

The templated synthesis and structure determination by synchrotron microcrystal diffraction of the novel small pore magnesium aluminophosphate STA-2 †

Graham W. Noble,^a Paul A. Wright^{*,a} and Åke Kvick^{*,b}

^a School of Chemistry, University of St. Andrews, The Purdie Building, North Haugh, St. Andrews, Fife, UK KY16 9ST

^b ESRF, BP220, 38043 Grenoble, CEDEX, France

A novel microporous aluminophosphate, STA-2, has been prepared by hydrothermal synthesis in the presence of the rationally designed template, $[(C_7H_{13}N)(CH_2)_4(NC_7H_{13})]^{2+}$ and in the absence and presence of sodium ions. Using sodium ions in the preparation results in the synthesis of crystals of STA-2 up to 50 μm in dimension, of sufficient quality to be studied by the new technique of microcrystal diffraction at a synchrotron X-ray source and with an area detector. Phase STA-2 is found to have symmetry $R\bar{3}$, $a = 12.726(2)$, $c = 30.939(6)$ Å at 200 K. Structure solution reveals it to be a small pore solid of the family of structural polytypes made up by the stacking of six-membered $Al_3P_3O_6$ rings, and possesses the most complex regular stacking sequence of any such structure known, which can be represented as ABAACACCB \bar{C} B \bar{B} in the usual convention. The stacking sequence is controlled by the size and shape of the templating molecule, the position of which, determined from the single-crystal diffraction, makes a close fit with the organic framework. Compound STA-2 is stable to thermal removal of the template molecule and has potential as a solid acid catalyst.

The use of organic bases and alkylammonium ions as structure-directing agents, or templates, for the crystallisation of microporous solids is one of the most fruitful routes to the synthesis of solids with desired features for adsorption and catalysis. For example, 33 different structural types of aluminophosphate-based zeotypes have been prepared by variation of the organic species and the conditions of temperature and pH used in the hydrothermal syntheses.¹⁻³ Each structure type has a unique combination of cages and channels, and therefore individual material properties. Our approach to broadening still further this range is to design and synthesise in our own laboratories organic bases likely to template new and useful inorganic structures. To this end we have explored the uses of templates of the form $[(CH_3)_3N(CH_2)_n(CH_3)_3]^{2+}$ (ref. 4) and $[(C_7H_{13}N)(CH_2)_n(NC_7H_{13})]^{2+}$,³ with $n = 3-10$, in the synthesis of magnesium aluminophosphates (MgAPOs). These templates are ideally suited to the preparation of aluminophosphates with cavities or channels bound by 12-membered rings. Using the latter series we synthesised for the first time two phases that were identified as being novel on the basis of their unique powder diffraction patterns, and which we reported as phases STA-1 and STA-2 (St. Andrews). Phase STA-1 was available as crystals of dimensions of up to 40 μm , which were large enough for single-crystal diffraction, and STA-1 became the first microporous framework structure to be solved by microcrystal diffraction at a synchrotron source.³ This method has enormous potential for crystal chemical investigations⁵⁻⁷ because many phases, including the majority of microporous ones, cannot be prepared as large enough crystals for conventional laboratory X-ray diffractometry. Phase STA-2, however, was only prepared as a powder of sub-micron dimensions, and its structure remained unsolved. In this paper, we report how microcrystals of STA-2 of sufficient quality for synchrotron-based microcrystal diffraction have been grown, and the structure has become the second new tetrahedrally co-ordinated microporous solid to be solved in this way.

† Dedicated to Professor Sir John Meurig Thomas on the occasion of his 65th birthday.

Experimental

Diquinuclidinium templates of formula $[(C_7H_{13}N)(CH_2)_n(C_7H_{13}N)]Br_2$, $n = 4$ or 5, were prepared by the Menshutkin reaction from quinuclidine and dibromoalkanes and converted into the hydroxide form as described previously.³ These were then used as structure-directing agents in the synthesis of MgAPOs by the sequential addition of aluminium hydroxide, magnesium acetate tetrahydrate, orthophosphoric acid and the diquinuclidinium hydroxide to distilled water using a mole ratio of 0.9:0.1:1.0:0.4:40 respectively. Once prepared the gel was transferred to a stainless steel, PTFE-lined autoclave and heated at 190 °C for 48 h. Preparations were also performed using unconverted template (in the bromide form) and additional sodium hydroxide in the stoichiometric ratio of 1:2. All chemicals were obtained from Aldrich except for the phosphoric acid (85 wt %) which was obtained from Prolabo.

Characterisation of the as-prepared and calcined STA-2 was performed initially using X-ray powder diffraction using a STOE STADIP laboratory diffractometer using Cu-K α 1 radiation with a primary monochromator. High resolution X-ray powder diffraction data were collected at room temperature in capillary mode on BM16 at the ESRF, Grenoble, on a sample of the as-prepared MgAPO-STA-2 powder. Thermogravimetric analysis (TGA) of the powder sample of STA-2 was performed using an SDT 2960 analyser from TA Instruments. Carbon-13 magic angle spinning (MAS) NMR spectra were obtained using a Bruker 400 MSL spectrometer. The ¹³C NMR of the template within STA-2 (δ 64.4, 56.4, 24.3 and 19.9 for the $n = 4$ template) corresponded closely with that observed with higher resolution in D₂O solution (δ 63.19, 54.79, 23.30 and 18.98). The chemical analysis of microcrystals of STA-2 was performed by selected area energy dispersive analysis of X-rays in an electron microscope (EDX). To check the stability of STA-2 with respect to template removal, a sample was calcined at 550 °C for 4 h in flowing nitrogen and 8 h in oxygen, the temperature having been raised to 550 °C using a ramp rate of 5 °C min⁻¹, and the microporosity was measured volumetrically using nitrogen adsorption at liquid nitrogen temperature.

Structure solution

Single-crystal diffraction data were collected on the Materials Science Beamline (ID-11, BL2) at the ESRF, Grenoble.^{8,9} A well formed rhombohedral crystal with edge lengths of 50 μm was glued to a fine glass fibre and mounted on the 3 circle fixed kappa Siemens diffractometer fitted with a Siemens SMART CCD detector. The X-ray wavelength used was 0.512 \AA obtained from a liquid nitrogen-cooled double crystal Si(111) monochromator. The wavelength was calibrated at an appropriate X-ray absorption edge. The crystal was cooled to 200 K with an Oxford Cryostream nitrogen gas flow system and the data were collected using the Siemens SMART CCD system. 900 Frames with an oscillation angle of 0.2° were collected with an X-ray exposure time of 2 s per frame. The data were integrated and corrected with the Siemens software adapted for synchrotron use. The structure was solved using the direct methods programs in the SHELXTL program package.¹⁰ The data statistics strongly indicated the trigonal space group $R\bar{3}$ with an overall mean absorption ($E \times E - 1$) value of 1.046; centric space groups have an expected value of 0.968 whereas non-centric space groups have a much lower value of 0.736. A total of 7925 reflections with a mean intensity/ σ (intensity) of 8.6 were obtained after integration. In the space group $R\bar{3}$ these represented 4287 reflections and 3673 had intensities above 3σ . Symmetry averaging yielded 1993 reflections with an inter-consistency index $R(\text{int})$ of 0.077. The resolution limit was 0.78 \AA . The indexing in the hexagonal cell resulted in a unit cell: $a = b = 12.726(2)$ and $c = 30.939(6)$ \AA , $F(000) = 1635$, $\mu = 0.19 \text{ mm}^{-1}$.

The structure could be refined successfully in this space group to an R factor $R(F) = 0.0757$ for 1593 reflections above 4σ and 0.0981 for all 1993 reflections. The goodness of fit $S = 1.307$ and the total number of refined parameters was 142. The largest extra-residual in the final difference map was 0.9 $e \text{ \AA}^{-3}$. No effort was made to locate the magnesium, which is expected on the basis of experience to substitute randomly for aluminium in the structure. All parameters were well behaved with the exception of those of one of the chain C-atoms in the template molecule. The atom was treated as three-fold disordered with fixed coordinates obtained from the Fourier-difference map. The isotropic temperature factor was allowed to vary. The structure solution was also tried in the triclinic space groups $P1$ and $P\bar{1}$, and although the refinement in $P\bar{1}$ was successful [$R(F) = 0.1061$ for 4287 reflections and 428 varied parameters], the standard deviations were twice those obtained in $R\bar{3}$ and the apparent disorder in the central part of the template molecule was still retained. Hydrogen-atom positions were generated using the TEXSAN suite of programs.¹¹ Attempts to refine them produced no significant improvement in $R(F)$ so the geometric positions were retained.

CCDC reference number 186/735.

Results and Discussion

Phase STA-2 was prepared from a gel of composition 0.4 $\text{R}(\text{OH})_2 : 0.1 \text{Mg}(\text{O}_2\text{CMe})_2 : 0.9 \text{Al}(\text{OH})_3 : \text{H}_3\text{PO}_4 : 40 \text{H}_2\text{O}$, when R represents the diquinuclidinium ion and the interconnecting chain of the template contained four or five methylene groups. The solid formed when the alkylammonium ion was used in its hydroxide form was indicated by scanning electron microscopy to consist of sub-micron particles with a poorly defined crystal shape, and laboratory X-ray powder diffraction [Fig. 1(a)] revealed the presence of some amorphous material. Attempts to increase the magnesium content of the solid by raising the Mg/P ratio in the gel to 0.15:1 resulted in the co-crystallisation of MgAPO-56, and the two solids could not be separated. Pure STA-2 was also prepared as the aluminophosphate, the cobalt aluminophosphate and the silicoaluminophosphate by appropriate variation of the gel chemistry, and the properties of

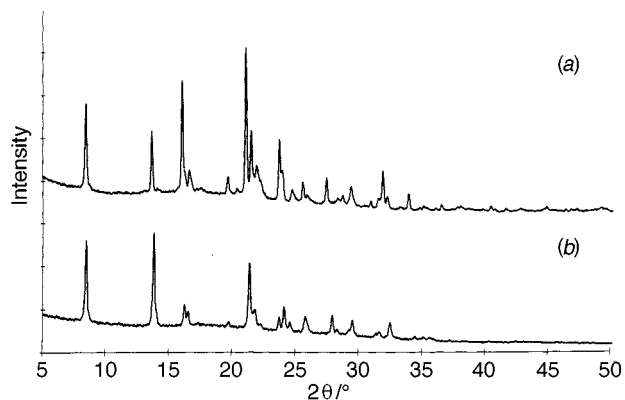


Fig. 1 Powder diffraction patterns of magnesioaluminophosphate STA-2 synthesised from the alkali free gel (a) as-prepared and (b) after calcination, using Cu-K α 1 radiation from a laboratory source

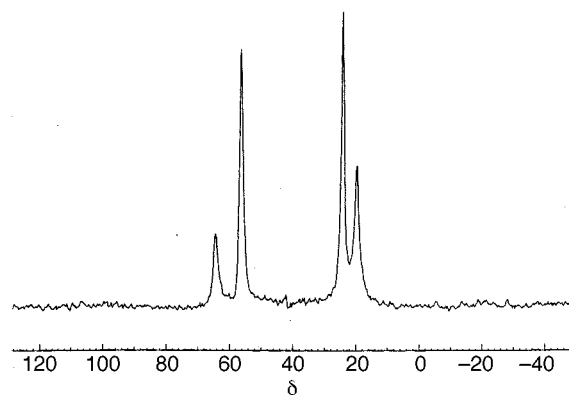


Fig. 2 Carbon-13 solid-state MAS NMR of the as-prepared MgAlPO-STA-2, showing that the included organic template remains intact

these materials will be reported later. Solid-state ^{13}C NMR of the MgAPO-STA-2, as-prepared, showed that the organic template had been incorporated intact (Fig. 2). Calcination of the sample in flowing oxygen was able to remove the template with retention of crystallinity [Fig. 1(b)]. Thermogravimetric analysis gave one weight loss peak at 100°C , presumably due to water loss, of 7.0 wt %, and a second, due to template removal, of 15.4 wt %. Nitrogen adsorption measurements on the calcined sample gave an isotherm mainly of Type I form, but also with some Type II characteristics, presumably because the particle size was very small and the external surface area was not negligible. From 'monolayer' or pore filling coverage, a void volume of $0.095 \text{ cm}^3 \text{ g}^{-1}$ was calculated from a mass/mass uptake of 0.084 g per g at $p/p_0 = 0.1$. However, we were not able to solve the structure from the powder diffraction data.

As part of a program of synthesis to examine the effects of alkali cations on the synthesis of MAPOs (and thereby to determine the necessity of converting the alkyl ammonium bromide into the hydroxide form using silver oxide) a hydrothermal synthesis was performed using as-prepared tetramethylene diquinuclidinium bromide and sodium hydroxide. The gel composition was adjusted so that the pH of the reaction gel was the same as that in the first set of experiments, performed in the absence of alkali-metal cations. Under these conditions, the product was a mixture of phases, including rhombs and hexagonal plates, of dimensions of up to 50 μm (Fig. 3). Powder diffraction indicated that the two crystal phases were MgAPO-56 and STA-2. The compound MgAPO-56 crystallised as well-formed hexagonal plates whereas STA-2 crystallised as rhombs of sufficient size and quality for micro-crystal diffraction and consequently a number of well formed crystals of STA-2 were chosen for examination at the ESRF at Grenoble. Selected area EDX chemical analysis on the STA-2 crystals indicated a framework composition close to $\text{Mg}_{0.15}$ -

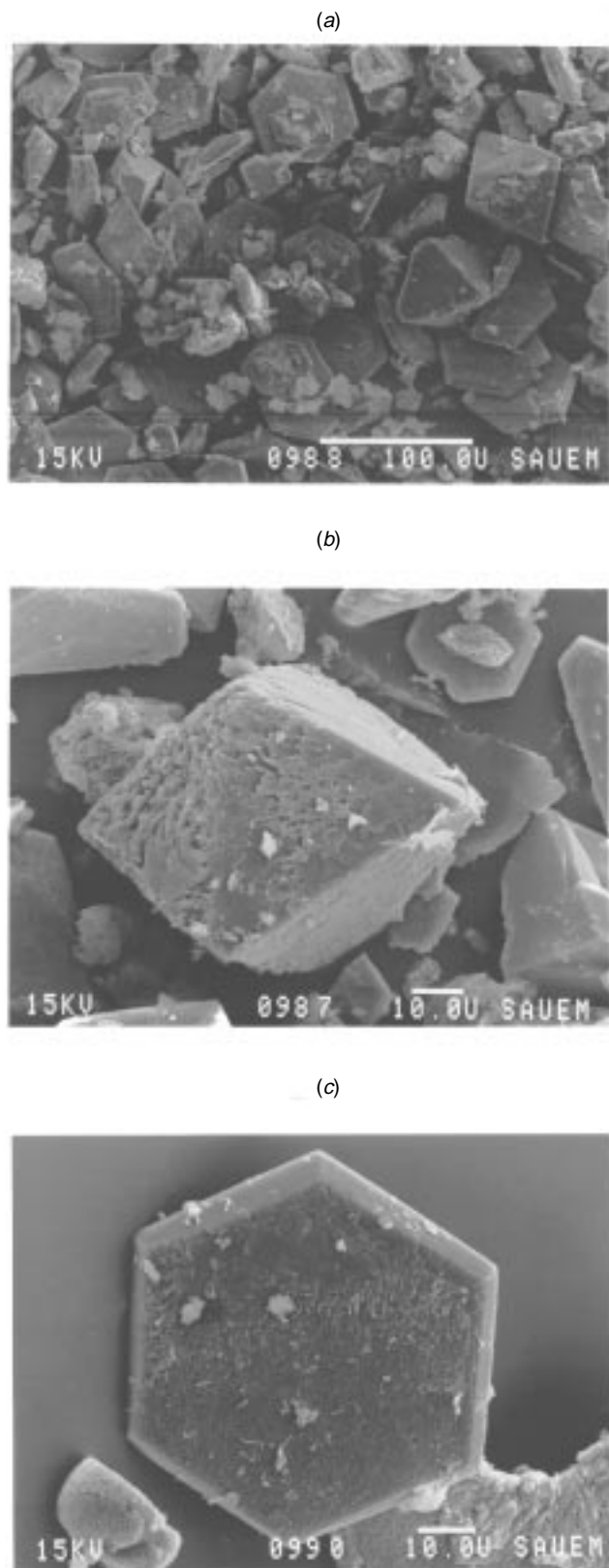


Fig. 3 Scanning electron micrographs of the separated coarse fraction of a preparation performed using sodium hydroxide to control the pH of the starting gel. (a) Mixture of MgAPO-56 and MgAPO-STA-2. (b) A single microcrystal of STA-2. (c) A single crystal of MgAPO-56

$\text{Al}_{0.85}\text{PO}_4$ in addition to traces of sodium. Assuming the template content to be similar to that measured on the powder samples, the as-prepared composition is likely to be $\text{Mg}_{0.15}\text{Al}_{0.85}\text{PO}_4 \cdot 0.083\text{R}^{2+} \cdot 0.625\text{H}_2\text{O}$, where the template charge is largely balanced by the negative charge on the framework.

Microcrystal diffraction was carried out at Grenoble at a temperature of 200 K in order to reduce the effects of thermal

Table 1 Atomic coordinates and principal mean square atomic displacements, U , for STA-2 at 200 K

Atom	x	y	z	$U_{\text{eq}}/\text{\AA}^2$
Al(1)	0.753 30(1)	0.757 22(13)	0.295 40(5)	0.016 20(40)
Al(2)	0.576 16(14)	0.902 30(14)	0.216 46(5)	0.020 34(41)
P(1)	0.577 83(12)	0.904 32(12)	0.114 44(5)	0.018 42(37)
P(2)	0.756 82(11)	0.001 27(10)	0.291 40(4)	0.015 12(36)
O(1)	0.613 76(11)	0.939 30(10)	0.161 68(4)	0.034 60(40)
O(2)	0.534 14(38)	0.753 25(36)	0.225 06(15)	0.033 95(36)
O(3)	0.792 83(38)	0.907 17(36)	0.293 95(17)	0.037 78(12)
O(4)	0.461 25(35)	0.927 99(41)	0.231 03(15)	0.035 33(41)
O(5)	0.701 43(39)	0.995 88(39)	0.247 20(15)	0.035 4(10)
O(6)	0.864 42(37)	0.122 40(36)	0.296 79(18)	0.041 9(12)
O(7)	0.668 92(44)	0.983 12(45)	0.326 74(16)	0.045 5(13)
O(8)	0.656 29(40)	0.009 23(38)	0.085 55(15)	0.035 64(38)
N(1)	0.000 00	0.000 00	0.102 48(42)	0.068 8(37)
C(1)	0.000 00	0.000 00	0.184 19(58)	0.098 5(71)
C(2)	-0.041 5(15)	0.082 7(14)	0.166 2(7)	0.121 6(53)
C(3)	-0.041 5(15)	0.078 7(14)	0.117 7(6)	0.118 6(53)
C(4)	-0.031 2	0.035 1	0.055 6	0.215 5(12)
C(5)	0.000 00	0.000 00	0.024 11(9)	0.188(17)
H(1)	0.000 0	0.000 0	0.214 7	—
H(2)	0.103 0	0.163 1	0.175 7	—
H(3)	-0.122 2	0.056 7	0.176 2	—
H(4)	0.009 0	0.158 0	0.106 9	—
H(5)	-0.122 6	0.049 8	0.107 5	—
H(6)	0.007 5	0.120 8	0.054 0	—
H(7)	-0.116 4	0.001 7	0.054 0	—
H(8)	0.085 1	0.032 2	0.024 9	—
H(9)	-0.021 1	0.026 3	-0.001 5	—

Symmetry $R\bar{3}$ (hexagonal setting), $a = 12.726(2)$, $c = 30.939(6)$ Å, λ 0.512 Å, T 200 K, hydrogen atom coordinates generated by the TEXSAN suite.¹¹

disorder of the included template. The as-prepared rather than the calcined sample was chosen for analysis because we were interested not only in the framework structure but also in the role the template molecules played in controlling the crystallisation. The structure was solved as detailed in the Experimental section. The atomic coordinates are given in Table 1 and relevant framework and template interatomic distances given in Table 2. Strict ordering of aluminium and phosphorus in the tetrahedral cation sites is revealed by the bond lengths; the average Al–O distances are 1.72 Å for Al(1) and 1.73 Å for Al(2) and the average P–O distances are 1.50 Å for P(1) and 1.49 Å for P(2).

To prove that the structure determined from the single-crystal diffraction is essentially the same as that of the powder sample of STA-2 prepared without alkali-metal cations the powder diffraction data collected at the ESRF were matched using the structural parameters determined by microcrystal diffraction, allowing the unit cell parameters and instrumental parameters (peak half-width, zero-point) to vary. The fit [Fig. 4, $R_{\text{wp}} = 0.114$, $R_p = 0.084$, with unit cell parameters at room temperature of $a = 13.0121(7)$ and $c = 30.406(2)$ Å] is sufficiently close to confirm it is the same phase, although further refinement is required to take into account the effects of particle size broadening and of additional structural disorder.

The framework structure (Fig. 5) can be viewed in terms of the building units and cavities that are arranged in columns parallel to the c axis [Fig. 5(b)] (in the hexagonal setting of the rhombohedral cell), with adjacent columns offset by $c/3$. Two ‘cancrinite’ or ϵ -cages, rotated by 60 °C with respect to each other, sandwich a double six-membered ring unit. Above and below this unit along c are cavities, approximately 17 Å in length, that contain the template cations. For small molecules, access to six other cavities is possible through eight-membered rings. Each column, as described above, is adjacent to six others, which are identical and shifted by $\pm c/3$, alternatively, going round the original column.

Table 2 Selected bond distances (Å) and angles (°)

Inorganic framework			
Al(1)–O(3)	1.714(4)	Al(2)–O(1)	1.760(5)
Al(1)–O(6)	1.687(4)	Al(2)–O(2)	1.715(4)
Al(1)–O(7)	1.731(5)	Al(2)–O(4)	1.711(4)
Al(1)–O(8)	1.751(5)	Al(2)–O(5)	1.722(5)
O(3)–Al(1)–O(6)	111.0(2)	O(1)–Al(2)–O(2)	109.8(2)
O(3)–Al(1)–O(7)	111.9(3)	O(1)–Al(2)–O(4)	110.3(2)
O(3)–Al(1)–O(8)	109.2(2)	O(1)–Al(2)–O(5)	108.2(2)
O(6)–Al(1)–O(7)	108.3(3)	O(2)–Al(2)–O(4)	110.3(2)
O(6)–Al(1)–O(8)	106.3(2)	O(2)–Al(2)–O(5)	110.4(2)
O(7)–Al(1)–O(8)	110.1(2)	O(4)–Al(2)–O(5)	107.8(2)
P(1)–O(1)	1.529(5)	P(2)–O(3)	1.483(4)
P(1)–O(2)	1.492(4)	P(2)–O(5)	1.524(5)
P(1)–O(4)	1.494(4)	P(2)–O(6)	1.473(4)
P(1)–O(8)	1.498(5)	P(2)–O(7)	1.497(5)
O(1)–P(1)–O(2)	109.7(3)	O(3)–P(2)–O(5)	109.5(3)
O(1)–P(1)–O(4)	110.1(3)	O(3)–P(2)–O(6)	109.8(3)
O(1)–P(1)–O(8)	110.0(3)	O(3)–P(2)–O(7)	110.2(3)
O(2)–P(1)–O(4)	108.6(3)	O(5)–P(2)–O(6)	108.4(3)
O(2)–P(1)–O(8)	110.1(3)	O(5)–P(2)–O(7)	110.8(3)
O(4)–P(1)–O(8)	108.3(3)	O(6)–P(2)–O(7)	108.1(3)
Organic bonds			
C(1)–C(2)	1.50(2)	N(1)–C(4)	1.62(1)
C(2)–C(3)	1.50(2)	C(4)–C(5)	1.22(2)
C(3)–N(1)	1.43(1)	C(5)–C(5)	1.49(5)

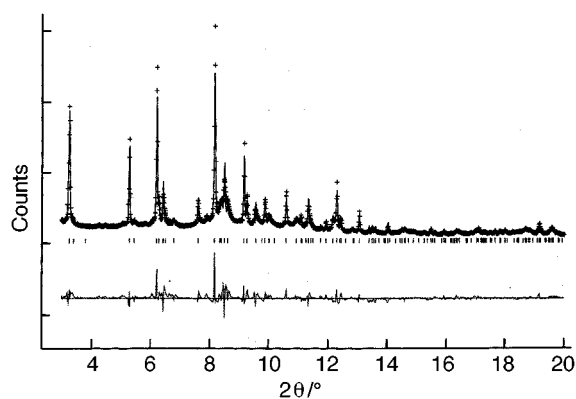


Fig. 4 Fitted experimental X-ray powder diffraction profile, $\lambda = 0.6004 \text{ \AA}$, collected at station BM16, at the ESRF, Grenoble. The data are matched using atomic coordinates derived from microcrystal diffraction, with the unit cell and profile parameters permitted to vary. Crosses represent observed data, the unbroken line the simulated profile and the broken line the difference ($R_{wp} = 0.114$, $R_p = 0.084$)

The framework structure of STA-2 is one of the family of zeolitic structure types, of which there are now 14 known (Table 3) which are best considered as made up of flat six-membered rings (the common description of rings made up of six tetrahedral cations and six oxygens) that are parallel to a hexagonal ab plane with lattice repeats of around 13 \AA . These six-rings may have their centres at only one of the $(0,0)$, $(\frac{1}{3}, \frac{1}{3})$ or $(\frac{2}{3}, \frac{2}{3})$ positions in the ab plane, and can link to other sets of six-rings above and below them in the c direction that may also have their centres at $(0,0)$, $(\frac{1}{3}, \frac{1}{3})$ or $(\frac{2}{3}, \frac{2}{3})$, which can be denoted as the A, B and C positions. The structures that are produced are then conveniently described in terms of repeating stacking sequences;¹³ for example cancrinite has the sequence AB, chabazite the sequence AABBC and AIPO-56 the sequence AABBCBB. Using this nomenclature, the framework structure of STA-2 has the sequence ABAACACCBCBB, the most complex of any yet reported. The energy differences between the different polytypes are likely to be small, and even random stacking of double six-rings has been observed.¹⁴ However, we see that

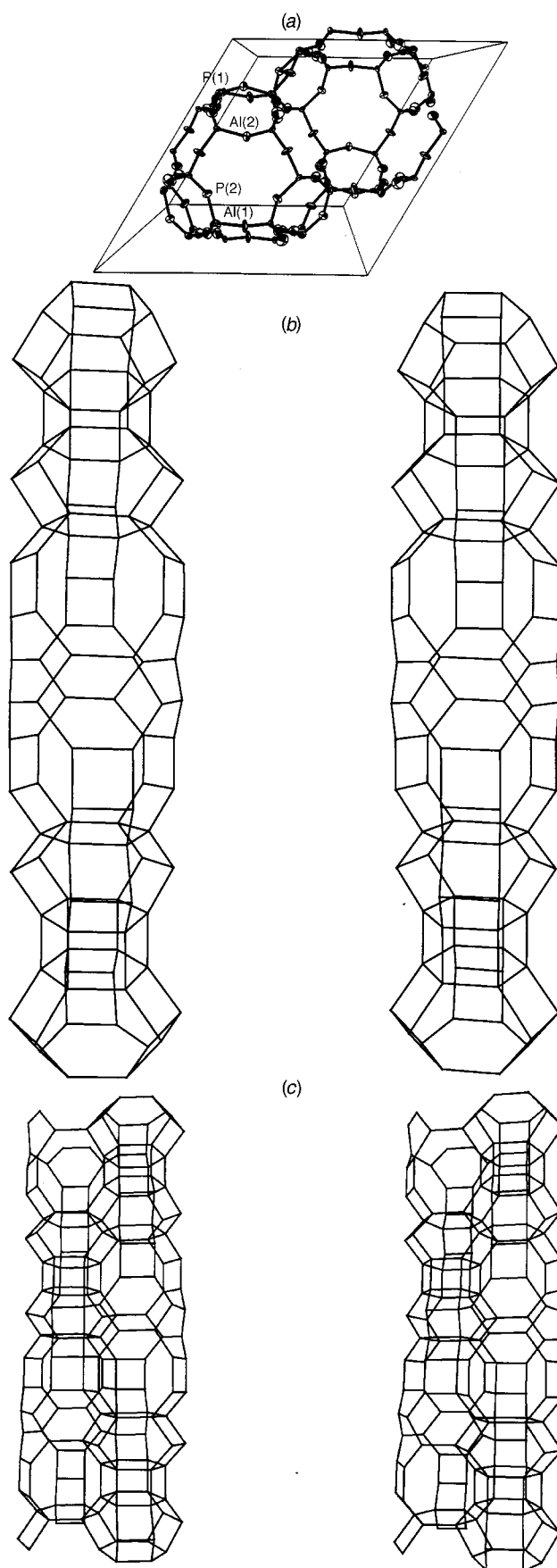


Fig. 5 (a) An ORTEP¹² representation of the framework structure, viewed down the $[001]_{\text{hexagonal}}$ axis. Stereoplots (b) and (c) show the column of secondary building units and cavities joined parallel to the c axis and the way in which adjacent columns are linked, respectively. For (b) and (c) only the tetrahedral connectivity is shown, oxygen positions being omitted for clarity

Table 3 Six-membered ring stacking polytypes

Name	Layers in repeat	Sequence	$a/\text{\AA}$	$c/\text{\AA}$	Framework density $10^{-3} T/\text{\AA}^3$
Cancrinite	2	AB	12.8	5.1	16.7
Offretite	3	AAB	13.3	7.6	15.5
Sodalite ^a	3	ABC	8.9	Cubic	17.2
Gmelinite	4	AABB	13.8	10.0	14.6
Losod	4	ABAC	12.9	10.5	15.8
Chabazite ^a	6	AABBCC	13.2	15.1	14.6
EAB	6	ABBACC	13.3	15.2	15.4
Erionite ^a	6	AABAAC	13.3	15.1	15.6
Liottite	6	ABABAC	12.8	16.1	15.7
Afghanite	8	ABABACAC	12.8	21.4	15.9
AIPO-56	8	AABBCCBB	13.8	19.9	15.7
Levyne ^a	9	AABCCABBC	13.3	23.0	15.2
AIPO-52	12	AABBCCAACCBB	13.7	29.7	15.2
STA-2 ^b	12	ABAACACCB	13.0	30.4	16.2

^a Both aluminosilicate and aluminophosphate analogues are known. ^b Unit cell dimensions taken from X-ray powder diffraction data obtained at room temperature. All other structural data taken from ref. 1.

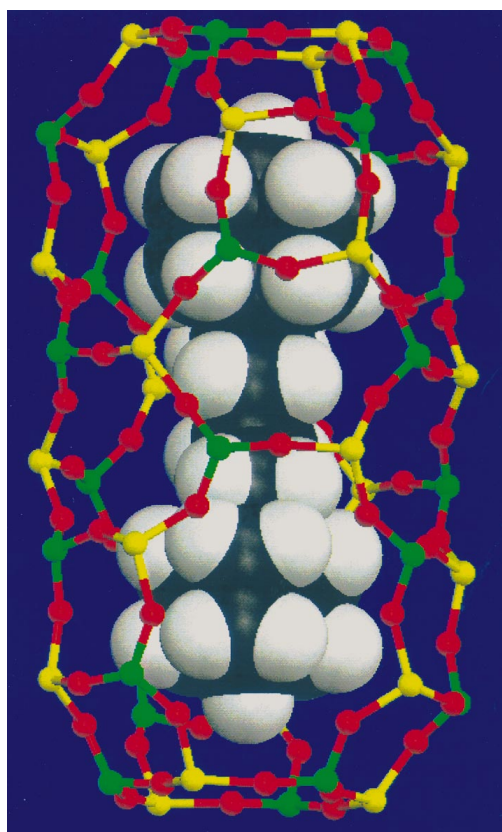


Fig. 6 The experimentally determined position of the template within the large cavities in STA-2, with the template represented by a space filling model and the inorganic framework represented by a ball and stick drawing for clarity. Hydrogen atoms on the template have been placed geometrically and a single (*trans*) orientation has been taken for the methylene chain of the template, which is in fact disordered about the triad axis. Aluminium, phosphorus and oxygen atoms are shown as yellow, green and red spheres respectively

very good crystals of MAPO-56 and STA-2 may be obtained, and this must be due to the templating action of the included organic cations.

The reason why such a complicated stacking sequence is produced in such a well-ordered way becomes clear when the experimentally-determined position of the diquinuclidinium cations is examined (Fig. 6). The position of the quinuclidinium fragments is particularly well described, although there is disorder in the positions of the atoms within the tetramethylene chain, as discussed in the Experimental section and seen in the

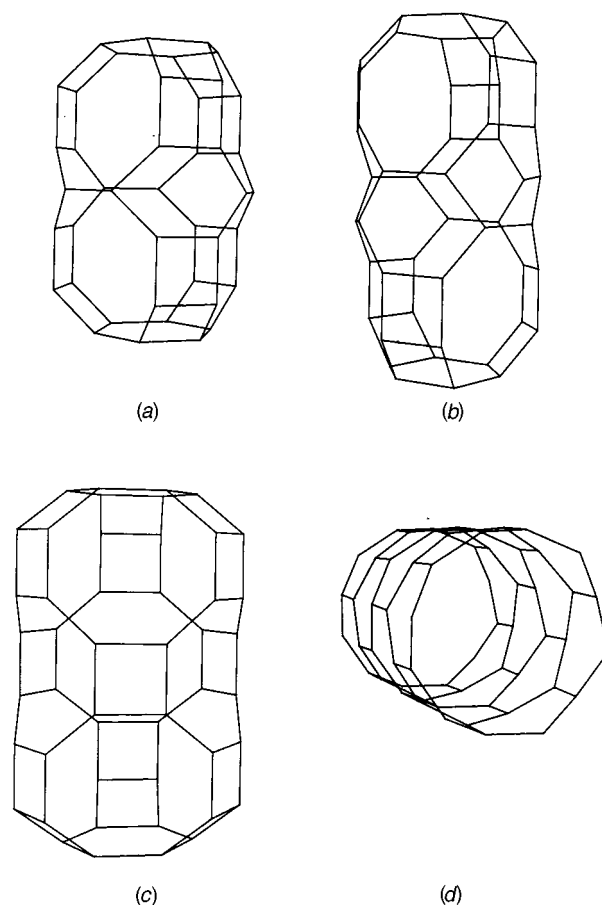


Fig. 7 Line representations (oxygen atoms removed for clarity), to approximately the same scale, of cavities within the structure types of (a) AIPO-17, (b) STA-2 and (c) AIPO-56 which are produced using diquinuclidine templates, with linking methylene chains containing three, four and five methylene groups. (d) The channel structure of AIPO-5, which is prepared if methylene chains containing six or more carbon atoms are present in templating molecules of the same kind

larger temperature factors and chemically inaccurate bond lengths C(4)–N(1) and C(4)–C(5), this is much smaller than usually observed for structures of this kind, and underlines the importance of the microcrystal technique, compared to the more usual powder diffraction method. The cations fit very closely in the large cavity within STA-2, and are stacked in a well ordered array throughout the structure. Both thermogravimetric analysis and crystallography indicate that each cavity is occupied by a template molecule. The reason that

MgAPO-56 co-crystallises with STA-2 under certain conditions becomes clear by considering the similarity in the cavity dimensions in the two solids. Although not identical, the dimensions of the cavity in the AFX structure type (Fig. 7) are very similar to those in STA-2 and very subtle effects must be responsible for determining which polytype will form. (It is of interest that SSZ-16, the aluminosilicate analogue to AFX, is templated by the same alkyl ammonium templates we have used for our magnesium aluminophosphates.¹⁵) Although STA-2 is prepared by the use of tetra- and penta-methylene diquinuclidinium ions it is interesting to note that with $n = 3$ the stacking sequence giving the erionite structure type is favoured, presumably because the cation is more satisfactorily co-ordinated within the smaller erionite cages (Fig. 7). On the other hand, with $n = 6$ the channel structure of the AFI structure type is favoured, because the template is too long to fit in the cavities of STA-2.

Conclusion

The study shows the sensitivity of crystal growth of microporous solids to precise conditions of the hydrothermal synthesis, and confirms that alkali-metal cations do not prevent the formation of microporous aluminophosphates. In the absence of the alkylammonium template, however, the alkali-metal cations are not able in this case to synthesise microporous materials.

On the atomic scale, the work underlines the role templates play in determining complex periodic stacking arrangements, and how single-microcrystal diffraction is a powerful tool not only to determine framework structures but also to locate organic templates. This should be of widespread applicability in experimental and computational studies aimed at the role and design of templates for the synthesis of targeted materials.¹⁶ Specifically, STA-2 is a new small pore polytype of the series of structures formed by the stacking and linking of six-membered rings (usually reported in terms of ABC type stacking). The material is stable to the removal of the template whereupon it becomes a solid acid catalyst for such chemical conversions as the methanol-to-light olefins reaction.[‡]

‡ Notes added at proof: (1) The zeotype STA-2 has been given the three letter code SAT by the IZA structure commission. (2) The structure of the zeolite SSZ-42, with a framework topology different to that of STA-2, has recently also been solved by microcrystal diffraction.¹⁷

Acknowledgements

We thank Drs R. E. Morris, P. Lightfoot, G. Vaughn and A. Finch for assistance in collecting the synchrotron powder diffraction data and for helpful discussions and we also gratefully acknowledge financial support from the Nuffield Foundation and the University of St. Andrews (to P. A. W. and G. W. N.).

References

- 1 W. M. Meier, D. H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types (Zeolites, 1996, 17)*, Elsevier, London, 4th edn., 1996.
- 2 D. E. Akporiaye, H. Fjellvag, E. N. Halvorsen, T. Haug and A. Karlsson, *Chem. Commun.*, 1996, 1553.
- 3 G. W. Noble, P. A. Wright, P. Lightfoot, R. E. Morris, K. J. Hudson, Å. Kvik and H. Graafsma, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 81.
- 4 P. A. Wright, C. Sayag, F. Rey, D. W. Lewis, J. D. Gale, S. Natarajan and J. M. Thomas, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3537.
- 5 M. Helliwell, V. Kaucic, G. M. T. Cheetham, M. M. Harding, B. M. Kariuki and P. J. Rizkallah, *Acta Crystallogr., Sect. B*, 1993, **49**, 413.
- 6 G. M. T. Cheetham and M. M. Harding, *Zeolites*, 1996, **16**, 245.
- 7 M. J. Gray, J. D. Jasper, A. P. Wilkinson and J. C. Hanson, *Chem. Mater.*, 1997, **9**, 976.
- 8 Å. Kvik and M. Wulff, *Rev. Sci. Instrum.*, 1992, **62**, 1073.
- 9 M. Krumrey, Å. Kvik and W. Schwegle, *ibid.*, 1994, **66**, 1715.
- 10 G. M. Sheldrick, SHELXTL, version 5.03, Program for the solution of crystal structures, University of Göttingen, 1993.
- 11 TEXSAN, Single Crystal Analysis Software, Version 1.6, Molecular Structure Corporation, The Woodlands, Houston TX, 1993.
- 12 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 13 G. R. Millward, S. Ramdas and J. M. Thomas, *Proc. R. Soc. London, Ser. A*, 1985, **399**, 57.
- 14 R. Szostak and K. P. Lillerud, *J. Chem. Soc., Chem. Commun.*, 1994, 2357.
- 15 R. F. Lobo, S. I. Zones and R. C. Medrud, *Chem. Mater.*, 1996, **8**, 2409.
- 16 D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas and G. J. Hutchings, *Nature (London)*, 1996, **382**, 604.
- 17 C.-Y. Chen, L. W. Finger, R. C. Medrud, P. A. Crozier, I. Y. Chan, T. V. Harris and S. I. Zones, *Chem. Commun.*, 1997, 1775.

Received 16th July 1997; Paper 7/05091G