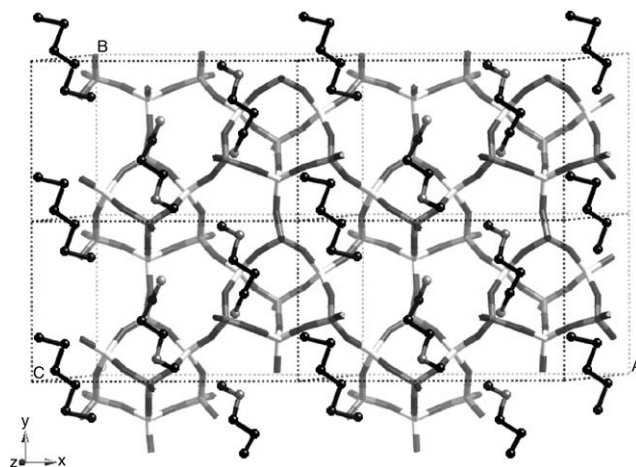


Fig. 2. Aluminophosphate layer and template molecules in MDAP-1 viewed along the (001) direction (C atoms: dark spheres, N atoms: light spheres, P tetrahedra: dark gray, Al tetrahedra: light gray). Half of MeDAP molecules are shown as *n*-hexane molecules (see text).

one P = O group. AlO_4 and $\text{PO}_3(=\text{O})$ tetrahedra alternate to form a two-dimensional network with a 4×6 net parallel to the *ab* plane (Fig. 2). Although 4×6 nets are relatively common in 2D layered aluminophosphates with $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$ stoichiometry, the sheet structure of MDAP-1 is unique and has never been reported. It is constructed from rows of capped six-membered rings, running parallel to the *b*-axis and connected via bridging oxygen atoms. The orientation of the capped P = O groups in a row is opposite to those of its neighboring rows. Such capped 6-MR units have been found in many 2D layered aluminophosphates. However, in most of these compounds, each capped 6-MR is connected to only 4 neighbors, thus delimiting a $4 \times 6 \times 8$ net. In MDAP-1, the originality of the network results from the fact that each capped 6-MR is linked to six neighbors.

Two types of doubly protonated organic molecules are located in the interlayer space and interact with oxygen atoms in the sheets via hydrogen bonding interactions. Molecules of the first type represent two thirds of organic molecules and occupy well-defined positions in the unit cell. Each of the two nitrogen atoms of the molecule interacts with one oxygen in the upper layer and one oxygen in the lower layer (Fig. 3a), with H-bond distances: $\text{N}(2)\dots\text{O}(16) = 2.72(2)$ Å, $\text{N}(2)\dots\text{O}(14) = 2.81(2)$ Å, $\text{N}(6)\dots\text{O}(16) = 2.88(2)$ Å and $\text{N}(6)\dots\text{O}(8) = 2.65(1)$ Å. These distances correspond to values usually found in layered aluminophosphates. The last-third of molecules is disordered. These molecules sit on a symmetry center of the crystal, though the MDAP molecule itself does not possess a center of symmetry. As mentioned in the experimental section, molecules are modeled by *n*- C_6 chains and occupy average positions in the interlayer space. Thus, distances between the carbon (nitrogen) atoms of the

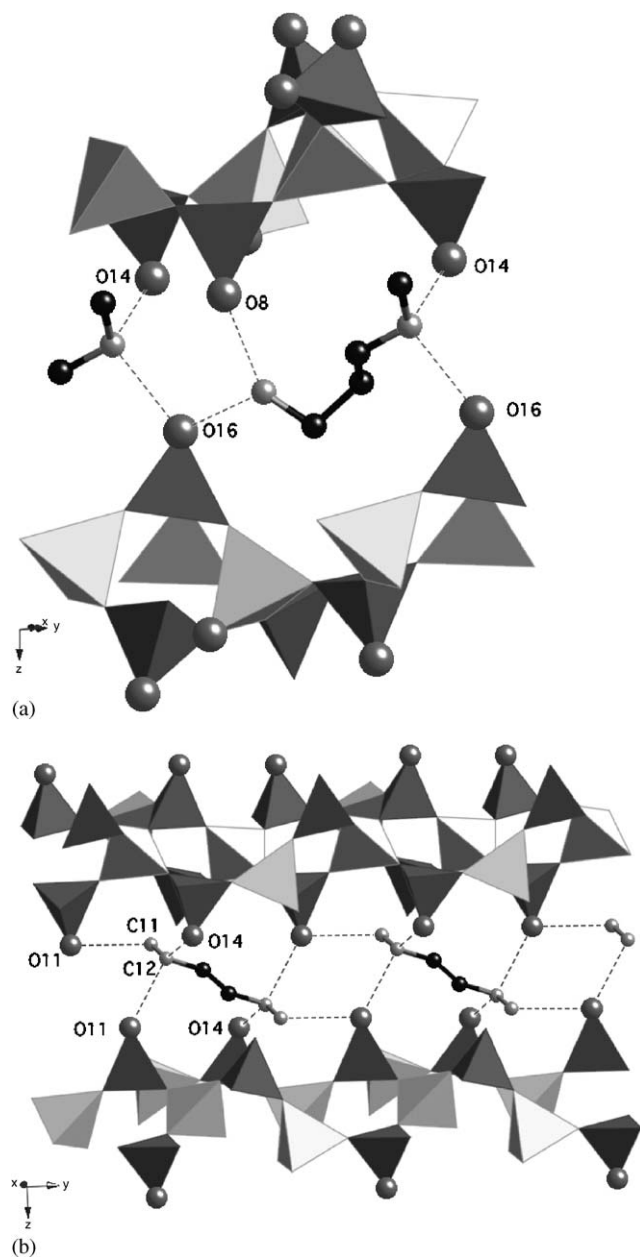


Fig. 3. Hydrogen bond scheme between ordered (a) and disordered (b) organic molecules and aluminophosphate sheets in MDAP-1 (P atoms: dark tetrahedra, Al atoms: light tetrahedra).

chain and oxygens of the aluminophosphate sheets can only be roughly estimated (Fig. 3b).

Characterization and structure description of MDAP-2: The chemical analysis of MDAP-2 gives Al/P = 0.99, in excellent agreement with the value obtained from the empirical formula in Table 4. The four major signals observed at ca. 24, 33, 39 and 44 ppm in the ^1H - ^{13}C CP/MAS NMR spectrum of the product (not shown) could be assigned to the four carbon atoms of the organic molecule, which indicates that MeDAP molecules are incorporated intact in the structure. Some peaks,

particularly that at 33 ppm, are clearly split and correspond to several crystallographically non-equivalent positions for the templating molecules. Thermogravimetric analysis of MDAP-2 shows a unique weight loss around 450 °C, corresponding to ca. 12.5 wt%. This value indicates that MDAP and water molecules are removed simultaneously from the pores (expected value 12.34 wt%). After removal of these molecules, the XRD pattern is characteristic of AlPO_4 -25, an aluminophosphate generally obtained upon calcination of AlPO_4 -21.

Actually, the structure of MDAP-2 is closely related to that of the microporous aluminophosphate AlPO_4 -21. The structure of AlPO_4 -21 (AWO framework type) was first reported by Bennett et al. [65] and Parise et al. [66]. AlPO_4 -21 could be obtained using various templating molecules, and crystallographic data reported in Table 4 are very similar to those reported by Parise et al. for AlPO_4 -21(en), synthesized with ethylenediamine [64]. The AWO framework-type contains infinite chains of edge-sharing 3- and 5-rings, connected together to form two-dimensional sheets with a $3 \times 4 \times 5 \times 8$ net. These sheets are bonded together in the perpendicular direction by crankshaft-shaped AlPO_4 chains, and the obtained network contains a three-dimensional pore system defined by 8-rings. All 3-rings units contain one tetrahedral P atom and two trigonal bipyramidal Al atoms sharing a hydroxyl group. This hydroxyl group neutralizes the charge of organic molecules located in the channels of the aluminophosphate.

In MDAP-2, one half of one of the trigonal bipyramids (atom Al(3)) is transformed into an octahedron by coordination of a water molecule on the Al atom (Fig. 4). As a consequence, hydroxyl groups present in 3-rings units bridge either 2 trigonal bipyramids or one bipyramid and one octahedron. The corresponding octahedron is highly distorted, the Al(3)–O(1W) distance (2.2 Å, see Table 6) being much longer than the others (1.806(4)–1.908(5) Å). A very

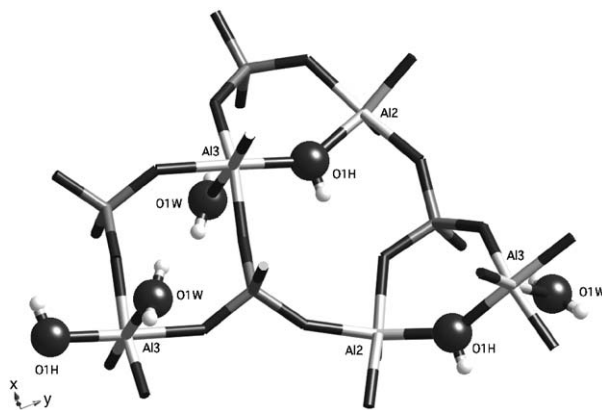


Fig. 4. Detail of the framework of MDAP-2 showing the partially occupied water position OW1 and the OH group (OH1) associated with the penta and hexacoordinated Al atoms.

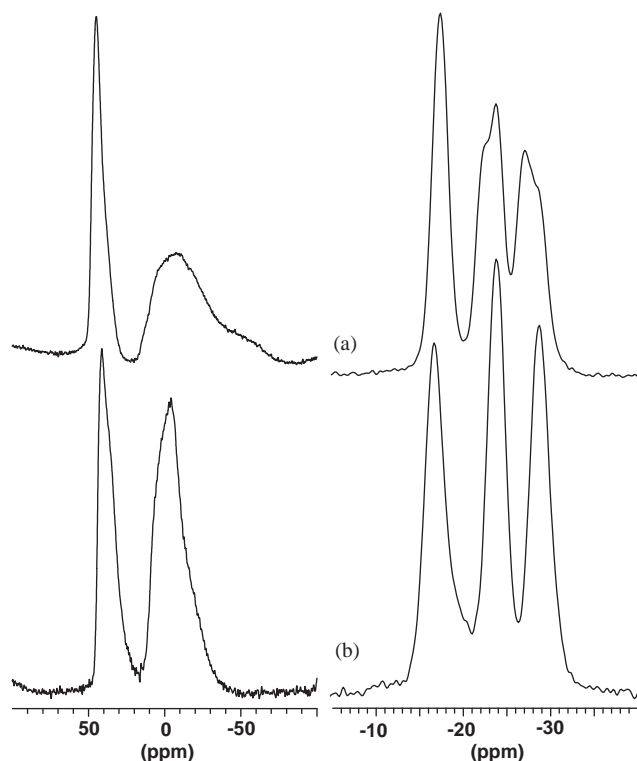


Fig. 5. ^{27}Al (left) and ^{31}P (right) NMR spectra of MDAP-2 (a) and $\text{AlPO}_4\text{-21}$ synthesized using N,N,N',N' -tetramethylethylenediamine (b).

similar situation is observed for $\text{AlPO}_4\text{-21(en)}$, if, in contrast to the interpretation of Parise et al. [66], one considers one of the disordered N -atoms of the ethylenediamine molecule as a sixth ligand of their $\text{Al}(2)$ atom ($\text{Al}(2) \dots \text{N}$ distance = 2.28 Å). The presence of an additional water molecule on $\text{Al}(3)$ was confirmed by ^{27}Al NMR (Fig. 5). The ^{27}Al NMR spectrum of MDAP-2 shows 2 main signals at ca. 40 and -10 ppm. The narrow line at 40 ppm can be unambiguously assigned to the tetrahedral $\text{Al}(1)$ atom. The other line is extremely broad and lies between +20 and -80 ppm. In the case of $\text{AlPO}_4\text{-21}$ synthesized with N,N,N',N' -tetramethylethylenediamine, the NMR signal around -10 ppm, which corresponds to the two 5-coordinate Al atoms in the framework, is relatively narrow (Fig. 5). In MDAP-2, the broad signal is interpreted as the superposition of two NMR lines attributed to 5- and 6-coordinate Al species, respectively. As in $\text{AlPO}_4\text{-21}$ synthesized with N,N,N',N' -tetramethylethylenediamine, the ratio between signals at ca. -10 and 40 ppm is close to 2, in agreement with the chemical formula of the aluminophosphate. However, due to the broadness and overlapping of the signals, it was not possible to estimate the ratio between 5- and 6 coordinate Al species. Broad signals like those observed in the spectrum of MDAP-2 usually characterize Al species with strong second-order quadrupolar coupling constants (C_Q) values. Such high C_Q values generally result

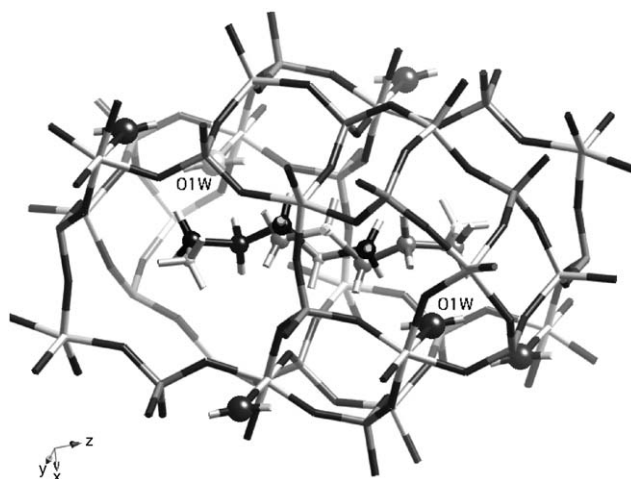


Fig. 6. Structure of MDAP-2 showing the arrangement of template and water molecules in the channels (see text).

from a highly distorted geometry around the Al atom, which supports the existence of the long $\text{Al}(3)\text{-O}(1\text{W})$ bond in the octahedron.

Templating molecules lie in the channels along the [001] direction. As seen in Fig. 6, the template is disordered because the molecule sits around a center of symmetry. The center of symmetry is located between the two N atoms and generates two symmetric MDAP molecules, each of them being half occupied. A second center of symmetry is present between the terminal N atoms of two molecules. The distance between the oxygen atom of the additional water molecule and the C(2) atom of the organic molecule (2.76 Å) is too short for a C–O contact. Therefore, the templating molecule and the water molecule cannot be present at the same time, and both positions are only half occupied. In Fig. 6, a possible arrangement is indicated. When the dimmed MeDAP molecule is present only the dimmed water molecule OW1 can be present and vice-versa. The unit cell contains the same number of MDAP molecules as there are water molecules attached to the octahedral Al. By contrast, there are only half as many template molecules as OH groups, but the neutrality of the framework is maintained because the diamine is doubly protonated. The localization of the template and its distribution in the channels are similar to those previously reported for $\text{AlPO}_4\text{-21(en)}$. In this compound, ethylenediamine molecules are also statically distributed over two positions. However, when one of the positions is not occupied, the aluminum atom in the 3-rings unit does not coordinate an additional water molecule.

If the template and water arrangement is randomly distributed, the symmetry will be locally reduced. The local reduction of the symmetry could be effectively

observed by solid state NMR. The ^{31}P MAS NMR spectrum of $\text{AlPO}_4\text{-21}$ synthesized using N,N,N',N' -tetramethylethylenediamine as templating molecule shows 3 distinct peaks assigned to the three crystallographically non equivalent P sites (Fig. 5). It has been reported that the position of these peaks could slightly vary, depending on the nature of the templating molecule in the channels. In the spectrum of MDAP-2, peaks are clearly split, particular those at ca. -24 and -29 ppm. This is the result of two different environments for P atoms in the framework, which is a direct consequence of the disorder of the template and water molecule.

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References

- [1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, *J. Am. Chem. Soc.* 104 (1982) 1146.
- [2] R.H. Jones, J.M. Thomas, R. Xu, Q. Huo, Y. Xu, A.K. Cheetham, D.J. Bieber, *J. Chem. Soc. Chem. Commun.* (1990) 1170.
- [3] S. Oliver, A. Kuperman, A. Lough, G.A. Ozin, *Chem. Mater.* 8 (1996) 2391.
- [4] I.D. Williams, J. Yu, Q. Gao, J. Chen, R. Xu, *J. Chem. Soc. Chem. Commun.* (1997) 1273.
- [5] D.J. Williams, J.S. Kruger, A.F. McLeroy, A.P. Wilkinson, J.C. Hanson, *Chem. Mater.* 11 (1999) 2241.
- [6] W. Yan, J. Yu, Z. Shi, R. Xu, *Inorg. Chem.* 40 (2001) 379.
- [7] N. Rajic, N. Zabukovec Logar, A. Golobic, V. Kaucic, *J. Phys. Chem. Solids* 64 (2003) 1097.
- [8] R.H. Jones, J.M. Thomas, R. Xu, Q. Huo, A.K. Cheetham, A.V.J. Powell, *J. Chem. Soc. Chem. Commun.* (1991) 1266.
- [9] A.M. Chippindale, A.V. Powell, L.M. Bull, R.H. Jones, A.K. Cheetham, J.M. Thomas, R. Xu, *J. Solid State Chem.* 96 (1992) 199.
- [10] J.M. Thomas, R.H. Jones, R. Xu, J. Chen, A.M. Chippindale, S. Natarajan, A.K. Cheetham, *J. Chem. Soc. Chem. Commun.* (1992) 929.
- [11] R.H. Jones, A.M. Chippindale, S. Natarajan, J.M. Thomas, *J. Chem. Soc. Chem. Commun.* (1994) 565.
- [12] K.R. Morgan, G. Gainsford, N.J. Millestone, *J. Chem. Soc. Chem. Commun.* (1995) 425.
- [13] P.A. Barrett, R.H. Jones, *J. Chem. Soc. Chem. Commun.* (1995) 1979.
- [14] D.A. Bruce, A.P. Wilkinson, M.G. White, J.A. Bertrand, *J. Chem. Soc. Chem. Commun.* (1995) 2059.
- [15] S. Oliver, A. Kuperman, A. Lough, G.A. Ozin, *J. Chem. Soc. Chem. Commun.* (1996) 1761.
- [16] I.D. Williams, Q. Gao, J. Chen, L. Ngai, Z. Lin, R. Xu, *J. Chem. Soc. Chem. Commun.* (1996) 1781.
- [17] D.A. Bruce, A.P. Wilkinson, M.G. White, J.A. Bertrand, *J. Solid State Chem.* 125 (1996) 228.
- [18] S. Oliver, A. Kuperman, A. Lough, G.A. Ozin, *Inorg. Chem.* 35 (1996) 6373.
- [19] K.R. Morgan, G.J. Gainsford, N.B. Milestone, *J. Chem. Soc. Chem. Commun.* (1997) 61.
- [20] Q. Gao, B. Li, J. Chen, S. Li, R. Xu, *J. Solid State Chem.* 129 (1997) 37.
- [21] A.M. Chippindale, A.R. Cowley, Q. Huo, R.H. Jones, A.D. Law, *J. Chem. Soc. Dalton. Trans.* 15 (1997) 2639.
- [22] S. Cheng, J.N. Tzeng, B.Y. Hsu, *Chem. Mater.* 9 (1997) 1788.
- [23] J. Yu, I.D. Williams, *J. Solid State Chem.* 136 (1998) 141.
- [24] M.A. Leech, A.R. Cowley, K. Prout, A.M. Chippindale, *Chem. Mater.* 10 (1998) 451.
- [25] L. Vidal, V. Gramlich, J. Patarin, Z. Gabelica, *Eur. J. Solid. State Chem.* 35 (1998) 345.
- [26] J. Yu, K. Sugiyama, K. Hiraga, N. Togashi, O. Terasaki, Y. Tanaka, S. Nakata, S. Qiu, R. Xu, *Chem. Mater.* 10 (1998) 3636.
- [27] N. Togashi, J. Yu, S. Zheng, K. Sugiyama, K. Hiraga, O. Terasaki, W. Yan, S. Qiu, R. Xu, *J. Mater. Chem.* 8 (1998) 2827.
- [28] L. Vidal, C. Marichal, V. Gramlich, J. Patarin, Z. Gabelica, *Chem. Mater.* 11 (1999) 2728.
- [29] P. Lightfoot, Z.A.D. Lethbridge, R.E. Morris, D.S. Wragg, P.A. Wright, A. Kvik, G.B.M. Vaughan, *J. Solid State Chem.* 143 (1999) 74.
- [30] A.M. Chippindale, R.I. Walton, *J. Solid State Chem.* 145 (1999) 731.
- [31] J. Yu, J. Li, K. Sugiyama, N. Togashi, O. Terasaki, K. Hiraga, B. Zhou, S. Qiu, R. Xu, *Chem. Mater.* 11 (1999) 1727.
- [32] K.O. Kongshaug, H. Fjellvag, K.P. Lillerud, *Microporous Mesoporous Mater.* 32 (1999) 17.
- [33] K.O. Kongshaug, H. Fjellvag, K.P. Lillerud, *J. Mater. Chem.* 9 (1999) 1591.
- [34] B. Wei, G. Zhu, J. Yu, S. Qiu, O. Terasaki, *Chem. Mater.* 11 (1999) 3417.
- [35] P. Feng, X. Bu, G.D. Stucky, *Inorg. Chem.* 39 (2000) 2.
- [36] H. Yuan, J. Chen, Z. Shi, W. Chen, Y. Wang, P. Zhang, J. Yu, R. Xu, *J. Chem. Soc. Dalton. Trans.* 13 (2000) 1981.
- [37] K. Maeda, A. Tuel, Ch. Baerlocher, *J. Chem. Soc. Dalton Trans.* 14 (2000) 2457.
- [38] H. Yuan, G. Zhu, J. Chen, W. Chen, G. Yang, R. Xu, *J. Solid State Chem.* 151 (2000) 145.
- [39] A. Tuel, V. Gramlich, Ch. Baerlocher, *Microporous Mesoporous Mater.* 41 (2000) 217.
- [40] W. Yan, J. Yu, Z. Shi, R. Xu, *J. Chem. Soc. Chem. Commun.* (2000) 1431.
- [41] A. Tuel, V. Gramlich, Ch. Baerlocher, *Microporous Mesoporous Mater.* 46 (2001) 57.
- [42] A. Tuel, V. Gramlich, Ch. Baerlocher, *Microporous Mesoporous Mater.* 47 (2001) 217.
- [43] W. Yan, J. Yu, Z. Shi, R. Xu, *Stud. Surf. Sci. Catal.* 35 (2001) 05-P-10 (CD-ROM).
- [44] A. Tuel, V. Gramlich, Ch. Baerlocher, *Microporous Mesoporous Mater.* 56 (2002) 119.
- [45] W. Yan, J. Yu, Y. Li, Z. Shi, R. Xu, *J. Solid State Chem.* 167 (2002) 282.
- [46] W. Tiely, Y. Long, P. Wenqin, *J. Solid State Chem.* 89 (1990) 392.
- [47] Q. Huo, R. Xu, S. Li, Z. Ma, J.M. Thomas, R.H. Jones, A.M. Chippindale, *J. Chem. Soc. Chem. Commun.* (1992) 875.
- [48] J. Yu, K. Sugiyama, S. Zheng, S. Qiu, J. Chen, R. Xu, Y. Sakamoto, O. Terasaki, K. Hiraga, M. Light, M.B. Hursthouse, J.M. Thomas, *Chem. Mater.* 10 (1998) 1208.
- [49] Y. Xu, B. Zhang, X. Chen, S. Liu, C. Duan, X. You, *J. Solid State Chem.* 145 (1999) 220.
- [50] W. Yan, J. Yu, R. Xu, G. Zhu, F. Xiao, Y. Han, K. Sugiyama, O. Terasaki, *Chem. Mater.* 12 (2000) 2517.

- [51] K. Maeda, A. Tuel, S. Caldarelli, Ch. Baerlocher, *Microporous Mesoporous Mater.* 39 (2000) 465.
- [52] W. Yan, J. Yu, R. Xu, Y. Han, K. Sugiyama, O. Terasaki, *Stud. Surf. Sci. Catal.* 135 (2001) 05-P-09 (CD-ROM).
- [53] W. Yan, J. Yu, Z. Shi, P. Miao, K. Wang, Y. Wang, R. Xu, *Microporous Mesoporous Mater.* 50 (2001) 151.
- [54] K. Wang, J. Yu, Z. Shi, P. Miao, W. Yan, R. Xu, *J. Chem. Soc. Dalton Trans.* 12 (2001) 1809.
- [55] S. Natarajan, J.C.P. Gabriel, A.K. Cheetham, *J. Chem. Soc. Chem. Commun.* (1996) 1415.
- [56] K.O. Kongshaug, H. Fjellvag, K.P. Lillerud, *Microporous Mesoporous Mater.* 40 (2000) 313.
- [57] J.B. Parise, *J. Chem. Soc. Chem. Commun.* (1984) 1449.
- [58] S.T. Wilson, B.M. Lok, C.A. Messina, E.M. Flanigen, in: D. Olson, A. Bisio (Eds.), *Proceedings of the Sixth International Zeolite Conference*, Reno, Butterworths, Guildford, UK, 1984, p. 97.
- [59] U. Lohse, E. Löffler, K. Kosche, J. Janchen, B. Parltitz, *Zeolites* 13 (1993) 549.
- [60] Q. Gao, S. Li, R. Xu, *J. Chem. Soc. Chem. Commun.* (1994) 1465.
- [61] G.M. Sheldrick, *SHELXTL PLUS*, program for the solution of crystal structures, University of Göttingen, Germany, 1986.
- [62] Ch. Baerlocher, *X-ray Rietveld System XRS-82*, Institute für Kristallographie und Petrographie, ETH, Zurich, Switzerland, 1982.
- [63] G.M. Sheldrick, *SHELX 93*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.
- [64] A. Tuel, unpublished work.
- [65] J.M. Bennett, J.M. Cohen, G. Artioli, J.J. Pluth, J.V. Smith, *Inorg. Chem.* 24 (1985) 188.
- [66] J.B. Parise, C.S. Day, *Acta Crystallogr. C* 41 (1985) 515.