SYNTHESIS AND STRUCTURE SOLUTION OF TRIETHYLENEDIAMINE DIRECTED MICROPOROUS MATERIALS

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Summary

By a combination of single crystal and high-resolution powder diffraction studies, the authors aimed to gain further insights into how the organic template molecules may direct the production of a specific microporous framework. Attention was focused on the use of cyclic mono and diamines as structure directing agents to produce small pore microporous materials. The zeolite analogue Chabazite, along with two novel framework types, were synthesised by the use of the triethylenediamine (DABCO) organic template. From an initial mixed phase sample, all three crystal morphologies have been successfully prepared in their phase pure form by optimising the synthesis conditions for each individual material. With the DAF-6 (Davy Faraday-6) pure AlPO phase isolated, the addition of different cations into the synthesis gel produced the CoAlPO Chabazitic phase and the calcium-substituted DAF-7 framework, to the authors' knowledge the first open framework structure containing calcium in a framework position.

1. Introduction

Several linear, branched and cyclic amines have been successfully used as templating agents in the synthesis of chabazite-type small pore aluminophosphates, for example triethylamine [1, 2] piperidine [3, 4] and cyclohexylamine [5, 6]. A number of triethylenediamine (DABCO) derivatives, for example 1.1'-alkylenedi(4-aza-1-azonia-2.5-dimethylbicyclo[2, 2, 2]octane are known to direct the formation of high-silica zeolite systems [7, 8]. In the amine form DABCO has also been used in the synthesis of three-dimensional open-framework Co^{2+} and Zn^{2+} phosphates [9] and more recently, a microporous cobalt-gallium phosphate [10] designated CGF by the Structure Commission of the International Zeolite Association.

The aim of the current work was to synthesise an aluminophosphate-based material with a small pore structure, using triethylenediamine (DABCO) in the amine form as a structure-directing agent. Our expectation was that the selected template would form a small pore type material quickly and in phase pure form, with little or no extraneous microporous phases. The Co^{2+}-substituted form would be synthesised, to endow the framework with some catalytic properties. The organic template used in this work is shown Fig.1.

One of the inherent problems with the detailed structural characterisation of these materials is the difficulty in obtaining a single crystal large enough for study using conventional laboratory single-crystal diffraction. A consequence of this is that many of the related structures have been solved by combining powder diffraction data and some single-crystal data and in some cases computer simulations as well [10 - 16]. With the introduction of the micro-crystal diffraction facility Station 9.8 at the Daresbury Synchrotron Radiation source [17] it is now routinely possible to collect diffraction data from crystals as small as 15 x 15 x 15μm.

2. Experimental

2.1. Synthesis

Cobalt-substituted aluminophosphate (CoAlPO) was prepared using triethylenediamine as the template. Cobalt and other heteroatoms were also substituted in the framework at the synthesis stage.

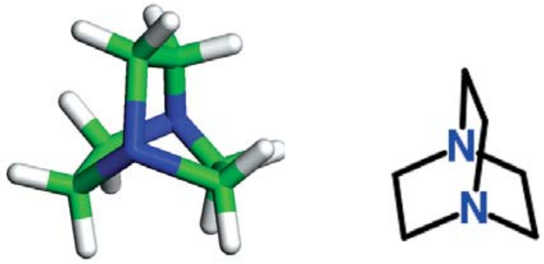


Fig.1. *Structure of the template species triethylenediamine (DABCO). The nitrogen site is shown in blue, the carbon in green and the hydrogens are white*

An aqueous gel was prepared using aluminium hydroxide, cobalt acetate tetrahydrate, 85% phosphoric acid, the template and distilled water. A small amount of water was added to the cobalt acetate until it dissolved. The remainder of the water was added to the phosphoric acid. The aluminium hydroxide was added to the acid/water mix, followed by the cobalt acetate solution; the template was added last.The initial gel composition for the synthesis was:

$0.9\ Al_2O_3 : 1.0\ P_2O_5 : 0.1\ Co(OAc)_2.4H_2O : 1\ DABCO : 40\ H_2O$

The gel was stirred vigorously after each addition to ensure thorough mixing. The resultant gel was then placed in a PTFE liner and heated hydrothermally in a stainless steel autoclave at 190°C for 24 hours.

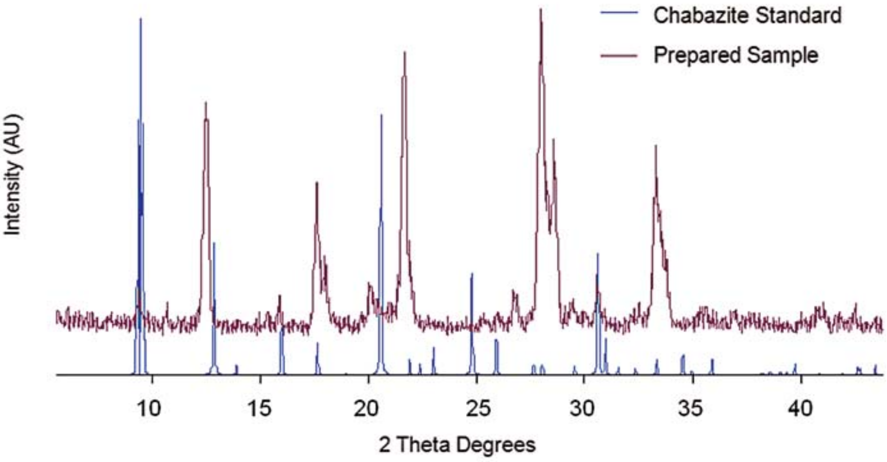


Fig.2. Powder X-ray diffraction patterns for a standard chabazite sample (blue) and the prepared sample (purple). It is clear that the prepared structure contains chabazite and an impurity phase. Intensities are arbitrary and the spectra have been offset vertically for clarity

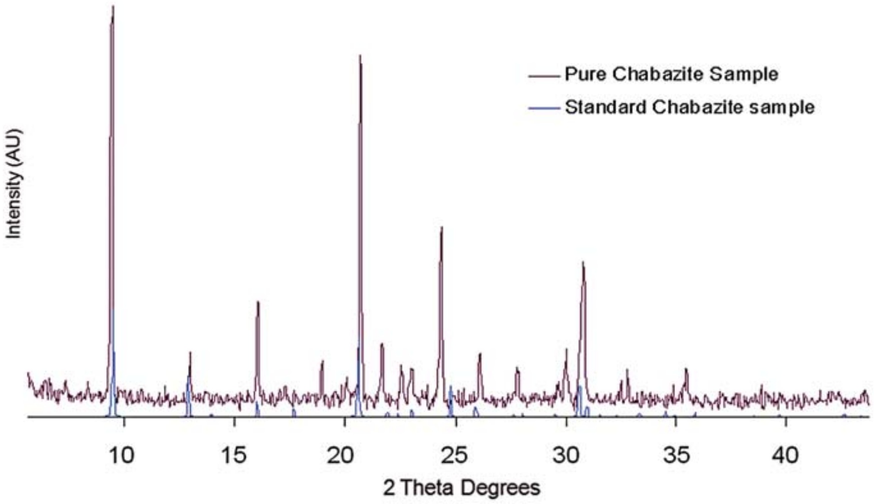


Fig.3. Powder X-ray diffraction patterns for a standard chabazite sample (blue) and the prepared CoAlPO sample (purple). Intensities are arbitrary and the patterns have been offset vertically for clarity

2.2. Characterisation

Phase purity was checked by powder diffraction, recorded with a Siemens D500 diffractometer. Single-crystal data for this work were collected at the microcrystalline diffraction facility on station 9.8 of the Daresbury SRS [17] with typical data collection times of around 4 to 6 hours. The crystal was mounted on a glass fibre, attached to a standard goniometer head. Data were collected at 150K, to minimise the thermal motion of the template. All structure solutions and refinements were carried out using the SHELXTL/SHELX-97 suite of programs [20]. All the data collections and post-collection integration data processing were performed by the SMART and SAINT software provided with the detector to give a final hkl file ready for solving. All of the direct method solutions were completed with the SHELX/SHELXTL suite of programs. SEM was taken by JEOL JSM-6480LV in University College London.

In this work, the X-ray Rietveld system (XRS-82) was used in the refinement of the X-ray powder data. In all refinements, the background was subtracted.

3. Results and discussions

3.1 Structure of pure AlPO, DAF-6 and DAF-7 by XRD, Single-crystal and SEM

The diffraction pattern is shown in Fig.2, along with the pattern for a standard chabazite sample generated from the Atlas of Zeolite Structure Types [18]. It is clear that the prepared structure contains chabazite and an impurity phase. Attempts to index all the reflections did not produce a unique solution, corroborating the optical microscope observations.

Examination by optical microscopy revealed three distinct crystal morphologies; two colorless, (hexagonal and rhombohedral crystal types) and one rectangular. The rectangular crystals are clearly blue, indicating their cobalt content. These distinct phases were separated for analysis by EDAX. This revealed the presence of calcium in the rhombohedral type crystals, approximately 12%. No traces of calcium were found in either of the other two morphologies, therefore establishing three distinct structures, A CoAlPO, pure AlPO and a calcium-containing phase.

Subsequently a pure phase was obtained for each of the three crystal morphologies and the CoAlPO phase was isolated at 170°C. The diffraction pattern is shown in Fig.3, along with the pattern for a standard chabazite sample. It is clear that the two spectra match very well, with no extra reflections in the sample, indicating that the only phase present is the Chabazite type material. The peak positions also match those expected from the Atlas of Zeolite Structures [19]. When studied with an optical microscope the sample is compiled of blue rectangular crystals. Optical pictures of the sample are shown in Fig.4. The crystal size of the sample ranged from 10 x 10 x 20mm to 30 x 30 x 40mm.

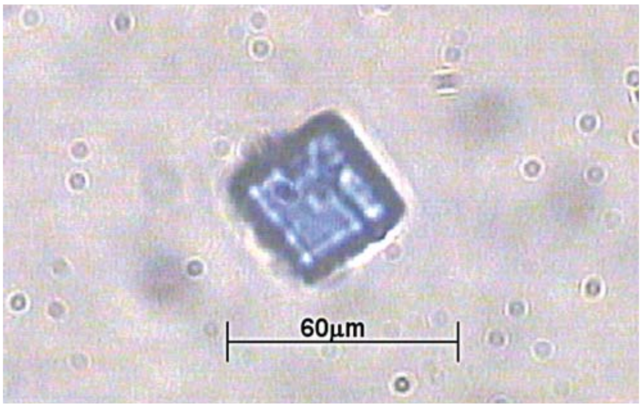


Fig.4. *Optical picture of a crystal form the Chabazite-type material*

A single crystal with dimensions 30 x 30 x 40mm was chosen and data were collected and analysed using the SHELXTL/SHELX-97 suite of programs [20], results shown in table below.

It was possible to obtain a precise structure for the chabazite material. The space group was found to be R3, with unit cell dimensions a = 13.747(8), c = 15.339(16). Initially we had found the symmetry of the as-prepared material to be $R\bar{3}$. Attempts were made to refine the structure in this space group; however, no satisfactory solutions were found for the disorder in the template.

Table 1. *Crystallographic details for the as-prepared Chabazite CoAlPO*

1	Chemical formula	$Al_{0.77}Co_{0.23}PO_4.N_{0.12}C_{0.34}$	
2	Formula weight	112.84	
3	Temperature	150(2) K	
4	Wavelength	0.69310Å	
5	Crystal system, space group	Hexagonal, R3	
6	Unit cell parameters	a = 13.747(8)Å	$\alpha = 90°$
		b = 13.747(8)Å	$\beta = 90°$
		c = 15.339(16)Å	$\gamma = 120°$
7	Cell volume	$2510(3)Å^3$	
8	Z	21	
9	Calculated density	$1.567g/cm^3$	
10	q range for data collection	2.1 to 29.3°	
11	Index ranges	h - 19 to 16, k - 8 to 19, l - 20 to 21	
12	Completeness to q = 29.3°	93.0%	
13	Reflections collected	5,846	
14	Independent reflections	2,880 (R_{int} = 0.0982)	
15	Reflections with $F^2 > 2s$	2,275	
16	Structure solution	direct methods	
17	Refinement method	Full-matrix least-squares on F^2	
18	Final R indices [$F^2 > 2s$]	R1 = 0.0634, wR2 = 0.1659	
19	R indices (all data)	R1 = 0.0754, wR2 = 0.1758	
20	Goodness-of-fit on F^2	1.098	
21	Largest and mean shift/su	0.138 and 0.023	
22	Largest diff. peak and hole	0.76 and - 0.90e $Å^{-3}$	

It is noted that removing the inversion centre also points to some cobalt ordering within the double six-ring. With the structure being refined in the space group R3 there are 4 T atom positions. The cobalt content was refined and the final value came to 23% cobalt substitution. Fractional coordinates and U_{iso} for the structure are given in Table 2 and a view of the structure is shown in Fig.5.

It was found that the template molecules were situated to one side of the framework cage and were well ordered, thus easily enabling the location and refinement of the DABCO molecule to accurately determine the position and orientation of the molecules (Fig.5). Hydrogen atoms of the template were given idealised positions using the HFIX/AFIX commands within SHELXL [20] and refined using isotropic displacement parameters. The final structure solution, refined in R3, clearly shows

Table 2. *Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the as-prepared Chabazite*

Atom	x	y	z	U_{iso}
Al(1)	0.99631(11)	0.22871(12)	0.65865(11)	0.0207(4)
Co1	0.99631(11)	0.22871(12)	0.65865(11)	0.0207(4)
Al(2)	1.23079(8)	0.23126(8)	0.45911(6)	0.0194(3)
Co(2)	1.23079(8)	0.23126(8)	0.45911(6)	0.0194(3)
P(1)	1.22973(8)	0.23111(9)	0.66360(6)	0.0137(2)
P(2)	1.23170(12)	0.00107(12)	0.46024(12)	0.0454(5)
O(1)	0.9027(4)	0.1011(5)	0.6852(3)	0.0674(17)
O(2)	1.1229(3)	0.2453(3)	0.6906(3)	0.0482(12)
O(3)	1.2709(3)	0.2695(3)	0.5608(3)	0.0269(9)
O(4)	1.3229(3)	0.3418(4)	0.3938(3)	0.0423(12)
O(5)	1.0951(4)	0.1968(4)	0.4453(4)	0.0718(18)
O(6)	1.2434(4)	0.1208(4)	0.4352(4)	0.0632(14)
O(7)	1.2672(7)	0.0127(7)	0.5460(7)	0.092(3)
O(8)	1.3144(5)	0.0217(5)	0.3934(4)	0.0823(17)
N(1)	1.0000	0.0000	0.1145(13)	0.131(6)
N(2)	1.0000	0.0000	0.272(2)	0.150(5)
C(1)	1.1090(17)	0.055(2)	0.1456(12)	0.092(7)
C(2)	1.138(3)	0.0940(15)	0.2279(13)	0.165(14)

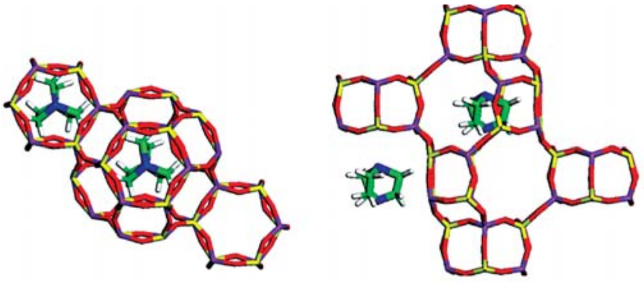


Fig.5. *Schematic views of the CoAlPO structure refined from data collected at 150K. 2 views are shown for clarity, and to clearly show the template location and orientation. Note only one template species per cage*

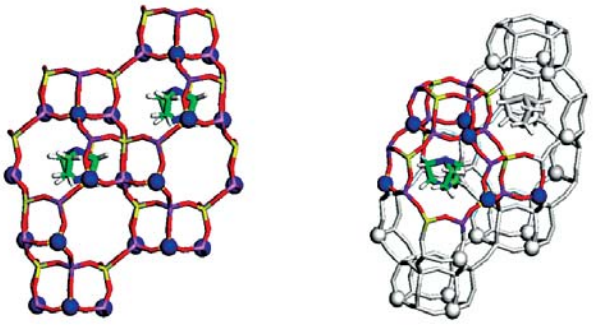


Fig.6. *Schematic showing the preferred cobalt sites, as blue spheres; the substituted aluminium site preference is in the lower ring of the double six-ring building unit*

the presence of only one ordered template within the cage, positioned off-centre towards one end.

Analysis of the Chabazite-related DAF-5 material by Sankar et al [21] also showed only one template contained within the cage, although the 4-piperidinopiperidine template used here occupies much more space within the cage, making a second spatially impossible.

The position of the DABCO template within the cage suggests an ordering of the substituted cobalt within the framework, with the cobalt preferentially substituting specific sites in the double six-rings. This is demonstrated by an imbalance in the substituted cobalt values on each of the aluminium sites, where a 1:4 cobalt substitution preference for one aluminium site is shown. The location of the preferred cobalt ion locations within the framework is shown in Fig.6.

Attention now focuses on the remaining two unidentified CaAlPO morphologies, and developing a phase pure synthetic route to one or both of these novel materials. As EDAX analysis identified one as a pure aluminophosphate and one containing calcium, two separate syntheses would be required. In order to obtain the pure aluminophosphate material as the major phase, a much shorter synthesis time and higher temperatures were required. The gel composition is shown below; it was heated at 190°C. The pH of the starting gel was 7.0.

$1.0\ Al_2O_3 : 1.3\ H_3PO_4 : 1.2\ DABCO : 40\ H_2O$

The CaAlPO phase was prepared using calcium carbonate as the calcium source. The gels were prepared in a similar manner to the CoAlPO synthesised earlier, using the compositions shown below. The pH of the starting gel was 7.0.

$0.80\ Al_2O_3 : 1.3\ H_3PO_4 : 0.20\ CaCO_3 : 1.2\ DABCO : 40\ H_2O$

The gel was heated in a PTFE liner under hydrothermal conditions in a stainless steel autoclave at 170°C for 3 days. White crystalline material was produced and suitable single crystals were obtained for microcrystal analysis.

X-ray diffraction patterns of the materials formed are shown in Fig.7 and Fig.8 respectively. A pure phase was

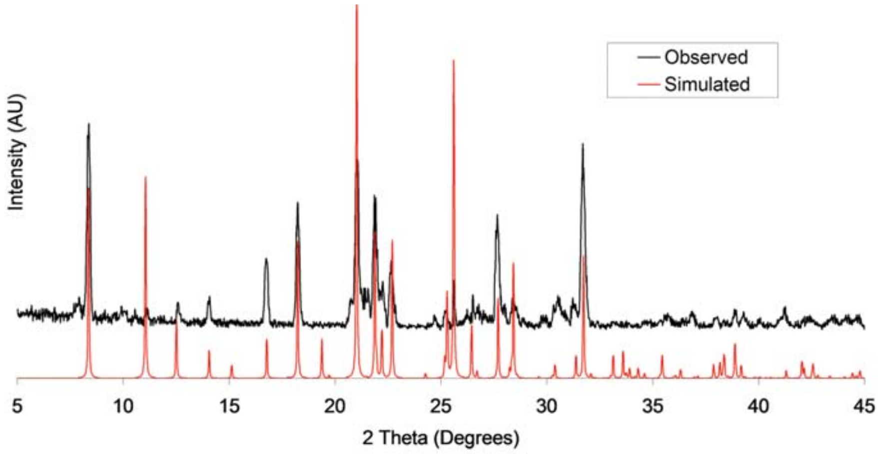


Fig.7. *Powder X-ray diffraction patterns for DAF-6 in the as-prepared form and simulated pattern from single-crystal analysis. Intensities are arbitrary and the spectra have been offset vertically for clarity*

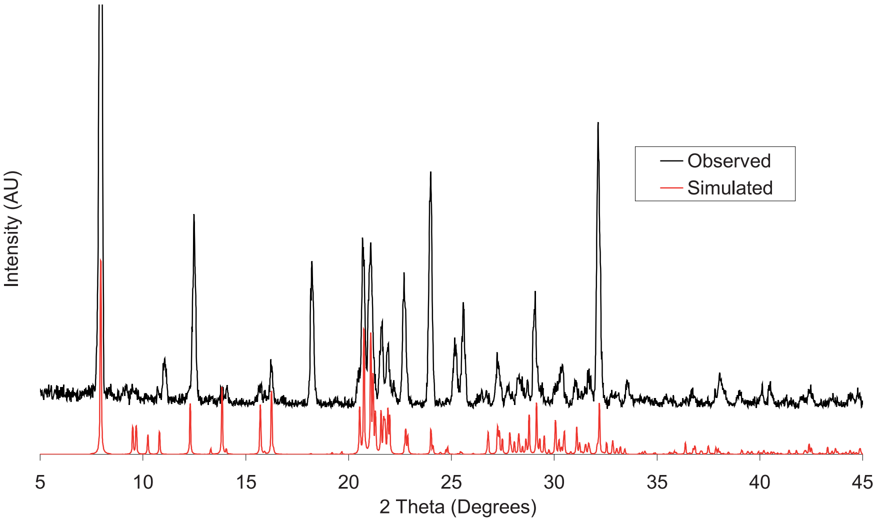
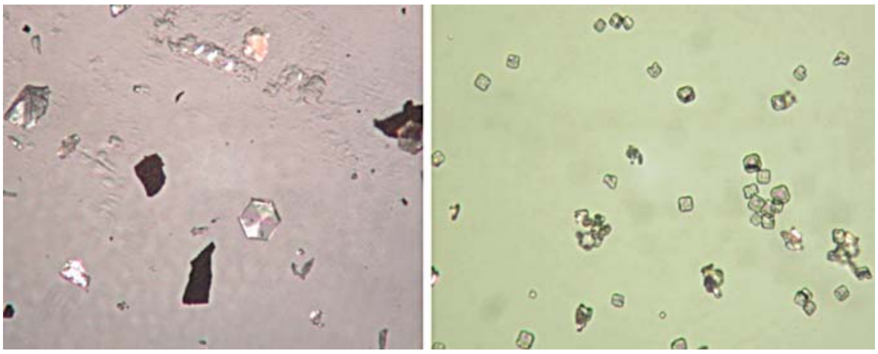


Fig.8. *Powder X-ray diffraction patterns for DAF-7 in the as-prepared form and simulated pattern from single-crystal analysis. Intensities are arbitrary and the spectra have been offset vertically for clarity*



(a) *(b)*

Fig.9. *Optical picture of the crystal morphology for the pure AlPO DAF-6 material (a) and DAF-7 CaAlPO material (b)*

produced for both gel compositions; the powder X-ray diffraction patterns were compared to the simulated XRD pattern from the single-crystal refinement. The crystals with hexagonal morphology were denoted as DAF-6, (Davy Faraday-6) and the rhombehedral shaped ones were referred to as DAF-7.

Optical pictures of the sample are shown in Fig.9. The crystal size of the samples ranged from 40 x 40 x 5mm to 40 x 30 x 10mm.

3.2. Structure solution of DAF-6

In order to determine the absolute structure and location of the template molecule inside the DAF-6 framework, single-crystal diffraction techniques were employed, using microcrystal diffraction techniques at Station 9.8, Daresbury SRS [17]. Crystallographic details for the refinement are given in Table 3; definitions of R1 and wR2.

The structure was refined in the space group R3c, with unit cell dimensions of a = 14.0612(7)Å and c = 42.403(2)Å. Within the structure two template molecule sites were found, both very disordered. Unfortunately the void space produced in this structure has only very small pore openings with only minimum access into the framework (Fig.10). However, two octahedrally coordinated aluminium sites were formed within the structure blocking what could have been a larger pore opening and creating a small cage inside the structure, as shown in Fig.10.

The Al^{3+} octahedral site shows four of the oxygen atoms connected to the phosphorus site, i.e. framework oxygens and two of the oxygens belonging to water molecules present in the voids created by the structure. The high quality single-crystal data enabled accurate location of the disordered template molecules. The octahedral aluminium along with the template molecules are shown in Fig.11.

Table 3. Crystallographic details for as-synthesised pure AlPO DAF-6

1	Chemical formula	$Al_{11}P_{12}N_8O_{48}$. $C_{12}H_{27}$	
2	Formula weight	1719.84	
3	Temperature	150(2) K	
4	Wavelength	0.6923Å	
5	Crystal system, space group	Trigonal, R3c	
6	Unit cell parameters	a = 14.0612(7)Å	$\alpha = 90°$
		b = 14.0612(7)Å	$\beta = 90°$
		c = 42.403(2)Å	$\gamma = 120°$
7	Cell volume	7,260.6(6)Å^3	
8	Calculated density	2.360g/cm^3	
9	q range for data collection	2.48 to 25.00°	
10	Completeness to q = 25.0°	94.0%	
11	Reflections collected	5,846	
12	Independent reflections	2,880 (R_{int} = 0.0982)	
13	Reflections with $F^2 > 2s$	2,275	
14	Structure solution	direct methods	
15	Refinement method	Full-matrix least-squares on F^2	
16	Final R indices [$F^2 > 2s$]	R1 = 0.0377, wR2 = 0.0968	
17	R indices (all data)	R1 = 0.0414, wR2 = 0.0986	
18	Goodness-of-fit on F^2	1.127	
19	Largest and mean shift/su	0.046 and 0.010	
20	Largest diff. peak and hole	0.504 and -0.667 e Å^{-3}	

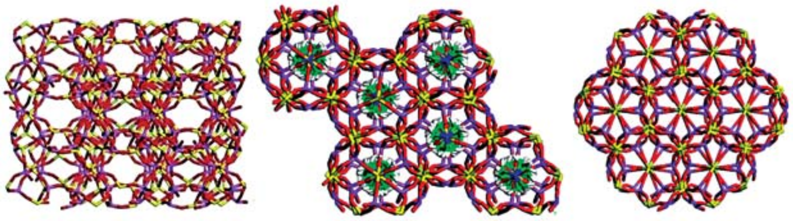


Fig.10. *Schematic showing the limited access into the framework for DAF-6. With the octahedral aluminium blocking the pore access and creating the cage structure, shown with and without the template*

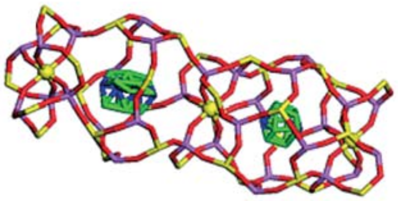


Fig.11. *Schematic showing the template location within the structure. The octahedral aluminium sites are shown here are yellow spheres. The hydrogen atoms have been omitted for clarity*

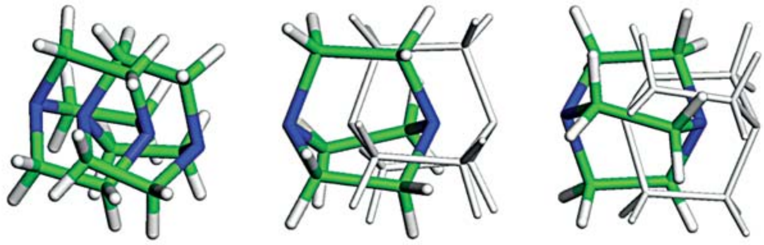


Fig.12. *Schematic of the first template site. The template is clearly shown disordered over two locations*

The disorder at the template locations is clearly visible in Fig.12, where only a general idea of how the template molecule is orientated can be shown. A more detailed study of the two template locations revealed a more accurate picture of the template orientation. In both cases it was found that the organic molecule was occupying two offset positions at each of the sites.

The second template site shows two possible orientations, not translated as in the first location, but rotated about the nitrogen positions as shown in Fig.13. Analysis of the bond lengths and angles clearly shows the presence of two aluminium octahedral sites within the structure (Table 4).

3.3. Structure solution of DAF-7

A crystal of size 40x30x10mm was studied and the structure was refined in the triclinic space group $P\bar{1}$. The cell dimensions were a = 9.5527(10) Å, b = 9.9126(10)Å, c = 12.2629(13) Å, and α = 69.832(3)°, β = 73.186(3)°, γ = 82.214(3)°. The disorder on the template molecule is such that only its general location within the framework can be determined and as such the hydrogens have been omitted for clarity. Crystallographic details for the refinement are given in Table 5; the structure solution and refinement were carried out using the SHELXTL/SHELX-97 suite of programs [20].

The DAF-7 structure appears to be more open and complex than the DAF-6 structure. There are 8-membered ring channels in two different directions, as shown in Fig.5. Furthermore one of the aluminum sites is fully occupied instead by Ca^{2+} ions. EDAX analysis of the crystal clearly shows that the rhombohedral

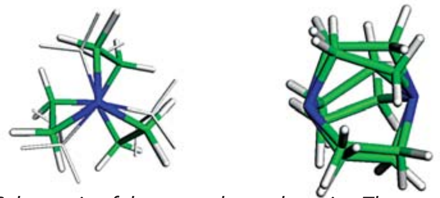


Fig.13. *Schematic of the second template site. The template is clearly shown disordered, with the rotation to the second template occupation about the nitrogen positions*

Table 4. *Selected bond lengths and angles for DAF6, highlighting the coordination geometry of the two octahedral aluminum sites*

Atom Pair	Bond Length (Å)	Average Bond Angle	Degrees
Al1 - O8	1.934(5)	O-Al-O	90.05
Al1 - O8B	1.934(5)		
Al1 - O13A	1.846(4)		
Al1 - O8A	1.934(5)		
Al1 - O13	1.846(4)		
Al1 - O13B	1.846(4)		
Al2 - O10	1.920(5)	O-Al-O	90.23
Al2 - O10D	1.920(5)		
Al2 - O12C	1.878(5)		
Al2 - O10C	1.920(5)		
Al2 - O12	1.878(5)		
Al2 - O12D	1.878(5)		

crystals have ~12% calcium present. We did not find any extra-framework Ca^{2+} ions in the structure solution.

Upon closer inspection of the structure and bond distances and angles (listed in Table 6), it is clear that one of the Al^{3+} sites is five-coordinate, with a water or a terminal hydroxyl group bonding to the underside to form the fifth and longest oxygen bond. The Ca^{2+} sites have octahedral coordination, with four of the oxygen atoms linked to phosphorus and two of the oxygen atoms belonging to either water molecules or terminal hydroxyl groups.

To the best of the author's knowledge this is the first report detailing an open framework structure containing Ca^{2+} in a framework position. Although calcium salts are added in the starting gel mixture in the synthesis of zeolites, in all other cases the calcium ions are located only in the extra-framework positions. The reason why Ca^{2+} ions can be incorporated in an open framework AlPO structure rather than silica may be related to the ease with which we have been able to replace an Al^{3+} ion by divalent cations in an AlPO rather than replace Si^{4+} ions in microporous silicates.

In addition, it appears that the template molecule DABCO has a large influence on the incorporation of Ca^{2+} ions, since attempts to reproduce this structure with framework calcium, using a different organic template molecules, did not result in similar compounds being formed. Further to this an attempt was made to substitute nickel into this structure type instead of calcium. Nickel was chosen as this will form an octahedral coordination similar to that of calcium. Unfortunately this failed and only produced AlPO-5 instead. The bond length and angles for the other T atom sites are not shown; they are as we would expect for a tetrahedral system. The average Al-O tetrahedral bond length is 1.72Å and the average P-O bond length is 1.53Å. The average for the template C-C bond lengths is 1.47Å and the C-N 1.51Å. The differences in the template values form the ideal probably arise from the large amount of disorder in the template molecule.

Table 5. *Crystallographic data and structure refinement details for the as synthesised CaAlPO material DAF-7*

1	Chemical formula	$CaAl_3P_4O_{18}.N_2C_6H_5$
2	Formula weight	638.02
3	Temperature	150(2)K
4	Wavelength	0.6931Å
5	Crystal system, space group	Triclinic, $P\bar{1}$
6	Unit cell parameters	a = 9.5527(10)Å α = 69.832(3)°
		b = 9.9126(10)Å β = 73.186(3)°
		c = 12.2629(13)Å γ = 82.214(3)°
7	Cell volume	1042.58(19) $Å^3$
8	Z	2
9	Calculated density	2.032g/cm^3
10	q range for data collection	2.2 to 24.0°
11	Completeness to q = 24.0°	95.2%
12	Reflections collected	5,238
13	Independent reflections	3,365 (R_{int} = 0.0361)
14	Reflections with $F^2 > 2s$	2,948
15	Structure solution	direct methods
16	Refinement method	Full-matrix least-squares on F^2
17	Data/restraints/parameters	3,365/454/327
18	Final R indices [$F^2 > 2s$]	R1 = 0.0675, wR2 = 0.1892
19	R indices (all data)	R1 = 0.0775, wR2 = 0.1931
20	Goodness-of-fit on F^2	1.053
21	Largest and mean shift/su	0.005 and 0.000
22	Largest diff. peak and hole	1.50 and -1.05 e $Å^{-3}$

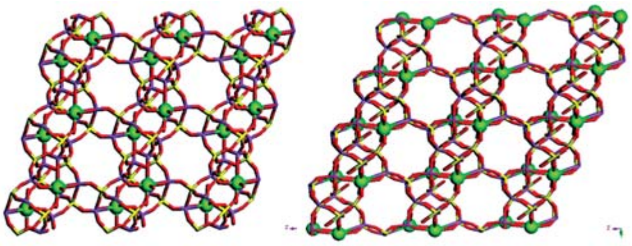


Fig.14. *Channel views of the DAF-7 structure. The calcium atoms are highlighted as green spheres*

Table 6. *Selected bond lengths and angles for DAF-7, highlighting the coordination geometry of the calcium and single aluminium site. Note the fifth Al-O bond is to a water molecule and not a framework oxygen*

Atom Pair	Bond Length (Å)	Average Bond Angle	Degrees
Ca1 - O6	2.237(5)	O-Ca-O	90.93
Ca1 - O9B	2.343(5)		
Ca1 - O16	2.238(5)		
Ca1 - O18	2.397(5)		
Ca1 - O14	2.270(5)		
Ca1 - O17	2.375(5)		
Al1 - O2	1.725(5)	O-Al-O	108.14
Al1 - O8	1.721(5)		
Al1 - O13C	1.743(6)		
Al1 - O12B	1.726(5)		
Al1 - O99w	2.257(19)	O-Al-Ow	76.46

4. Conclusions

In this paper two new framework structures have been presented, highlighting the importance of both the template species used in the synthesis and the choice of divalent cation to be substituted into the framework.

The synthesis routes followed in this research produced three distinct crystal morphologies, with three very different structures. The initial synthesis mixture contained 20% cobalt and small amounts of calcium salt, at this time an impurity, with DABCO as the template molecule. This mixture resulted in three types of crystal morphologies: blue rectangular crystals with the other two colourless but one rectangular and the other rhombohedral, later designated DAF-6 and DAF-7. The single-crystal study of the rectangular crystals (clearly seen as blue crystals in the optical microscope, whereas both DAF-6 and DAF-7 were colourless) revealed that this is similar to CoAlPO-34 or CoAlPO-44 (chabazite type); it is interesting to note that there is only one DABCO molecule present in the chabazite cage.

In order to confirm that some of the structures reported here are new, we performed the analysis involving the estimation of coordination sequence and comparing them with other known structures in

Table 7. *Fractional Coordinates, occupancy and equivalent isotropic displacement parameters (Å^2) for as-prepared DAF-7*

Atom	x	y	z	U_{iso}
Ca(1)	0.64139(14)	2.30295(14)	0.64366(11)	0.0170(4)
Al(1)	0.7328(2)	1.9768(2)	0.42870(16)	0.0167(5)
Al(2)	1.42482(19)	1.66133(19)	0.85102(15)	0.0129(4)
Al(3)	0.97441(19)	1.52849(19)	0.67907(15)	0.0131(4)
P(1)	1.24411(17)	1.69196(17)	0.66350(14)	0.0138(4)
P(2)	1.31654(17)	1.58303(17)	1.12806(13)	0.0142(4)
P(3)	0.96142(17)	1.71683(16)	0.42894(13)	0.0131(4)
P(4)	0.53225(18)	1.96547(18)	0.68306(14)	0.0178(4)
O(1)	1.3173(5)	1.6469(5)	0.9948(4)	0.0197(10)
O(2)	0.8655(6)	1.8515(5)	0.3925(4)	0.0264(11)
O(3)	1.1004(5)	1.6121(5)	0.7072(4)	0.0201(10)
O(4)	0.8960(5)	1.6406(5)	0.5651(4)	0.0186(10)
O(5)	1.3123(6)	1.6450(6)	0.7703(4)	0.0300(12)
O(6)	0.5992(5)	2.0679(5)	0.7153(5)	0.0268(11)
O(7)	1.1671(5)	1.5159(6)	1.1918(4)	0.0298(12)
O(8)	0.6321(6)	1.9228(6)	0.5765(4)	0.0373(14)
O(9)	1.3481(5)	1.6591(6)	0.5580(4)	0.0282(11)
O(10)	0.9399(6)	1.6202(5)	0.3605(4)	0.0269(11)
O(11)	0.5005(7)	1.8275(6)	0.7892(4)	0.0409(15)
O(12)	1.2019(6)	1.8517(5)	0.6348(5)	0.0334(12)
O(13)	0.3887(6)	2.0280(7)	0.6519(5)	0.0408(14)

Atom	x	y	z	U_{iso}
O(14)	0.6593(7)	2.3071(6)	0.8230(5)	0.0381(14)
O(15)	1.4323(7)	1.4612(8)	1.1404(5)	0.0521(18)
O(16)	0.8826(5)	2.2529(6)	0.5955(5)	0.0351(13)
O(17)	0.6191(6)	2.5581(5)	0.5818(5)	0.0310(12)
O(18)	0.3803(6)	2.3260(6)	0.6805(5)	0.0339(12)
O(99)	0.902(2)	1.985(2)	0.5222(17)	0.062(5)
N(1)	1.0971(9)	1.0933(9)	1.0080(7)	0.073(2)
C(2A)	1.2538(12)	1.0457(12)	0.9726(10)	0.029(3)
C(2B)	1.0820(12)	1.2504(11)	0.9473(10)	0.027(3)
C(2C)	1.0544(13)	1.0653(14)	1.1412(10)	0.044(3)
N(4)	1.2561(13)	1.2285(13)	1.0653(11)	0.060(3)
C(3C)	1.1462(16)	1.1434(17)	1.1755(10)	0.049(3)
C(3B)	1.1748(18)	1.3305(12)	0.9805(14)	0.062(4)
C(3A)	1.3475(12)	1.1250(17)	1.0062(14)	0.056(4)
N(4')	1.277(3)	1.152(3)	1.086(2)	0.059(4)
C(3B')	1.243(3)	1.289(2)	0.996(3)	0.053(6)
C(3A')	1.352(2)	1.047(3)	1.023(3)	0.064(7)
N(4")	1.187(3)	1.211(3)	1.134(3)	0.052(4)
C(3C")	1.023(3)	1.212(5)	1.164(3)	0.060(5)
C(3B")	1.290(4)	1.233(5)	1.012(3)	0.055(4)
C(3A")	1.225(5)	1.053(4)	1.166(3)	0.063(5)
C(2A")	1.148(4)	0.982(2)	1.116(3)	0.049(5)
C(2C")	0.975(3)	1.184(3)	1.070(3)	0.049(5)
C(2B")	1.228(4)	1.192(4)	0.933(2)	0.046(4)

the zeolite atlas, the program Kriber [22] was used. The analysis clearly revealed that the structure of the crystals with rectangular morphology is identical to that of Chabazite and the other two types are unique and new, thus justifying a new nomenclature.

The study also shows that template molecule choice is extremely important in this system and that the inclusion of the template molecule DABCO has a large influence on the incorporation of Ca^{2+} ions, since attempts to reproduce this structure with the framework-substituted calcium ions always failed when using some other organic template molecule. Also other divalent metals were tried in this synthesis, to replace the calcium in the framework; these also failed and produced only AlPO-5, suggesting a unique relationship between the calcium ions and the DABCO molecule in this synthesis.

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