TRIETHYLAMINE TEMPLATE LOCATION WITHIN CoAlPO-34 TYPE MATERIALS BY HIGH-RESOLUTION POWDER DIFFRACTION AND SINGLE-CRYSTAL DIFFRACTION TECHNIQUES

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Summary

A detailed structural study into the effects of substituted cobalt concentration within the aluminophosphate material CoAlPO-34 on the uptake of the template within the framework structure has been performed. The structure is classed as "small pore", with an aperture of ca 3.8Å, and has a structure analogous to that of the naturally occurring mineral Chabazite. Both high-resolution powder diffraction (HRPD) and single-crystal diffraction (SCD) techniques in the form of micro-crystal diffraction facilities at the Daresbury Synchrotron Source have made it possible to collect high-quality diffraction data for the range of crystalline CoAlPO-34 samples. The results showed the template location and ordering within the structure at the various substituted cobalt concentrations up to the Co:T site ratio of 1:6 expected to produce two template molecules per cage. The location of the single organic template molecule within the microporous framework is clearly shown.

Key words: *Template, location, high resolution X-ray diffraction, single-crystal difraction.*

1. Introduction

Aluminophosphate framework structures analogous to the naturally occurring mineral Chabazite were first synthesised in 1984. Lok et al. of Union Carbide [1] synthesised a series of silicon-substituted aluminophospahte materials (SAPO's) and this was followed by the substitution of divalent metal ions into the AlPO framework, where the Al^{3+} is replaced by divalent Co, Mn, Zn, Mg, Fe, etc, forming MeAlPO's. These materials still command large amounts of interest today, particularly in the area of shape selective-catalysis [2, 3]. Of particular interest are the chabazitic (CHA) systems, i.e. the structure types -34, -44, and -47, differing only in chemical composition and the template species used in synthesis, and type -18 (AEI) which has a similar structure differing only in how the double six-rings stack (Fig.1). These systems are known to be effective catalysts for the conversion of methanol to light olefins, in particular being selective for ethene over higher olefins [4 - 6] which attracted considerable attention. Initially type-34 materials were prepared using tetraethylammonium hydroxide (TEAOH) as the template [1] but, since this initial synthesis several other templates have been successfully used, including morpholine [7, 8], piperidine [9] and triethylamine [10, 11]. Most of the resultant synthesis gels react under similar conditions, while some require changes in temperature, pH and time to form the specific structure. In this study all the structures are of the AlPO-34 type synthesised using triethylamine as the structure-directing agent.

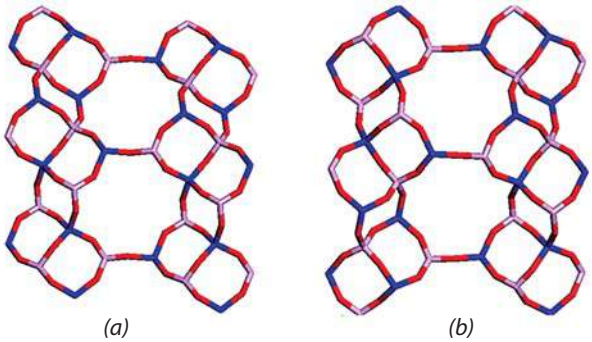


Fig.1. *A section of the CHA (Chabazite) type framework is given in (a) as found in structure types -34, -44, and -47. (b) Shows the AEI structure as in type -18. The main difference is in the stacking of the double 6-rings. The Co/Al sites are shown in blue*

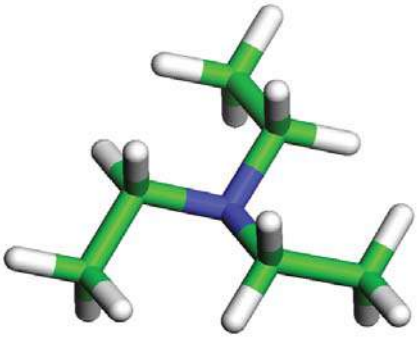


Fig.2. *Structure of the template species triethylamine. The nitrogen site is shown in blue, the carbon in green and the hydrogen's are white*

Uncertainty over the factors influencing the synthesis of these materials still exists; the presence or absence of a heteroatom within the synthesis gel can radically alter the structure of the resulting material. The relationship between the template and cobalt concentration is explored through the Triethylamine-templated CoAlPO-34 structure. Lewis et al [16] showed computationally that this system contains 2 template molecules per cage, but little crystallographic information has been obtained [16]. Several authors have calculated the number of template molecules located within the Chabazite-type cage of heteroatom-substituted AlPO-34 by employing single-crystal or thermogravimetric studies [14]. Usually one or two templates are found per cage; depending on which template was used and the type of heteroatom substituted into the framework, this number can vary.

Results for morpholine show that 2 templates are usually found per cage [12, 13]. However Marchese et al [13] showed that there are 1.5 molecules of morpholine per cage but also two molecules of water; this suggests that 50% of the cages might be occupied by 2 molecules of morpholine; the rest will have 1 molecule of morpholine and 4 molecules of water. If triethylamine is used as the templating agent, thermogravimetric analysis of the synthesised SAPO-34 in the presence of HF shows there are two template molecules present per cage. Computational studies [17] have shown that 2 triethylamine molecules can fit comfortably within the cage. Synthesis of heteroatom-substituted AlPO-34 with tetraethylammonium hydroxide [2, 12, 18] and 1-propylamine [7] showed only one template molecule per chabazite cage.

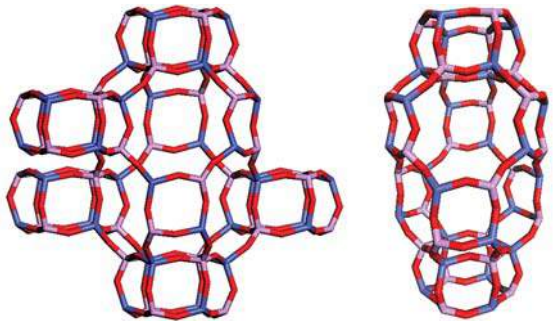


Fig.3. *A model of the CHA (Chabazite) type framework. The Co/Al sites are shown in blue, the phosphorus in purple and the bridging oxygen atoms are red*

Table 1. *Summary of the crystal size obtained for each sample prepared. Powder samples are defined here as having a particle size smaller than 15 x 15 x 15μm*

Co^{2+} concentration (%) at synthesis	Powder	Single crystal
10	Yes	No
15	Yes	Yes
20	Yes	Yes
25	Yes	No

Lewis et al [16] reported that, energetically, it is preferential for two template molecules to be found in each cage. The calculations show a significant increase in stability over a single template occupation. Xu et al [14] synthesised CoAPSO-34 and SAPO-34 using triethylamine in the presence of HF; thermogravimetric analysis showed the presence of two molecules per cage. Using computational techniques they also showed that two triethylamine molecules fit comfortably inside the chabazite cage. There are however, only limited single-crystal data reported for heteroatom-substituted AlPO-34 synthesised from in the absence of HF [16].

In paper we will compare the number and locations of the template molecules within the chabazite cages as a function of cobalt concentration. The CoAlPO-34 structures were synthesised with triethylamine as the structure-directing agent (Fig.2).

The structure of chabazite is comprised of double six-rings, with 3 sets of four rings attached to each six-membered ring (6-membered with respect to the number of T-atoms, a conventional notation used when describing such structures). Two of these secondary units join together to form a cage structure with intersecting 8-membered ring channels. The cage units then join together to form the 3-dimensional microporous network, (Fig.3). The 8-rings channels have a pore aperture of approximately 3.8 x 3.8Å.

One of the problems with the detailed structural characterisation of these materials is that they rarely form large enough single crystals for study using standard laboratory single-crystal diffraction techniques. As a result of this, many of the related structures have been solved by the combination of powder diffraction and single-crystal data, as well as computer simulations in some cases [19 - 25]. However, with the advent of micro-single-crystal diffraction facilities such as Station 9.8 at the Daresbury Synchrotron Radiation Source, it is now routinely possible to collect diffraction data from crystals as small as 15 x 15 x 15μm. For this study, however even crystals of this size were not available for all the samples prepared, necessitating the use of both single microcrystal diffraction and high-resolution powder diffraction

techniques to identify the number of templates and their location inside the CoAlPO-34 structure. The prepared samples are summarised in Table 1.

2. Experimental

2.1. Synthesis

Samples of the CoAPlO material were synthesised hydrothermally using triethylamine as the template species. In this case a solution was first made from the Co(acetate)$_2$ and some of the water. The aluminium source was combined with 85% phosphoric acid and the remaining water; this was thoroughly stirred before the addition of the cobalt acetate solution. The resultant gel was mixed until homogenous and the template was added at the final stage.

Table 2. *Gel compositions (moles) used in the synthesis of CoAPlO-34 with different cobalt concentrations*

Co	Al	P	H_2O	Template
0.10	0.90	1	60	2.0
0.15	0.85	1	60	2.0
0.20	0.80	1	60	2.0
0.25	0.75	1	60	2.0

The gel was then mixed again until homogenous and then sealed in a PTFE liner within a stainless steel autoclave and heated under autogenous pressure at 170°C for 4 days. The product is recovered by filtration and the blue crystallites were dried at 100°C for 24 hours. The gel compositions used for the cobalt concentrations are given in Table 2. Phase purity was checked by powder diffraction recorded with a Siemens D500 diffractometer. The diffraction patterns are shown in Fig.4. All patterns are similar to that of the mineral chabazite, indicating the only phase presents being the Chabazite-related CoAlPO-34 material. The peak positions also match those expected as in the Atlas of Zeolite Structures [26]. When studied using an optical microscope the samples split into two groups, with cubic blue crystals, where large crystals are formed, consistent with previous Chabazite-type samples. Fine powders are obtained in the second case. Optical pictures of the samples are shown in Fig.5.

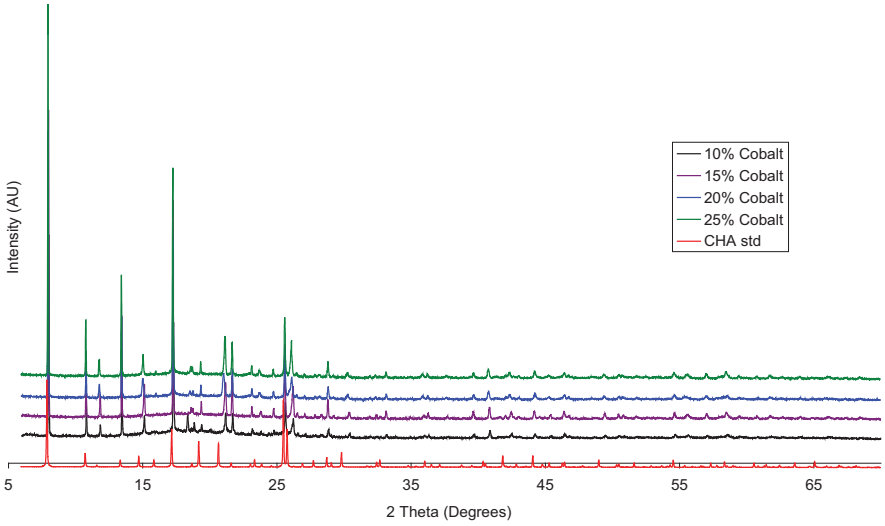


Fig.4. *XRD patterns for CoAlPO-34 synthesised with differing cobalt concentrations. Intensities are arbitrary and the spectra have been offset vertically for clarity*

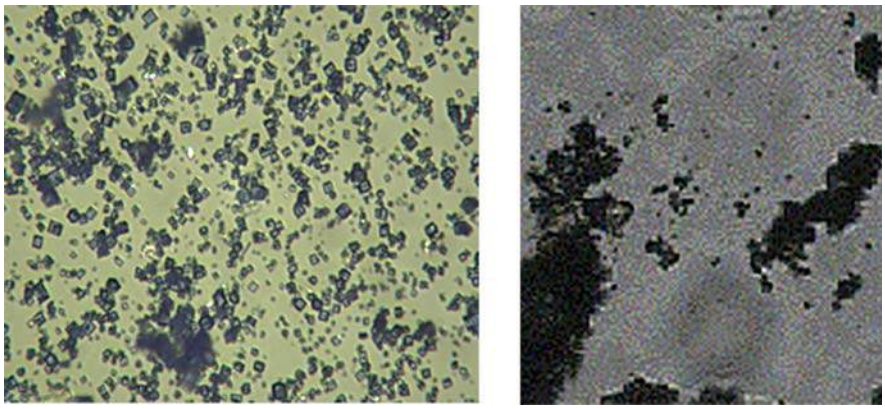


Fig.5. *Optical images showing the different crystalline sizes obtained. Picture upper shows the distinct single crystals obtained for the 15% and 20% cobalt substituted CoAPlO-34 samples. Picture lower is representative of the fine powder obtained in all other concentrations for substituted cobalt CoAlPO-34 material*

2.2. Data collection

2.2.1 Single-crystal diffraction data collection

As some single crystals of the prepared material were available, single-crystal diffraction was used to locate the template molecules inside the CoAPO-34 framework and provide supporting data to the powder analysis. Single crystal analysis of all prepared samples was not possible, as crystals of sufficient size were not always obtained. The data for the crystals were collected on Station 9.8 of Daresbury SRS using a Bruker SMART CCD area detector diffractometer equipped with

a silicon (111) crystal monochromator. A hemisphere of data was collected in each case at a temperature of 150K, employing a wavelength of 0.6892Å. The data were analysed via a least-squares refinement combined with direct methods, using the SHELXTL/SHELX-97 suite of programs [29].

2.2.2. High-resolution powder diffraction data collection

High-resolution powder diffraction data were collected on station 2.3 at the Daresbury SRS [28]. The data were collected at room temperature in capillary mode. The step size was 0.01° and the time for each step was 4s; the data were collected from 6 to 70° 2θ with a wavelength of 1.30029Å. Two patterns were collected and the data summed. The data were analysed by Rietveld profile refinement using XRS-82, the X-ray Rietveld system suite of programs [30].

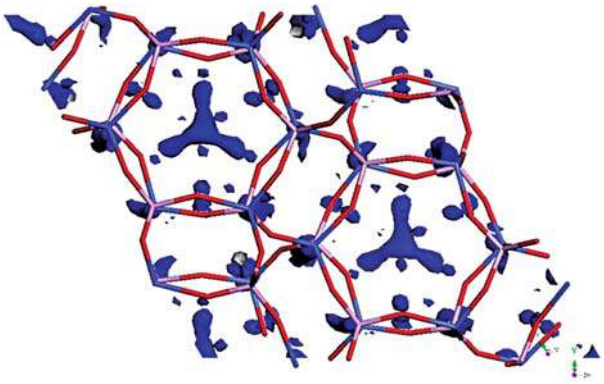


Fig.6. *The observed electron density map clearly shows the template location within the cage. The framework has been overlaid for clarity and shows the Al/Co positions in blue*

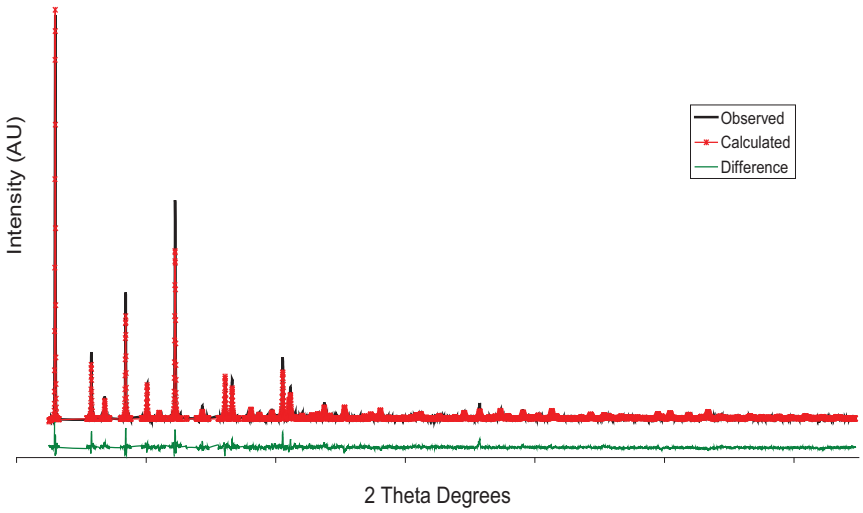


Fig.7. *Best fit between calculated XRD pattern employing XRS-82 program for HRPD data of the 10% Co sample of CoAlPO-34. Collected at station 2.3, SRS, Daresbury Laboratory, using a wavelength of 1.30029Å*

2.3. Data analysis

In order to maintain consistency and allowing for the fact that a single crystal is not always representative of the overall bulk sample, all the cobalt-substituted concentrations were refined using the Rietveld method, with the single-crystal studies in support. As the powder patterns obtained for each sample closely matched, each pattern was refined from the same initial starting model. This model was taken from the single-crystal data and was used to provide the atoms only for all the powder samples and also the initial cell dimensions and space group. The space group $R\bar{3}$ was used for each of the structures.

The first step for the refinement with XRS-82 is the estimation and subtraction of the background; this is done by linear interpolation between selected points before subtraction. This more effectively models the background function, particularly in this case the slight "hump" due to the amorphous scattering from the glass/quartz typically found when the samples are analysed in capillary mode. A pseudo-Voigt function was used to describe the peak shape [30]. In the initial stages, refinement of the peak shape function was performed before the inclusion of cell parameters and zero-point error. Once all these parameters had converged, the framework atomic coordinates were refined. In order to achieve a stable refinement, a few constraints were applied. In particular, the Al-O and P-O distances were restrained to 1.77Å and 1.53Å, with esd's of 0.02 and 0.01 respectively. The former distance is longer than the standard Al-O bond distance to take into account the cobalt substitution on the aluminium sites. Associated with this were some bond angle restraints, i.e. the O-P-O and O-Al-O angles were restrained to 109° (esd 0.80) and the Al-O-P restrained to 145° (esd 8.0). After successfully refining the framework, a 3-dimensional electron density map was generated to reveal the location of the template molecules within the structure. With the template species now included within the model, again with restraints, (distances N-C 1.48Å, esd 0.01, and C-C 1.54Å, esd 0.01. Angles C-N-C 110°, esd 1.0. and N-C-C 109°, esd 1.0.), further refinement was performed to accurately determine the template location. The hydrogen atoms on the template were geometrically placed.

In the final cycles of refinement a further electron density map was generated to check for any density unaccounted for within the structure. At this point it also becomes possible to remove the framework bond restraints; all atomic and displacement parameters were then refined to convergence. The initial cell and space group information and the starting coordinates for the framework atoms were provided by the high quality single-crystal data collected for the 15% cobalt-substituted CoAlPO-34 material. The framework coordinates were directly transferred to the Rietveld refinement for the 15% cobalt-substituted CoAlPO-34 HRPD data. This structure model was refined to completion and the final framework atom positions were then used as the starting model for the subsequent powder refinements for all other substituted cobalt concentrations.

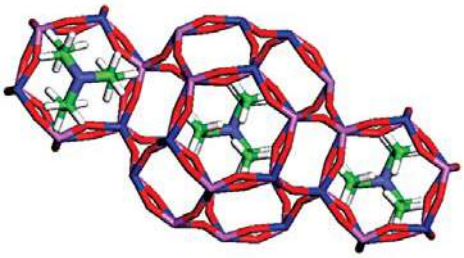


Fig.8. *View of the 10% CoAlPO-34 structure, showing the position and orientation of the template within the cage structure. Al/Co sites are shown in blue*

3. Results and discussion

3.1. High-resolution powder diffraction study of 10% cobalt in CoAlPO-34

The structure was refined from a starting model as described above using XRS-82, in the space group $R\bar{3}$. The final refined unit cell parameters were a = 13.857Å and c = 14.872Å. The final model was refined to convergence, producing final agreement factors (esd's) given in Table 3. The observed, calculated and difference profiles are shown in Fig.7. The generated difference Fourier map (difference election density map generated to help locate the template species) was generated after the framework atom positions and displacement parameters were refined. The generated 3-dimensional map clearly identifies the positions of the template carbon atoms in the chabazitic cage, and suggests only one template per cage (Fig.6). The coordinates for the carbon atoms were then added to the model and their locations refined to convergence. With the template molecule accurately located, the model was refined to convergence with the hydrogen atoms being placed last, geometrically. The final bond distances and angles are all chemically reasonable, with the final wR_p closely matching the expected value. The final R factors are shown in Table 3 and the final difference X-ray profile is shown in Fig.6.

With the structure being refined in the space group $R\bar{3}$ there are only 2 T atom positions, and as such it is not

Table 3. *Atom x, y, z coordinates and isotropic thermal parameters for the as prepared 10% CoAlPO-34. The cobalt occupancy here refines to 8.9%*

Atom	x	y	z	Occupancy	U_{iso}
P1	0.44153	0.33860	0.22688	1.00000	1.40665
Al1	0.67258	0.56636	0.23528	0.91000	2.88348
Co1	0.67258	0.56636	0.23528	0.08900	2.88348
O1	0.54232	0.45136	0.20221	1.00000	4.97041
O2	0.34700	0.31442	0.16321	1.00000	4.97041
O3	0.46982	0.24673	0.21967	1.00000	4.97041
O4	0.40550	0.33933	0.32213	1.00000	4.97041
N1	0.66667	0.44467	0.74130	0.33333	3.79955
C2	0.69171	0.46220	0.63769	1.00000	3.79955

Table 4. *Selected bond lengths and angles for the as-synthesised 10% CoAlPO-34 framework material*

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.53	O1 - P1 - O2	108.8
P1 - O2	1.51	O1 - P1 - O3	110.7
P1 - O3	1.51	O1 - P1 - O4	110.8
P1 - O4	1.50	O2 - P1 - O3	109.2
		O2 - P1 - O4	109.7
		O3 - P1 - O4	107.4
Al1 - O1	1.78	O1 - Al1 - O2*A	108.7
Al1 - O2*A	1.73	O1 - Al1 - O3*A	108.5
Al1 - O3*A	1.77	O1 - Al1 - O4*A	111.9
Al1 - O4*A	1.69	O2*A - Al1 - O3*A	110.7
		O2*A - Al1 - O4*A	108.2
		O3*A - Al1 - O4*A	108.6
		P1 - O1 - Al1	147.9
		P1 - O2 - Al1*A	153.3
		P1 - O3 - Al1*B	150.3
		P1 - O4 - Al1*C	144.1
N1 - C1	1.51	C1 - N1 - C1*A	113.1
C1 - C2	1.55	N1 - C1 - C2	112.0

Table 5. *Final agreement factors for the 15% cobalt-substituted CoAlPO-34 material*

R Factor	Value
Profile, (R_p)	0.242
Profile, Weighted, (wR_p)	0.144
Profile, Statistically Expected, (R_e)	0.135

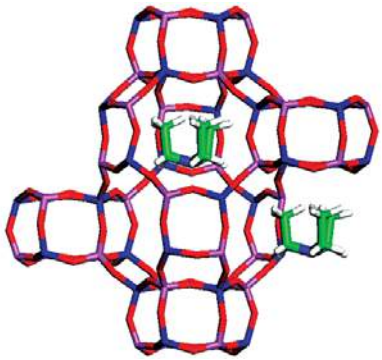


Fig.9. *View of the 10% CoAlPO-34 structure showing the position of the single triethylamine template molecule. The Al/Co sites are shown in blue*

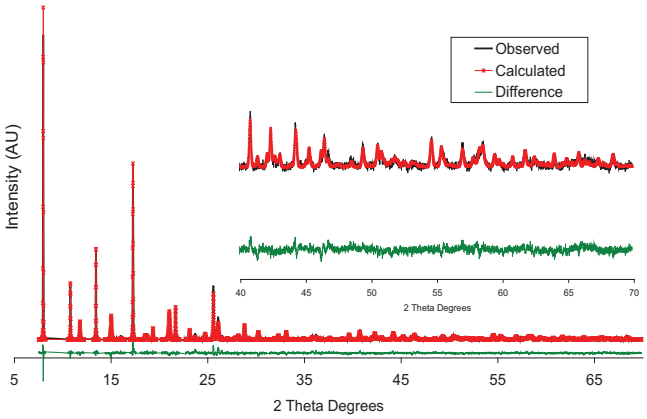


Fig.10. *HRPD data for the 15% Co sample of CoAlPO-34, showing the best fit between calculated XRD pattern and observed data, employing XRS-82 program. Collected at station 2.3, SRS, Daresbury Laboratory using a wavelength of 1.30029Å*

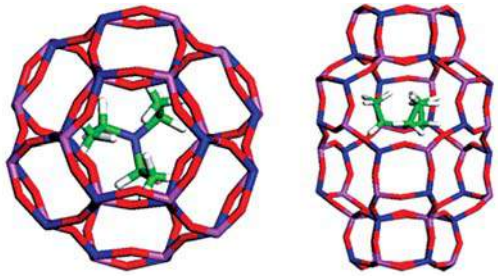


Fig.11. *View of the 15% CoAlPO-34 structure, showing the position of the single triethylamine template molecule. The Al/Co sites are shown in blue*

possible to assign separate positions to the Al and Co ions; therefore the Al site was refined with a partial occupancy of Al and Co (with (Al + Co) = 1). The cobalt content was refined and the final value matched closely the amount incorporated in the initial synthesis gel. The atomic coordinates and bond lengths and angles are given in Tables 3 and 4 respectively. The final structure derived from the Rietveld analysis clearly shows the presence of a highly ordered single template molecule contained within the cage of the framework. The atom coordinates and selected bond lengths are shown in Tables 4 and 5 respectively.

3.2. High-resolution powder diffraction study of 15% cobalt in CoAlPO-34

The initial cell dimensions were again refined along with the zero-point correction before refining the structural model. The final framework atomic coordinates from the 10% CoAlPO-34 refinement provided the starting point and this model was then refined in the same manner as the 10% data, in the space group $R\bar{3}$, with the template molecule located by the difference electron density map generated once the framework atoms had stabilised. The fully refined and converged Rietveld difference patterns are shown in Fig.10. The final refined unit cell parameters were, a = 13.832Å c = 14.921Å. The cobalt content cobalt refined to 16.6%. The template was easily located from the generated 3-dimensional density map, and again shows a single template molecule occluded within the chabazitic cage (Fig.11). Again a good correlation between the final wR_p and the expected value was obtained and the bond distances and angles are all acceptable and chemically reasonable. Final agreement factors are shown in Table 5. The atom coordinates and selected bond lengths and angles are shown in Tables 6 and 7 respectively.

3.3. High-resolution powder diffraction study of 20% Cobalt in CoAlPO-34

The refinement followed the previously established route in the space group $R\bar{3}$. The refined cell parameters obtained for the 20% CoAlPO-34 material are a = 13.831Å, and c = 14.933Å. The difference profile is shown in Fig.12 and the final agreement R-factors are given in Table 8.

The structural model obtained is shown in Fig.13. Again we find evidence for only a single triethylamine template molecule within the structural chabazitic cage. The atomic coordinates and selected bond distances and angles are given in Tables 9 and 10 respectively.

Table 6. *Atom x, y, z coordinates and isotropic displacement parameters for the as prepared 15% CoAlPO-34. The cobalt occupancy here refines to 16.6%*

Atom	x	y	z	Occupancy	U_{iso}
P1	0.44351	0.33840	0.22358	1.00000	1.29710
Al1	0.67072	0.56249	0.23301	0.83300	1.04874
Co1	0.67072	0.56249	0.23301	0.16600	1.04874
O1	0.54138	0.45126	0.19611	1.00000	2.24358
O2	0.34605	0.31291	0.16285	1.00000	2.24358
O3	0.47424	0.24780	0.21279	1.00000	2.24358
O4	0.41138	0.33711	0.32124	1.00000	2.24358
N1	0.66670	0.33330	0.73384	0.33333	3.79955
C1	0.68452	0.24229	0.76079	1.00000	3.79955
C2	0.70463	0.19545	0.67334	1.00000	3.79955

Table 7. *Selected bond lengths and angles for the as-synthesised 15% CoAlPO-34 framework material*

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.52	O1 - P1 - O2	107.9
P1 - O2	1.51	O1 - P1 - O3	110.1
P1 - O3	1.52	O1 - P1 - O4	111.9
P1 - O4	1.52	O2 - P1 - O3	109.1
		O2 - P1 - O4	110.5
		O3 - P1 - O4	106.9
Al1 - O1	1.77	O1 - Al1 - O2*A	107.8
Al1 - O2*A	1.73	O1 - Al1 - O3*A	107.9
Al1 - O3*A	1.76	O1 - Al1 - O4*A	112.8
Al1 - O4*A	1.73	O2*A - Al1 - O3*A	109.4
		O2*A – Al1 - O4*A	109.1
		O3*A - Al1 - O4*A	109.5
		P1 - O1 - Al1	143.3
		P1 - O2 - Al1*A	153.8
		P1 - O3 - Al1*B	147.1
		P1 - O4 - Al1*C	149.4
N1 - C1	1.46	C1 - N1 - C1*A	112.7
C1 - C2	1.54	N1 - C1 - C2	105.8

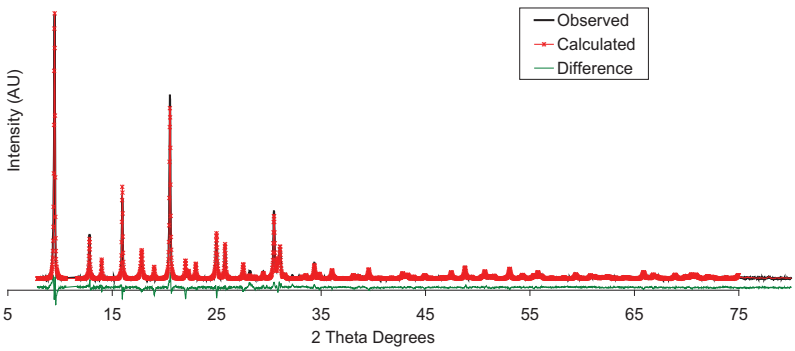


Fig.12. *HRPD data for the 20% CoAlPO-34 sample, showing the best fit between calculated XRD pattern and observed data, employing XRS-82 program. Collected at station 2.3, SRS, Daresbury Laboratory using a wavelength of 1.300291Å*

Table 8. *Final agreement factors for the 15% cobalt-substituted CoAlPO-34 material*

R Factor	Value
Profile, (R_p)	0.259
Profile, Weighted, (wR_p)	0.141
Profile, Statistically Expected, (R_e)	0.156

3.4. High-resolution powder diffraction study of 25% cobalt in CoAlPO-34

The atomic coordinates and selected bond angles and distances are given in Tables 12 and 13 respectively and are all chemically reasonable and what we would expect. The final structural model obtained is shown in Fig.15 and clearly shows the location of the single template molecule within the cage structure.

With all the structures solved and refined in the space group $R\bar{3}$, the inclusion of the centre of inversion at the centre of the chabazite cage places a symmetry-equivalent triethylamine template molecule on either side of this in order to conform to the overall symmetry of the system. However this places the two equivalent, adjacent molecules very close together, resulting in N... N separation distances shorter than an actual bond length rather than the separation of 2 adjacent groups. The separation distances are shown in Figs.16 and 17.

By lowering the symmetry for the refinement from $R\bar{3}$ to R3 we will remove the inversion point, and therefore subsequent data analysis in this revised symmetry should eliminate the second equivalent template molecule. To achieve this we went back to the two initial single crystal-studies at 15% and 20% substituted CoAlPO-34. These along side a representative powder data set, were re-analysed in the lower symmetry space group R3.

3.5. Single-crystal study of CoAlPO-34 material

Single-crystal data were collected on station 9.8 at the Daresbury SRS as described earlier and solved by direct

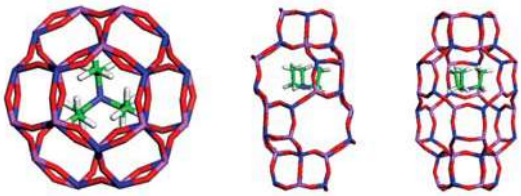


Fig.13. *View of the 20% CoAlPO-34 structure, showing the position of the single Triethylamine template molecule. The Al/Co sites are shown in blue*

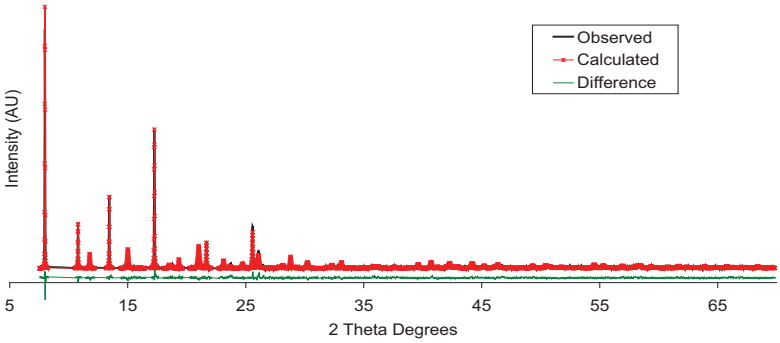


Fig.14. *HRPD data for the 25% CoAlPO-34 sample, showing the best fit between calculated XRD pattern and observed data*

Table 9. *Atom x, y, z coordinates and isotropic displacement parameters for the as prepared 20% CoAlPO-34. The cobalt occupancy here refines to 19.62%*

Atom	x	y	z	Occupancy	U_{iso}
P1	0.44330	0.33859	0.22378	1.00000	1.57755
Al1	0.67001	0.56222	0.23280	0.80380	1.34932
Co1	0.67001	0.56222	0.23280	0.19620	1.34932
O1	0.54033	0.45148	0.19728	1.00000	2.53303
O2	0.34597	0.31343	0.16327	1.00000	2.53303
O3	0.47510	0.24873	0.21229	1.00000	2.53303
O4	0.41015	0.33693	0.32110	1.00000	2.53303
N1	0.66670	0.33330	0.73380	0.33333	3.79955
C1	0.68160	0.23970	0.76020	1.00000	3.79955
C2	0.69550	0.19050	0.67180	1.00000	3.79955

Table 10. *Selected bond lengths and angles for the as-synthesised 20% CoAlPO-34 framework material*

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.52	O1 - P1 - O2	107.9
P1 - O2	1.51	O1 - P1 - O3	109.9
P1 - O3	1.52	O1 - P1 - O4	111.7
P1 - O4	1.52	O2 - P1 - O3	109.4
		O2 - P1 - O4	109.8
		O3 - P1 - O4	107.7
Al1 - O1	1.76	O1 - Al1 - O2*A	107.9
Al1 - O2*A	1.73	O1 - Al1 - O3*A	108.2
Al1 - O3*A	1.78	O1 - Al1 - O4*A	112.6
Al1 - O4*A	1.74	O2*A - Al1 - O3*A	109.6
		O2*A - Al1 - O4*A	108.6
		O3*A - Al1 - O4*A	109.7
		P1 - O1 - Al1	143.9
		P1 - O2 – Al1*A	153.6
		P1 - O3 - Al1*B	146.2
		P1 - O4 - Al1*C	148.4
N1 - C1	1.45	C1 - N1 - C1*A	112.5
C1 - C2	1.53	N1 - C1 - C2	105.5

methods with the SHELX suite of programs [29]. With the structure being refined in the space group R3, there are 4 T atom positions. Discrete positions for the Al and P atoms in the framework were immediately apparent from the different bond distances, ca 1.78 and 1.55Å respectively. The cobalt content for each structure was refined and the final values came to 15.12% and 21% for the 15 and 20% cobalt substitution respectively (substitution figures at synthesis stage). The final R-factors for both refinements were acceptable for a framework material with template molecules occluded in the pores, which have a relatively high level of thermal motion. Crystallographic details for each refinement are given in Table 14.

The space group was forced down from $R\bar{3}$ to R3 to remove the inversion centre. A previous study of the structurally similar CoAPSO-44 material had found the symmetry of the as-prepared material to be $P\bar{1}$ with a lowering of symmetry seen in the double six-rings. Attempts were made to refine this structure in this space group and resolve fully the template and cobalt ordering within the system; however, no satisfactory results were obtained. It is noted that, in the CoAPSO-44 structure solution, K^+ ions were included in the synthesis, and these were found to reside between the template molecule and adjacent double six-rings. This difference can be attributed to the slight distortion of the framework caused by the increased strain imparted on the framework by the K^+ ions.

3.5.1. Single-crystal study of 15% cobalt in CoAlPO-34

The reduction in symmetry has clearly shown that the second template suggested in the initial analysis is no longer present and it was just the symmetry equivalent with the triethylamine disordered over the two sites within the cage, instead the template occupies one site exclusively and not two simultaneously. The structural model for the 15% CoAlPO-34 is shown in Fig.18 with the

Table 11. *Final agreement factors for the 25% CoAlPO-34 composition*

R Factor	Value
Profile, (R_p)	0.248
Profile, Weighted, (wR_p)	0.145
Profile, Statistically Expected, (R_e)	0.115

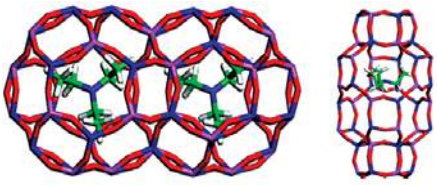


Fig.15. *View of the 25% CoAlPO-34 structure showing the position of the single triethylamine template molecule. The Al/Co sites are shown in blue*

Table 12. *Atom x, y, z coordinates and isotropic displacement parameters for the as prepared 25% cobalt inclusion. The cobalt occupancy here refines to 22.3%*

Atom	x	y	z	Occupancy	U_{iso}
P1	0.44519	0.34279	0.22306	1.00000	0.87196
Al1	0.67061	0.56453	0.23484	0.77637	1.32738
Co1	0.67061	0.56453	0.23484	0.22313	1.32738
O1	0.54072	0.45600	0.19719	1.00000	1.98367
O2	0.35017	0.31757	0.16043	1.00000	1.98367
O3	0.47553	0.25181	0.21206	1.00000	1.98367
O4	0.40997	0.33967	0.31989	1.00000	1.98367
N1	0.66670	0.33330	0.64072	0.33333	3.79955
C1	0.67604	0.23430	0.67234	1.00000	3.79955
C2	0.74936	0.26420	0.75869	1.00000	3.79955

Table 13. *Selected bond lengths and angles for the as-synthesised 25% CoAlPO-34 framework*

Atom Pair	Bond Length (Å)	Bond Angle	Degrees
P1 - O1	1.51	O1 - P1 - O2	106.8
P1 - O2	1.50	O1 - P1 - O3	111.7
P1 - O3	1.51	O1 - P1 - O4	112.1
P1 - O4	1.51	O2 - P1 - O3	108.2
		O2 - P1 - O4	110.7
		O3 - P1 - O4	107.1
Al1 - O1	1.75	O1 - Al1 -O2*A	106.6
Al1 - O2*A	1.74	O1 - Al1 - O3*A	108.0
Al1 - O3*A	1.83	O1 - Al1 - O4*A	114.2
		O2*A - Al1 -O3*A	110.2
		O2*A - AL1 -O4*A	107.6
		O3*A - Al1 -O4*A	110.0
		P1 - O1 - Al1	142.3
		P1 - O2 -Al1*A	153.1
		P1 - O3 -Al1*B	146.1
		P1 - O4 - Al1*C	147.7
N1 - C1	1.51	C1 - N1 - C1*A	110.4
C1 - C2	1.55	N1 - C1 - C2	110.4

20% data shown in Fig.19. The final atomic coordinates are given in Tables 15 and 16 for the 15% and 20% CoAlPO-34 structures respectively.

Hydrogen atoms located on the organic template molecule were given idealised positions using the HFIX/AFIX commands within SHELX. All the other atoms, as is the case for both refinements, were refined with anisotropic displacement parameters with no constraints. Fractional co-ordinates and U_{iso} for the 15% cobalt structure are given in Table 15.

3.5.2. Single-crystal study of 20% cobalt in CoAlPO-34

Further to resolving the number and location of the template molecules within the structure, distinct cobalt ordering was also found. The cobalt in these systems substitutes on the aluminium T sites located on the bottom of the double six-rings, shown in Fig.20.

3.6. High-resolution powder diffraction data

The structure was again refined as described above using XRS-82, but this time from a starting model in the space group R3. This reduction doubles the T atom site refinement and also shows some cobalt ordering within the system. The final refined unit cell parameters were a = 13.832 and c = 14.933. The final model was refined to convergence, producing final agreement factors given in Table 18. The observed, calculated and difference profiles are shown in Fig.21.

With the lower symmetry the difference electron density map was generated as before in order to locate the template molecule. The map clearly showed the presence of only a single template molecule in the framework. This was added to the model and the refinement taken to completion. A second map was generated to check for any residual electron density unaccounted for. This final map confirmed only one organic molecule in the structure, as no large electron density peaks were discovered. The final structural model is presented in Fig.22. The final agreement R-factors are given in Table 17. Again we see similar cobalt ordering from the HRPD data to that found in the single

Table 14. *Crystallographic details for CoAlPO-34*

Cobalt Concentration	15%	20%
Chemical formula	$C_{0.86}Al_{0.73}Co_{0.13}N_{0.14}O_{3.43}P_{0.86}$	$C_{0.86}Al_{0.70}Co_{0.16}N_{0.14}O_{3.43}P_{0.86}$
Formula weight	121.02	121.69
Temperature	150(2)K	150(2)K
Wavelength	0.6872Å	0.6872Å
Crystal system, space group	Trigonal, R3	Trigonal, R3
Unit cell parameters	a = 13.837(2) Å α = 90°	a = 13.808(2) Å α = 90°
	b = 13.837(2) Å β = 90°	b = 13.808(2) Å β = 90°
	c = 14.765(3) Å γ = 120°	c = 14.881(3) Å γ =120°
Cell volume	2448.2(7)Å^3	2457.2(8)Å^3
Z	21	21
Calculated density	1.724g/cm^3	1.727g/cm^3
q range for data collection	2.1° - 29.3°	2.2 - 30.5°
Completeness to q = 29.3°	93.3%	94.8%
Reflections collected	5693	5926
Independent reflections	2552 (R_{int} = 0.1339)	3014 (R_{int} = 0.1409)
Reflections with $F^2 > 2$⍁	2,168	2,138
Structure solution	direct methods	direct methods
Final R indices [$F^2 > 2s$]	R1 = 0.0706, wR2 = 0.1954	R1 = 0.0754, wR2 = 0.2007
R indices (all data)	R1 = 0.0772, wR2 = 0.2042	R1 = 0.0985, wR2 = 0.2192
Goodness-of-fit on F^2	1.034	1.033
Largest and mean shift/su	0.000 and 0.000	0.029 and 0.025
Largest diff. peak and hole	1.26 and -0.79 e	0.76 and -0.82 e Å^{-3}

Refinement method Full-matrix least-squares on F^2

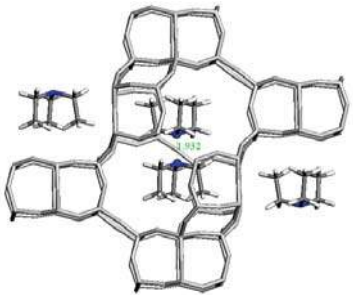


Fig.16. *The N… N separation distance for the crystallographically equivalent template molecule located either side of the centre of inversion. This distance is measured at 1.932Å for the 10% cobalt material*

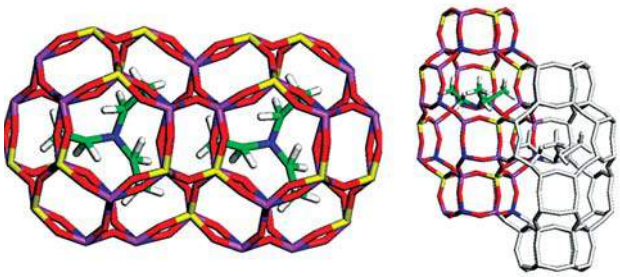
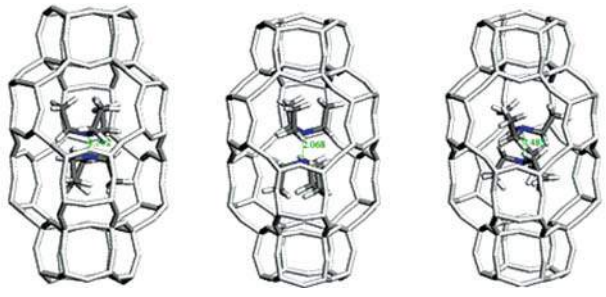


Fig.18. *View of the 15% CoAlPO-34 structure refined in R3. 2 views of 2 cage units are shown for clarity, and to show clearly the template location and orientation. There is only one template molecule per cage*



15% Cobalt *20% Cobalt* *25% Cobalt*

Fig.17. *N… N separation distances of 1.502Å, 2.068Å and 2.485Å for 15%, 20% and 25% substituted CoAlPO-34 respectively*

-crystal analysis, with the cobalt selectively substituting for aluminium on only the bottom of the double six-rings (Fig.23). The atomic coordinates, occupancies and displacement parameters are shown in Table 18.

3.7. Effect of cobalt concentration on cell parameters

As the incorporation of cobalt into the aluminophosphate framework in place of aluminium increases, as well as putting a strain in the structure, we would also expect the inclusion of a greater amount of the template acting as a charge balance. The framework strain is due to the differing bond lengths between aluminium and cobalt. For each substituted cobalt, four Al-O bonds (1.73Å) are replaced by four much longer (1.94Å) Co-O bonds. This cobalt inclusion into the aluminophosphate framework has been shown to have adverse effects, and can lead to the collapse of the structure upon calcinations once the template is removed [15].

Table 15. *Fractional x, y, z coordinates, U_{iso} and occupancy for as-prepared 15% CoAlPO-34 material. Note the Cobalt substitution refined to 15.7%*

Atom	x	y	z	Uiso	Occupancy
P1	1.22875(14)	0.22330(13)	1.02728(9)	0.0236(4)	1
P2	1.55892(13)	0.66163(13)	0.91215(10)	0.0236(5)	1
Al1	1.00445(13)	0.22897(13)	1.03231(9)	0.0222(7)	0.686
Co1	1.00445(13)	0.22897(13)	1.03231(9)	0.0222(7)	0.314
Al2	1.32917(12)	0.43799(12)	0.90759(10)	0.0242(6)	1
O1	1.1100(5)	0.1953(5)	1.0132(4)	0.0444(15)	1
O2	1.3096(4)	0.3222(4)	0.9725(4)	0.0429(13)	1
O3	1.4574(4)	0.5529(4)	0.9407(4)	0.0408(13)	1
O4	1.2227(5)	0.4699(5)	0.9334(4)	0.0404(13)	1
O5	1.5850(5)	0.6585(5)	0.8140(4)	0.0475(16)	1
O6	1.6547(4)	0.6787(5)	0.9733(4)	0.0489(15)	1
O7	1.2619(6)	0.2584(6)	1.1259(4)	0.0475(16)	1
O8	1.2459(5)	0.1258(5)	1.0042(4)	0.0484(16)	1
N1	1.0000	0.0000	0.671(7)	0.44(7)	0.333
C1	1.121(3)	0.082(3)	0.719(3)	0.34(3)	1
C2	1.234(5)	0.116(4)	0.7775(19)	0.43(4)	1

Table 16. *Fractional x, y, z coordinates U_{iso} and occupancy for as-prepared 20% CoAlPO-34 material. Note the cobalt concentration refined to 17.4%*

Atom	x	y	z	Uiso	Occupancy
P1	0.89214(9)	0.32821(8)	1.23175(7)	0.0251(3)	1
P2	1.32743(8)	0.43581(8)	1.34911(6)	0.0240(3)	1
Al1	0.89633(7)	0.55975(8)	1.22765(6)	0.0261(3)	0.652
Co1	0.89633(7)	0.55975(8)	1.22765(6)	0.0261(3)	0.348
Al2	1.10314(8)	0.44224(8)	1.35520(6)	0.0207(3)	1
O1	0.7811(2)	0.5717(3)	1.2627(2)	0.0406(9)	1
O2	1.0068(2)	0.6553(3)	1.2939(2)	0.0410(9)	1
O3	0.8624(2)	0.4176(3)	1.2494(2)	0.0398(9)	1
O4	0.9819(3)	0.3462(3)	1.2946(3)	0.0510(12)	1
O5	1.2127(3)	0.4207(3)	1.3304(3)	0.0513(12)	1
O6	1.4210(3)	0.5559(3)	1.3339(3)	0.0545(13)	1
O7	1.3321(3)	0.4045(4)	1.4458(2)	0.0458(11)	1
O8	0.9212(4)	0.3235(3)	1.1343(2)	0.0492(12)	1
N1	1.0000	0.0000	1.239(3)	0.40(3)	0.333
C1	1.079(2)	0.1390(10)	1.2399(17)	1.00(3)	1
C2	1.1172(12)	0.2213(17)	1.1490(8)	0.301(12)	1

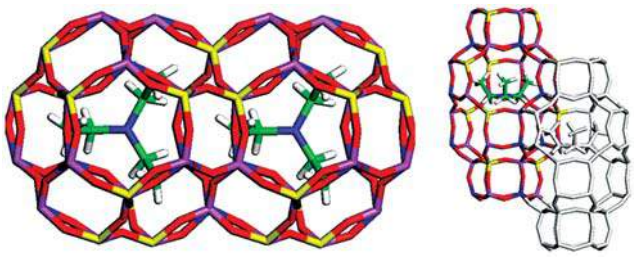


Fig.19. *Views of the 20% CoAlPO-34 structure refined in R3. 2 views of 2 cage units are shown for clarity, and to show clearly the template location and orientation. Again only one template molecule per cage is found, as seen with the 15% cobalt sample*

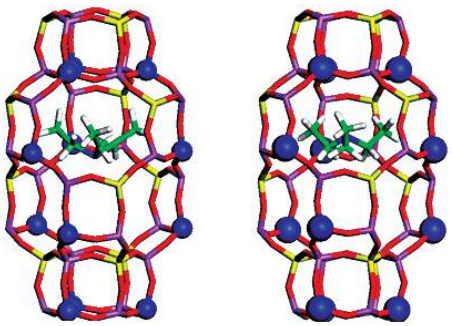


Fig.20. *Distinct cobalt ordering can be seen in both the 15 (left) and 20% (right) cobalt samples, where the cobalt substitutes for aluminium in only one of the double six-rings*

Table 17. *Final agreement factors for the 20% CoAlPO-34 material, in the lower symmetry space group R3*

R Factor	Value
Profile, (R_p)	0.269
Profile, Weighted, (wR_p)	0.163
Profile, Statistically Expected, (R_e)	0.156

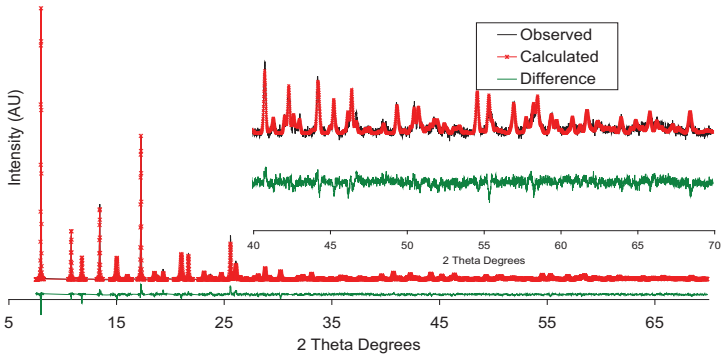


Fig.21. *HRPD data for the 20% CoAlPO-34 material refined in the lower space group R3. Showing the best fit between calculated and observed XRD patterns employing XRS-82. Collected at station 2.3, SRS, Daresbury Laboratory using a wavelength of 1.300291Å*

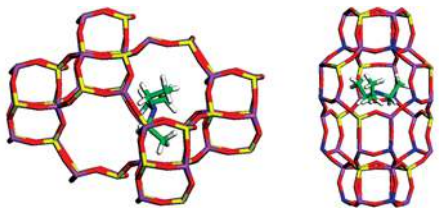


Fig.22. *Views of 20% CoAlPO-34 structure refined in R3. The template location is shown clearly, confirming only one template molecule per cage*

Table 18. *Atom x, y, z coordinates and isotropic displacement parameters for the as-prepared 20% CoAlPO-34 material. The cobalt occupancy here refines to 20%, i.e a Co:Al site ratio of 1:5*

Atom	X	Y	Z	Occupancy	U_{iso}
P1	0.44312	0.34092	0.22437	1.000	0.13048
P11	0.66598	0.55806	0.44402	1.000	0.13048
Al1	0.66816	0.56288	0.23265	1.000	0.87540
Al11	0.44436	0.34122	0.43552	0.666	0.87540
Co11	0.44436	0.34122	0.43552	0.333	0.87540
O1	0.54532	0.44984	0.18927	1.000	0.24889
O11	0.78312	0.57832	0.45904	1.000	0.24889
O2	0.34454	0.31510	0.16780	1.000	0.24889
O21	0.64840	0.63339	0.50696	1.000	0.24889
O3	0.46439	0.24220	0.21888	1.000	0.24889
O31	0.58359	0.43860	0.46695	1.000	0.24889
O4	0.41930	0.35605	0.32117	1.000	0.24889
O41	0.65088	0.58198	0.34616	1.000	0.24889
N1	0.66670	0.33330	0.72844	0.333	3.79955
C1	0.74622	0.29823	0.75922	1.000	3.79955
C2	0.79239	0.26784	0.67595	1.000	3.79955

In this work, however, we are comparing the level of template inclusion within the structure against the substituted cobalt concentration; instability upon calcination is therefore of little concern. Four different cobalt concentrations have been presented, and all studies have shown the inclusion of only one template within the chabazitic cage at all these varying concentrations. The cell parameters and the volumes obtained are shown in Table 19.

Although the cell dimensions change, particularly the c axis, there is an insignificant change in the cell volume. We would expect to see some increase in cell volume if two template molecules were to be included at higher Cobalt concentrations. The cell volume here remains almost constant, suggesting only minor changes to accommodate the larger cobalt loading on the framework and not the gradual introduction of a second template molecule to the chabazitic cage.

4. Conclusions

From the range of samples produced we were able to collect high quality data both from HRPD and a limited concentration range with microcrystal diffraction. From this we found evidence both in the original $R\bar{3}$ space group and the subsequent reduction to R3 that only a single triethylamine template molecule was occluded within the cages.

The template molecule was quite easily found in the density map as it was not badly disordered, unusual for these systems as the template normally has a high thermal motion. However, it is clear that the template does partially occupy two sites within the chabazitic cage, but not at the same time due to the separation distance between the two nitrogen atoms. Lowering the symmetry confirms this. In the work by Lewis et al [16] it was stated that, with the triethylamine template, the Chabazite phase is only likely to form when the Co:T site ratio reaches 1:6, this in turn gives 2 templates. However the ratio in this work is around 1:12 Co:T sites and we find only on template molecule in the as-prepared phase pure Chabazite. Some cobalt ordering was discovered in the double

Table 19. *Cell parameters and volumes for CoAlPO-34 structures with differing substituted cobalt concentrations*

Co concentration (%) At synthesis	Co concentration % Refined	a/Å	c/Å	Volume/Å^3
10	8.9	13.858	14.872	2473.4
15	16.6	13.832	14.921	2472.3
20	19.62	13.831	14.933	2473.9
25	22.31	13.832	14.932	2474.1

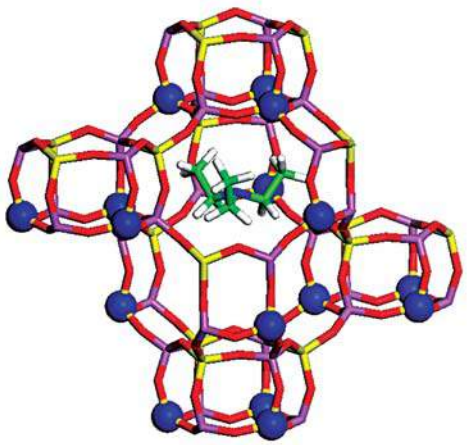


Fig.23. *View of the structure refined in R3. The cobalt ordering is highlighted as blue spheres*

six-rings, and was highlighted once the symmetry had been lowered to the space group R3. We see the cobalt substituting for aluminium only on the lower of the double six-rings. Efforts to resolve this further in $P\bar{1}$ produced no satisfactory results. To conclude, this systematic study over a range of triethylamine templated CoAlPO-34 materials does provide more evidence for the inclusion of only 1 triethylamine molecule per cage. We found only a single template molecule within the cage and no significant change in cell dimensions or volume, which could indicate changes like the inclusion of a second molecule.

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