SYNTHESIS AND STRUCTURE SOLUTION OF SMALL PORE ALUMINOPHOSPHATES

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Summary

By utilising template molecules known to produce Zeotype framework materials, two new synthesis routes leading to the production of DAF-4 and DAF-5 were presented. To reproduce the microporous material DAF-4 the template molecule successful in the synthesis of the pure SiO_2 structural analogue, LEV, was used and produced the phase pure material DAF-4. To reproduce the DAF-5 microporous material, the template used was chosen for its shape, which closely matched that used previously, differing only in the nitrogen atom positions. A phase pure sample of DAF-5 was produced.

Key words: *Small pore aluminophosphates, structure solution.*

1. Introduction

Zeolite analogues containing transition metals are highly desirable for industrial processes. As a result of this, hetero-atom substituted small pore aluminophosphates have attracted considerable attention in recent years due to their wide range of substitution chemistry, leading to the production of solid catalysts with a range of functionality [1 - 3].

Alongside efforts to produce zeolite analogues utilising the template molecule used in the formation of high-silica zeolites, the search for new microporous AlPO materials has led to many interesting developments. The useful properties of these materials have directed research efforts into their development and template role in synthesis and especially the rational design of new structures. One such design used the molecule 4-piperidinopiperidine as predicted by the computer methodology ZEBEDDE [3] as the template to produce a microporous framework with a structure analogous to that of the mineral Chabazite. This template was used for the synthesis of a cobalt-substituted aluminophosphate, [5] which was shown to have a chabazite-type structure containing one 4-piperidinopiperidine molecule per cage fully occupying the cage. The material produced was designated DAF-5.

Knowing that this template produces a Chabazite-type framework, it was decided that a template would be used with a slightly different structure, by keeping the same overall structure shape but moving one of the nitrogen atoms to the 4^{th} positions to make 4,4-bipiperidine. With this we aimed to produce a second synthetic route to the material DAF-5.

The structure of the pure silaceous zeolite Levyne was reported in the early nineties by McCusker [6], using the organic molecule adamantanamine as the templating species. Both the aluminosilicate and pure silaceous forms have been reported [7] but only the structurally analogous aluminophosphate DAF-4 has been reported utilising 2-methylcyclohexane as the structure-directing template [1]. Knowing that the pure SiO_2 form was produced with the adamantanamine template, a cobalt-substituted AlPO was synthesised with the Levyne-type structure.

2. Synthesis and methods

A cobalt-substituted aluminophosphate (CoAlPO) was prepared using 4,4-bipiperidine as the template molecule. Cobalt was chosen as the substituting heteroatom for reasons previously stated.

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, and the template was added last. 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 195°C for 20 hours. The initial gel composition for the synthesis was

$$0.7\ Al_2O_3 : 1.0\ P_2O_5 : 0.3\ Co(OAc)_2 : 1\ Template : 30\ H_2O$$

Phase purity was checked by powder diffraction,

recorded with a Siemens D500 diffractometer at University College London.

The same initial gel composition was again used for the adamantanamine synthesis, but the hydrothermal synthesis conditions were optimised at 170°C for 4 days.

The samples produced were blue crystals with dimensions up to approximately 40x20x20µm. The crystals used for the diffraction experiment were too small for a conventional laboratory X-ray source and therefore the single-crystal studies were performed at station 9.8 of Daresbury SRS, using a Bruker SMART CCD diffractometer. The structure was then solved and refined using the SHELX-97 suite of programmes [8].

3. Results and discussion

The diffraction patterns for the two as-prepared samples are shown in Figures 3 and 4. It is clear in both cases that the prepared sample patterns match closely with those of their respective framework standard, type. The bipiperidine material matches the Chabazite standard and the adamantanamine material matches the simulated pattern generated from the single-crystal solution by the programme PowderCell 2.3.

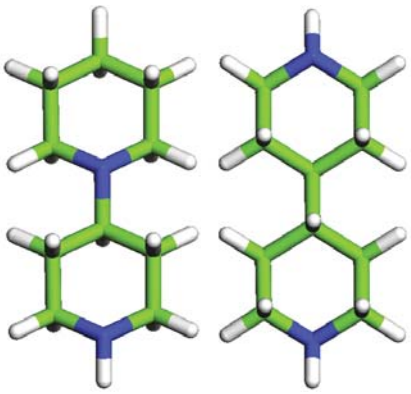
Both the powder X-ray patterns obtained show the single crystal data to be representative of the bulk sample.

3.1. Bipiperidine templated material

The structure was found to be analogous to that of the chabasitic DAF-5 structure and was solved and refined in the space group $R\bar{3}$. The crystallographic details are given in Table 1.

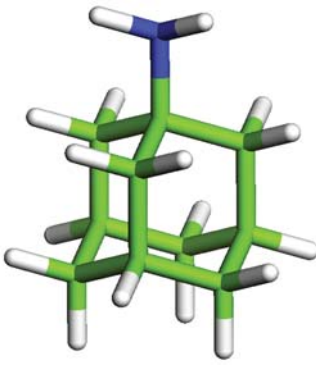
The substituted cobalt content refines to 35%, giving a much higher cobalt substitution to that previously obtained in the original DAF-5 synthesis where optimum conditions produced a 20% Co substitution.

The atom positions and selected bond lengths are shown in Tables 2 and 3 respectively. All the values obtained from the refinement are chemically reasonable. The position of the template is clearly visible within the framework structure, despite the obvious 3-fold disorder due



(a)

Figure 1. *Structure of 4-piperidinopiperidine (a) Structure of 4,4-bipiperidine (b). Carbon atoms shown in green and nitrogen in blue*



(b)

Figure 2. *Structure of adamantanamine. Carbon atoms are shown in green and nitrogen in blue*

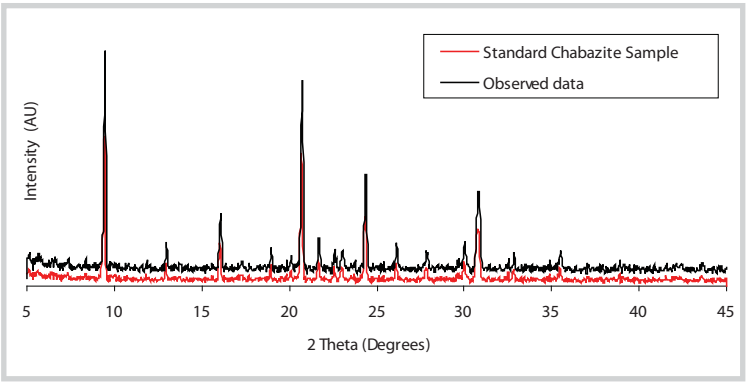


Figure 3. *Powder X-ray diffraction patterns for the as-prepared Bipiperidine-templated sample (Black) and a standard Chabazite sample. Intensities are arbitrary and the patterns have been offset for clarity*

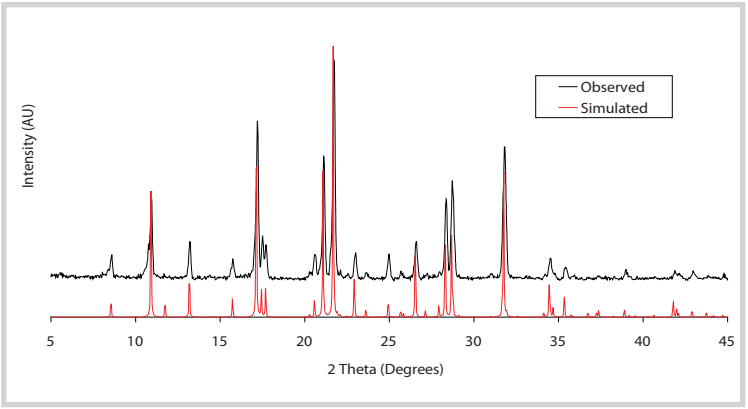


Figure 4. *Powder X-ray diffraction patterns for the as-prepared adamantanamine-templated sample (Black) and the simulated powder pattern. Intensities are arbitrary and the patterns have been offset for clarity*

to its position in the centre of the cage, where it occupies a position similar to that found with the 4-piperidinopiperidine structure as reported by G.Sankar et al [5]. Again we see only a single template molecule present within the cage. The template location is shown in Figure 5, the hydrogen atoms have been omitted for clarity.

The disorder at the template location is clearly visible in Figure 6, where the orientation of the template molecule is shown. The

Table 1. *Crystallographic details for the CoAlPO CHA (Bipiperidine template) structure*

Chemical formula	$Al_{0.65}Co_{0.35}PO_4N_{0.33}C_{1.667}H_{333}$
Formula weight	135.29
Temperature	150(2)K
Radiation, wavelength	Synchrotron, 0.6929Å
Crystal system, space group	Trigonal, $R\bar{3}$
Unit cell parameters	a = 13.5732(2) Å α = 90°
	b = 13.5732(2) Å β = 90°
	c = 15.4406(4) Å γ = 120°
Cell volume	2463.54(8) Å^3
Z	21
Calculated density	1.915g/cm^3
Absorption coefficient μ	1.520mm^{-1}
F(000)	1394
Diffractometer	ω rotation with narrow frames
θ range for data collection	3.1 to 29.4°
Index ranges	h-17 to 19, k-19 to 12, l-18 to 21
Completeness to θ = 29.4°	91.6%
Reflections collected	5,566
Independent reflections	1,494 (R_{int} = 0.0199)
Reflections with $F^2 > 2\sigma$	1,406
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0996, 20.4589
Data/restraints/parameters	1,494/30/81
Final R indices [$F^2 > 2\sigma$]	R_1 = 0.0693, wR_2 = 0.1959
R indices (all data)	R_1 = 0.0723, wR_2 = 0.1985
Goodness-of-fit on F^2	1.135
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.88 and -0.88eÅ^{-3}

Table 2. *Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for CoAlPO CHA, (Bipiperidine template)*

Atom	x	y	z	U_{iso}
Al1	0.67309(7)	0.57063(7)	0.73932(5)	0.0282(3)
Co1	0.67309(7)	0.57063(7)	0.73932(5)	0.0282(3)
P1	0.43880(8)	0.34057(8)	0.72732(6)	0.0288(4)
O1	0.5419(4)	0.4538(4)	0.7089(3)	0.0762(16)
O2	0.3940(4)	0.3399(4)	0.8169(2)	0.0543(10)
O3	0.3501(4)	0.3254(4)	0.6615(3)	0.0649(13)
O4	0.4704(4)	0.2494(4)	0.7176(3)	0.0605(11)
N1	0.6667	0.3333	0.5620(8)	0.147(6)
C1	0.621(2)	0.4077(19)	0.5226(7)	0.159(6)
C2	0.604(2)	0.390(2)	0.4231(6)	0.178(6)
C3	0.6667	0.3333	0.3837(4)	0.190(7)

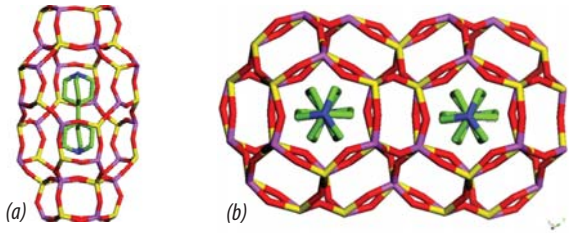


Figure 5. *Structure of CoAlPO CHA determined from single-crystal X-ray diffraction. The location and disorder of the template are clearly shown in (a) and (b). The hydrogen atoms have been omitted for clarity*

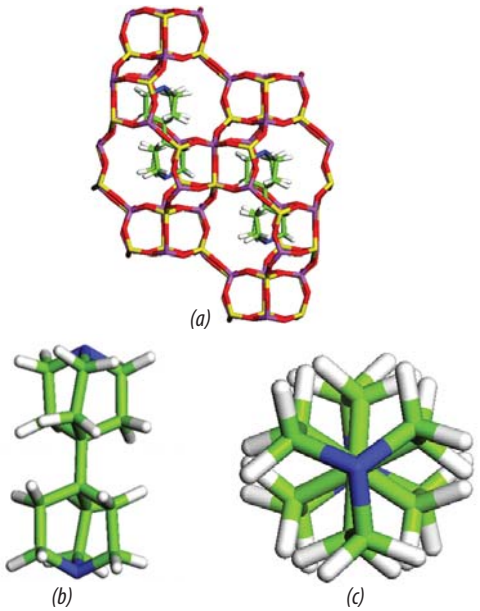


Figure 6. *The template disorder determined from single-crystal X-ray diffraction. The location and disorder of the template are clearly shown in (a), (b) and (c). The hydrogen atoms have been omitted for clarity*

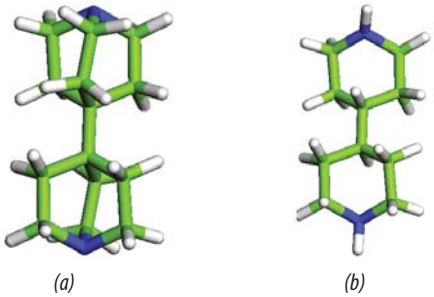


Figure 7. *The template disorder determined from single-crystal X-ray diffraction: The 3-fold disorder present at the template location (a) and one of the three contributing orientations (b)*

Table 3. *Selected bond lengths and angles for the CoAlPO CHA (Bipiperidine template). The Co partially occupies the Al T sites*

Atom pair	Bond length (Å)	Bond angle	Degrees
Al1-O1	1.756(4)	O1-Al1-O2A	112.3(2)
Al1-O3B	1.764(4)	O1-Al1-O4C	106.0(3)
Al1-O2A	1.797(4)	O2A-Al1-O4C	113.4(2)
Al1-O4C	1.814(4)	O1-Al1-O3B	105.4(2)
P1-O1	1.500(4)	O2A-Al1-O3B	108.0(2)
P1-O3	1.509(4)	O3B-Al1-O4C	111.6(2)
P1-O2	1.509(3)		
P1-O4	1.506(4)	O1-P1-O2	110.3(3)
		O1-P1-O4	108.7(3)
N1-C1	1.547(12)	O2-P1-O4	111.4(2)
N1-C1F	1.547(13)	O1-P1-O3	106.5(3)
N1-C1C	1.547(12)	O2-P1-O3	109.0(3)
C1-C2	1.553(12)	O3-P1-O4	110.9(3)
C2-C3	1.527(13)		
C3-C2F	1.527(13)		
C3-C2C	1.527(13)		
C3-C3G	1.557(12)		

Table 4. *Crystallographic details for the CoAlPO LEV (adamantanamine template) structure*

Chemical formula	$Al_{0.78}Co_{0.22}PO_4N_{0.22}C_{222}H_{333}$
Formula weight	162.88
Temperature	150(2)K
Radiation, wavelength	Synchrotron, 0.6843Å
Crystal system, space group	Hexagonal, R $\overline{3}c$
Unit cell parameters	a = 13.4256(6) Å α = 90°
	b = 13.4256(6) Å β = 90°
	c = 45.184(3) Å γ = 120°
Cell volume	7053.1(6) Å^3
Z	54
Calculated density	2.071g/cm^3
Absorption coefficient μ	1.257mm^{-1}
F(000)	4,428
θ range for data collection	1.90 to 29.22°
Index ranges	H - 19 to 10, k - 15 to 19, l - 60 to 62
Completeness to θ = 25°	99%
Reflections collected	15,623
Independent reflections	2,300 (R_{int} = 0.0461)
Reflections with $F^2 > 2\sigma$	2,008
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0744, 65.4886
Data/restraints/parameters	2,300/31/108
Final R indices [$F^2 > 2\sigma$]	R_1 = 0.0667, wR_2 = 0.1778
R indices (all data)	R_1 = 0.0735, wR_2 = 0.1816
Goodness-of-fit on F^2	1.155
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.949 and -0.914eÅ^{-33}

Table 5. *Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for CoAlPO, LEV (adamantanamine template)*

Atom	x	y	z	U_{iso}
Al1	0.90620(7)	0.3333	0.0833	0.0163(3)
Co1	0.90620(7)	0.3333	0.0833	0.0163(3)
Al2	0.77118(7)	0.00432(6)	0.035179(17)	0.0176(2)
Co2	0.77118(7)	0.00432(6)	0.035179(17)	0.0176(2)
P1	0.6667	0.09653(8)	0.0833	0.0161(3)
P2	1.00567(6)	0.23703(7)	0.035059(18)	0.0175(2)
O1	0.7701(2)	0.2129(2)	0.08934(8)	0.0414(8)
O2	0.9740(3)	0.3142(3)	0.05193(7)	0.0397(7)
O3	0.9185(2)	0.1114(2)	0.04049(7)	0.0371(7)
O4	0.6848(3)	0.0410(3)	0.05588(6)	0.0367(7)
O5	1.0076(2)	0.2690(3)	0.00272(6)	0.0367(7)
O6	1.1222(2)	0.2565(3)	0.04492(6)	0.0319(6)
N1	1.0000	0.0000	0.07964(10)	0.081(9)
N1'	0.8754	-0.2369	0.17026(10)	0.063(5)
C1	1.0000	0.0000	0.11229(10)	0.059(2)
C2	0.9408	-0.1220	0.12369(10)	0.0749(18)
C3	0.9363	-0.1225	0.15770(10)	0.0673(16)
C_4	0.8763	-0.0604	0.16772(10)	0.081(2)

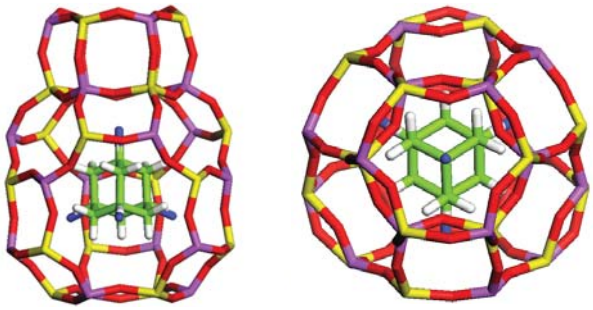
three different orientations of the template can be clearly seen, with the rotation through the long axis of the molecule about the nitrogen positions.

Although only one third occupied in any of the positions shown in a) of Figure 7, the molecule has a shape as shown in b).

3.2. Adamantanamine-templated material

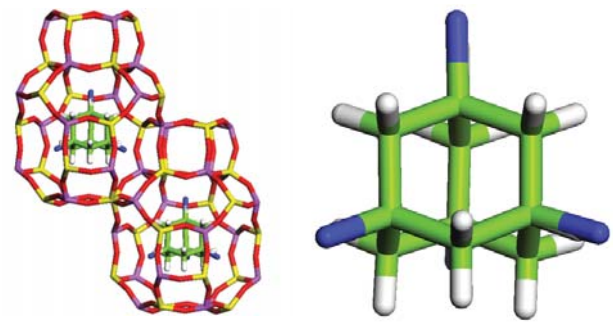
As the original microporous synthesis using adamantanamine was a pure silica form, we expected the space group for the CoAlPO system to differ, and this was true, as the structure was solved and refined by direct methods in Rc compared to the previous Rm. The unit cell dimension of the c axis is double that found for the pure siliceous material and similar to that for DAF-4. The substituted cobalt content refines to 22%. The crystallographic details are given in Table 4.

Despite the template disorder within the system, a good final refined model was obtained, with a low R-factor of 7.35% and clearly showing the presence of only one template molecule occluded within the cage



(a) *(b)*

Figure 8. *Views of the CoAlPO structure refined from data collected at 150K. The template location and orientation are clearly shown in (a) and (b). Note only one template species per cage; the substituted cobalt has been omitted for clarity but partially occupies some of the aluminium sites*



(a) *(b)*

Figure 9. *Schematic views of the location of the template molecules (a) highlighting the presence of a single molecule per cage (b). The enlarged template shows the disorder present within the system*

Table 6. *Selected bond lengths and angles for the CoAlPO LEV (adamantanamine template). The Co partially occupies the Al T sites. The average bond lengths for the N-C and C-C bonds are given, as the variation was small*

Atom pair	Bond length (Å)	Bond angle	Degrees
P1 - O1	1.507(3)	O1-P1-O1a	109.7(3)
P1 - O1a	1.507(3)	O1a-P1-O4a	111.27(17)
P1 - O4	1.527(3)	O1-P1-O4	111.26(17)
P1 - O4a	1.527(3)	O1-P1-O4a	106.87(19)
P2 - O2	1.508(3)	O1a-P1-O4	106.86(19)
P2 - O3	1.517(3)	O4-P1-O4a	110.9(2)
P2 - O5	1.519(3)		
P2 - O6	1.518(2)		
Al1 - O1	1.753(3)	O1-Al1-O1b	109.0(2)
Al1 - O2	1.773(3)	O1-Al1-O2	111.36(15)
Al1 - O1b	1.753(3)	O1-Al1-O2b	108.47(16)
Al1 - O2b	1.787(3)	O1b-Al1-O2b	111.37(15)
Al2 - O3	1.787(3)	O1b-Al1-O2	108.47(16)
Al2 - O4	1.742(3)	O2-Al1-O2b	108.2(2)
Al2 - O5c	1.773(3)		
Al2 - O6d	1.762(3)		
N - C	1.475		
C - C	1.501		

structure although the disorder does suggest it is freely rotating within the confines of the cage. The refined structure and the location of the disordered template are shown in Figure 8.

With the final structure refined in the space group $R\bar{3}c$, it is not possible to identify any cobalt ordering within the system. Attempts were made to lower the symmetry in order to resolve this but no satisfactory solutions could be found. Therefore, the Co Occupancy was refined on both the aluminium T sites with the Co+Al occupancies = 1 for each T atom position.

The disordered template location is clearly shown in Figure 9 and shows how the single template molecule is located within the cage. The result obtained does suggest that the template can freely rotate within the confines of this position but suggests that the nitrogen group points into the double six-ring.

Analysis of the bond lengths and angles for the DAF-4 type material does not give clear indication of an aluminium site preference within the structure, but does hint that slightly more has substituted on the Al2 site, as shown by the slightly longer bond lengths for this site.

4. Conclusion

In this work two framework analogues of known structures have been presented, showing new synthetic routes to the known aluminophosphate materials DAF-4 and DAF-5. In both cases single-crystal structure solution was used to provide the clearest possible insight into the framework structure obtained and the number and location of the structure-directing template molecules within the cages of the material. The structure of the adamantanamine-templated material is analogous to the pure SiO_2 Levyne structure and matches closely the crystallographic data obtained for the original DAF-4 synthesis, both space group and cell dimensions. A quicker synthesis was achieved than for the pure microporous material, 4 days as opposed to 7 [1].

As seen with the DAF-5 synthesis by Sankar et al. [5] in this synthesis a single but bulky bipiperidine template molecule was found, emphasising the importance of template shape upon the synthesis of materials alongside the charge-balancing effects.

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