Co-templating and modelling in the rational synthesis of zeolitic solids†

Maria Castro,[a] Raquel Garcia,[a] Stewart J. Warrender,[a] Alexandra M. Z. Slawin,[a] Paul A. Wright,*[a] Paul A. Cox,[b] Antoine Fecant,[c] Caroline Mellot-Draznieks[d] and Nicolas Bats[c]

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A 'co-templating' strategy supported by molecular modelling has been used to prepare, for the first time, silicoaluminophosphates with the SAV and KFI framework topologies, each of which has a three-dimensionally connected pore system with high specific volume.

Although structure direction by organic 'templates' is an essential route to the preparation of many zeolites, it remains a challenge to choose a template for a desired topology. To our knowledge, there are no examples where a novel framework type has been synthesised using an organic molecule chosen specifically for that purpose. The approach of Lewis *et al.*[1] to build a molecule computationally within the pores of a zeolite is attractive, but until now has only succeeded in designing new templates for existing aluminophosphate frameworks. The method is most promising for application to structures containing pores where the space to be occupied by the organic molecule is well-defined. For this reason, the synthesis of cage structures with novel compositions, or structures where these would not be expected by simple modifications of known preparations, appears to be a designed synthesis goal that is both worthwhile and achievable.

It has been observed by ourselves and others that azamacrocycles are highly effective structure-directing agents (SDAs) for the synthesis of aluminophosphate-based structures that contain cages.[2,3] In particular, tetramethylcyclam directs the crystallisation of substituted aluminophosphates with the STA-6 (framework type **SAS**) and STA-7 (**SAV**) structures (Fig. 1). The crystallising phase is STA-6 for silicoaluminophosphate (SAPO) and metalloaluminophosphates (MAPO, M(II) = Mg, Fe, Mn), and STA-7 for CoAPO and ZnAPO compositions. Of the two framework types, **SAV** is favoured for applications in adsorption and catalysis because it has a three-dimensionally connected pore space *via* openings limited by rings containing eight tetrahedral cations (8-membered rings, 8MRs). It is also desirable to prepare it as a SAPO (rather than as a CoAPO or ZnAPO) because SAPOs are usually more stable once calcined and contain well-defined Brønsted acid sites. Indeed, SAPO-34 (**CHA**) and SAPO-18 (**AEI**), which have structures closely related to that of STA-7, are active and selective catalysts for the methanol-to-olefins reaction:[4,5] **CHA**, **AEI** and **SAV** structure types are all composed of double 6-membered rings (D6Rs) attached differently by 4MRs.

SAPO STA-7 is therefore an attractive target for synthesis. Its structure differs from that of STA-6 due to it possessing two types of cage rather than one. The templating activity of tetramethylcyclam in CoAPO STA-7 occurs *via* inclusion within the larger of the two cages; modelling indicates that it cannot fit into the smaller cage.[2] A second organic base that would fit closely into the smaller cage should therefore favour crystallisation of the SAPO STA-7 structure. Remarkably, addition of tetraethylammonium cations (TEA^+) directs the crystallisation to pure STA-7 rather than STA-6; the co-base also reduces the amount of macrocycle needed for pH control.‡ Furthermore, together with TEA^+, cyclam itself directs the formation of STA-7. To investigate the role of co-bases further, two other examples, selected on the basis of size, di-*n*-propylamine (DPA) and diisopropylamine (DIPA), were added to SAPO syntheses containing cyclam or tetramethylcyclam as the primary SDA. In each case, the product was mainly STA-6 with minor admixed STA-7 (estimated visually to be 10–20%). The cyclam/TEA^+ combination is therefore best for the synthesis of SAPO STA-7 in terms of cost and purity, and this combination can be used to prepare silicoaluminophosphates with Si/(Al + Si + P) values from 0.04 to 0.20. Solid state NMR and CHN elemental analysis indicate that cyclam and TEA^+ are included intact, and SAPO STA-7 samples prepared in this way give a ^{29}Si MASNMR resonance at −91.6 ppm, indicating that silicon is included into the framework by replacing phosphorus. For a sample with a Si/(Al + Si + P) value of 0.11, elemental and TGA analysis gave a unit cell composition of $(NC_8H_{20})_{1.8}(N_4C_{10}H_{26})_{1.8}(H_2O)_{11}[Al_{24}P_{18.5}Si_{5.5}O_{96}]$. Single crystal diffraction[6]

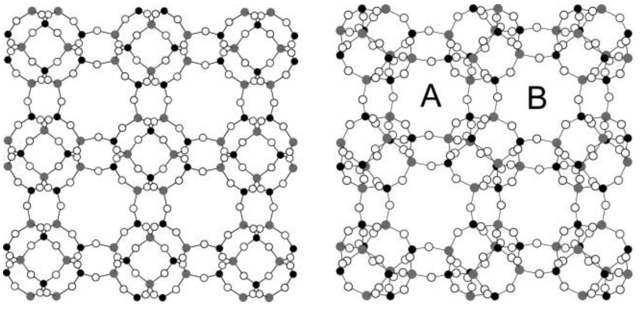

Fig. 1 The structures of STA-6 (left) and STA-7 (right) both contain cages: STA-6 has only one type, whereas STA-7 has two different types, A and B (aluminum atoms are gray, phosphorus black and oxygen white).

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[a] *School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, Fife, UK KY16 9ST. E-mail: paw2@st-andrews.ac.uk; Fax: +44 1334 463808; Tel: +44 1334 463793*
[b] *School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Road, Portsmouth, UK PO1 2DT*
[c] *IFP-Lyon, BP. 3, 69390, Vernaison, France*
[d] *Davy–Faraday Laboratories, Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS*

† Electronic supplementary information (ESI) available: Solid state NMR spectra, XRD patterns and Rietveld refinements, N_2 77 K isotherms and modelling details. See DOI: 10.1039/b705377k

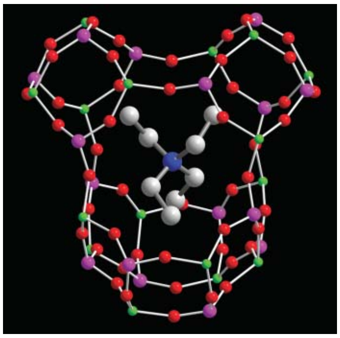

Fig. 2 The measured configuration of TEA ions in the smaller cages of STA-7, as determined from SXRD. One of two symmetry-related configurations is shown. Hydrogen atoms are omitted for clarity.

of cyclam/TEA$^+$ SAPO STA-7 showed that the TEA$^+$ cations adopt the tg.tg configuration within the smaller cages (Fig. 2), but it was not possible to locate the cyclam precisely, although electron density found within a disk in the larger cage could be attributed to disordered cyclam molecules.

Calcination gives crystalline SAPO STA-7 with a pore volume of 0.29 cm^3 g^{-1}. Rietveld refinement of the STA-7 framework (Al–O 1.74(2) Å, (Si,P)–O 1.54(2) Å) gives a good fit to the data ($P4/n$, a = 18.6931(7) Å, c = 9.4191(5) Å, R_{wp} = 7.8%, R_p = 5.4%). The properties of SAPO STA-7 as an adsorbent and a catalyst will be described elsewhere.

The experimental results demonstrate that the addition of TEA ions directs the synthesis towards SAPO STA-7. By modelling their lowest energy configurations in the smaller cage of the STA-7 structure, using a combined Monte Carlo-Simulated Annealing approach,[7] some idea of the role of TEA$^+$ can be obtained. While the large cage is occupied by cyclam, the binding energies of DPA, DIPA and TEA$^+$ in the smaller cage are found to be -83.6, -124.9 and -125.6 kJ mol^{-1}, respectively. The modelled position of TEA$^+$ is close to the position measured experimentally, but that of the DPA protrudes from the smaller cage, where it interferes with the templating effect of the cyclam. The higher selectivity of TEA$^+$ to STA-7 compared to DIPA is attributed to the better fit to the symmetry of the cage.

Having prepared the SAPO form of STA-7 for the first time by using a co-templating strategy, the approach was developed in attempts to synthesise, as an aluminophosphate, a structure type that had not previously been prepared as an $AlPO_4$-based solid, but which had been observed as an aluminosilicate zeolite: ZK-5 (framework type **KFI**)—one of the first synthetic zeolites to be discovered.[8] Like the **SAV** (and also **CHA** and **AEI**) framework types, **KFI** is built up from D6Rs only, but with a different stacking arrangement (Fig. 3). Furthermore, the (001) surface of the **SAV** structure is topologically identical to the ⟨100⟩ surfaces of **KFI**. It was therefore thought likely that an $AlPO_4$-based **KFI** structure could be prepared under similar gel compositions to those that give the substituted (MAPO, SAPO) versions of $AlPO_4$-18 and -34, and STA-7, if suitable structure directing agents could be found.

The ZK-5 structure, like that of STA-7, has two types of cages. In ZK-5, these are the so-called α-cage (also found in the structure of zeolite A and the isostructural $AlPO_4$-42 (**LTA**)) and a smaller cage found in the structure of zeolite merlinoite (**MER**). Previous studies have shown that the azaoxacryptand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (K222) is a good template for $AlPO_4$-42 and its substituted derivatives,[3] and must reside in the α-cage.

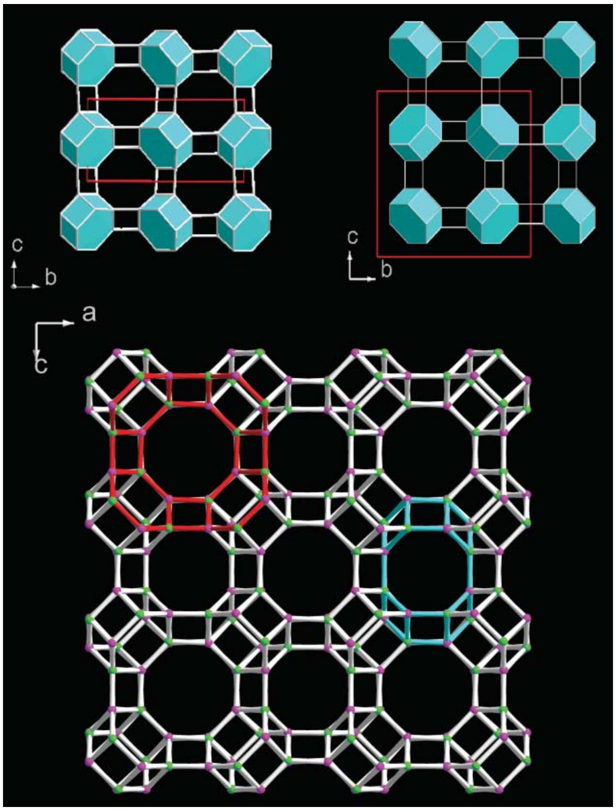

Fig. 3 Above: The structures **SAV** (left) and **KFI** (right), both made up entirely of D6Rs (in blue), can be distinguished when viewed along the a-axis. In **SAV**, layers are stacked along the c-axis by a simple translation, whereas in **KFI** adjacent layers are related by a mirror plane perpendicular to the c-axis. Below: The **KFI** structure, with oxygen atoms omitted, and with α- and **MER** cages outlined in red and cyan, respectively.

Using the co-templating approach, a selection of readily available amines and alkylammonium cations were screened computationally for their fit within the **MER** cages of a theoretical $AlPO_4$ composition of the **KFI** structure type: tetramethylammonium (TMA$^+$), TEA and tetrapropylammonium (TPA$^+$) cations and the amines methylamine (MA), ethylamine (EA), propylamine (PA), dimethylamine (DMA), diethylamine (DEA), DPA, DIPA, triethylamine (TREA) and diisopropylethylamine (DIPEA)).[10] The non-bonding energies are given in Fig. 4. The most favorable (-177.8 kJ mol^{-1}) was observed for TEA$^+$ in the tt.tt configuration (Fig. 4), but a number of the potential SDAs gave favorable energies. To examine the usefulness of this modelling approach, TEA$^+$ was examined as a potential co-template with K222 in syntheses from a magnesioaluminophosphate gel of composition: x R : 0.108 K222 : 0.2 $Mg(OAc)_2$: 0.8 $Al(OH)_3$: H_3PO_4 : 40 H_2O, where R refers to the co-base. MgAPO preparations are known to crystallise rapidly and give highly crystalline solids. Remarkably, powder diffraction showed that the phase pure product had the desired **KFI** structure type. ^{13}C MASNMR of as-prepared MgAPO (**KFI**) indicated that both TEA and K222 were present. To test the co-template selectivity,

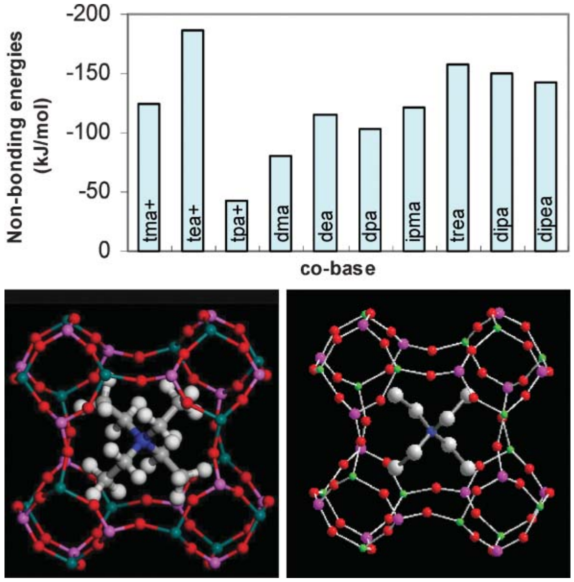

Fig. 4 Above: A histogram of the non-bonding energies of potential co-templates for the **MER** cages of the $AlPO_4$-**KFI** structure indicates that tetraethylammonium ions have most negative energies. Below: The modelled position of the TEA^+ cations within the **MER** cages of the $AlPO_4$-**KFI** structure (left) and that observed experimentally (right). In the latter, one of two symmetry-related positions is shown.

TMA^+, TEA^+ and TPA^+, and the amines DPA, DIPA, TEA and DIPEA, were also tried as co-templates with K222 under similar conditions. All except TMA^+ gave MgAPOs with the **LTA** structure type; TMA^+ favours the formation of MgAPO-20 (**SOD**).

The **KFI** framework structure of MgAPO (K222/TEA^+) was confirmed by single crystal diffraction[9] and the TEA^+ cation located within the **MER** cages in the configuration predicted by modelling. It was not possible to locate the K222 cryptand due to disorder. Combining TGA and chemical analysis, and assuming full occupancy of the **MER** cages by TEA^+, gave a unit cell composition of $(NC_8H_{20})_6(N_2C_{18}O_6H_{38})(NH_4)_2(H_2O)_{40}$-$[Mg_{10}Al_{38}P_{48}O_{192}]$. Using the K222/$TEA^+$ combination, CoAPO(**KFI**) and SAPO(**KFI**) compositional variants were also obtained. These new solids are designated STA-14 materials (St. Andrews material 14). SAPO STA-14 (Si/(Al + Si + P) = 0.1) is of particular interest because it is stable to template removal, giving a solid with a pore volume of 0.31 $cm^3\ g^{-1}$. Structural refinement of the calcined form in *Pn*-3*n* gave an acceptable fit to the powder XRD data.

These two rational syntheses indicate that a co-templating approach is viable for structures containing more than one cage type, where at least one of the organic additives has been observed to function as an SDA for one of the cages. Many such structures are known, either as hypothetical nets[11] or in a limited compositional range (as phosphates but not silicates, for example). These offer attractive targets for synthesis by careful choice of available templates.

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Notes and references

‡ Synthesis gels were prepared by mixing the reactants and adjusting the initial pH to between 7 and 8 by the addition of co-base. The gels were then heated at 190 °C for 2–5 d in Teflon-lined autoclaves. In a typical synthesis of SAPO STA-14, 1.00 g of phosphoric acid (85%) was mixed with 9 g of water and 1.11 g of aluminium hydroxide hydrate. To this solution, 0.075 g of fumed silica and K222 was added, and it was stirred until homogeneous. Then, co-template (TEA-OH) was added until a final pH of 7 was attained. Gel ratios: x (TEA^+) : 0.108 K222 : $Al(OH)_3$: 0.8 H_3PO_4 : 0.2 SiO_2 : 40 H_2O. For STA-7 synthesis, the process was similar with typical ratios of gel: x (TEA^+) : 0.108 cyclam : $Al(OH)_3$: 0.8 H_3PO_4 : 0.2 SiO_2 : 40 H_2O.

Products were characterised by powder XRD on a STOE Stad/p diffractometer using Cu $K_{\alpha 1}$ X-rays. Inorganic chemical analysis was performed by EDX on a JEOL JSM-5600 SEM with an Oxford INCA Energy 200 analyser, and the organic component was measured on a Carlo Erba EA 1110 CHNS analyser. ^{13}C MASNMR spectra were obtained with cross polarisation on a 300 MHz Varian spectrometer, contact time 1 ms, acquisition time 20 ms, recycle delay 1 s, spinning speed 4.1 kHz. TGA was performed under flowing oxygen at 5 °C min^{-1}, and the XRD of the calcined samples was measured in 0.7 mm quartz glass capillaries sealed after dehydration at 200 °C. N_2 adsorption was performed at 77 K on dehydrated samples using an automated HIDEN gravimetric porosimeter.

Modelling and energy minimisation of 'templates' in the **SAV** and **KFI** structures were performed using Monte Carlo-Simulated Annealing routines within the program Discover.[10] A model of the $AlPO_4$ (**KFI**) framework was first obtained by energy minimisation using the GULP[12] program. Frameworks were held fixed, and short range forces were calculated using the Universal forcefield.

1 D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas and G. J. Hutchings, *Nature*, 1996, **382**, 604.
2 V. Patinec, P. A. Wright, P. Lightfoot, R. A. Aitken and P. A. Cox, *J. Chem. Soc., Dalton Trans.*, 1999, **22**, 3909; P. A. Wright, M. J. Maple, A. M. Z. Slawin, V. Patinec, R. A. Aitken, S. Welsh and P. A. Cox, *J. Chem. Soc., Dalton Trans.*, 2000, **8**, 1243.
3 L. Schreyeck, F. D'Agosto, J. Stumbe, P. Caullet and J. C. Mougenel, *Chem. Commun.*, 1997, 1241; M. J. Maple, E. F. Philp, A. M. Z. Slawin, P. Lightfoot, P. A. Cox and P. A. Wright, *J. Mater. Chem.*, 2001, **11**, 98.
4 W. G. Song, J. F. Haw, J. B. Nicholas and C. S. Heneghan, *J. Am. Chem. Soc.*, 2000, **122**, 10726; W. G. Song and J. F. Haw, *J. Am. Chem. Soc.*, 2001, **123**, 4749.
5 J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow, P. L. Gai-Boyes, R. P. Townsend and C. M. Lok, *J. Phys. Chem.*, 1994, **98**, 10216.
6 Crystal data for SAPO STA-7: $M_{r(SXRD)}$ = 3700.55, dimensions 0.030 × 0.0280 × 0.010 mm, tetragonal, space group *P*4/*n*, *Z* = 1, ρ_{calcd} = 1.883 g cm^{-3}, *F*(000) = 1878, $2\theta_{max}$ = 25.35°, *a* = 18.656(15) Å, *c* = 9.378(7) Å, *V* = 3264(4) $Å^3$, *T* = 93(2) K. A total of 22423 reflections were collected, of which 2985 were independent (R_{int} = 0.2217). The structure was solved using SHELX97. The structure was refined to final *R*1 = 0.1027 for 2057 data [$I > 2\sigma(I)$], w*R*2 = 0.2180 for all data, GOF = 1.180 and residual electron density max./min. = 0.594/−0.559 e $Å^{-3}$. CCDC 642713. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705377k.
7 A. P. Stevens, S. H. Gorman, C. M. Freeman and P. A. Cox, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2065.
8 W. M. Meier and G. T. Kokotailo, *Z. Kristallogr.*, 1965, **121**, 211.
9 Crystal data for MgAPO STA-14: $M_{r(SXRD)}$ = 7743.63, dimensions 0.030 × 0.030 × 0.010 mm, cubic, space group *Pn*-3*n*, *Z* = 1, ρ_{calcd} = 1.903 g cm^{-3}, *F*(000) = 3950, $2\theta_{max}$ = 25.33°, *a* = 18.9056(17) Å, *V* = 6757.3(11) $Å^3$, *T* = 93(2) K. A total of 55683 reflections were collected, of which 1034 were independent (R_{int} = 0.1899). The structure was solved using SHELX97. The structure was refined to final *R*1 = 0.1320 for 958 data [$I > 2\sigma(I)$], w*R*2 = 0.3030 for all data, GOF = 1.288 and residual electron density max./min. = 0.723/−1.180 e $Å^{-3}$. CCDC 642714. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705377k.
10 *Discover Version 3.0*, Accelrys Inc, San Diego, USA, 1995.
11 M. D. Foster, A. Simperler, R. G. Bell, O. Delgado-Friedrichs, F. A. A. Paz and J. Klinowski, *Nat. Mater.*, 2004, **3**, 234.
12 J. D. Gale, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 629.