The structure and location of 18-crown-6 ether in zeolites RHO and ZK-5

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Abstract

The use of organic additives presents the greatest versatility and control of zeolite synthesis in order to prepare novel architectures for desired applications. Despite this prospect, there is little clarity of how organic additives are involved in framework assembly and the range of behaviours that are available. To address this issue, we have considered zeolites RHO and ZK-5 which can both be prepared using 18-crown-6 ether as an additive. Previously, this additive has shown to employ different structure directing behaviours to assemble a variety of zeolites. We have used high resolution powder X-ray diffraction and Rietveld refinement to determine structural models for zeolites RHO and ZK-5 with 18-crown-6 ether occluded in the framework. In doing so, we can observe the identity, location and orientation of the occluded additive and reason the structure directing behaviour in synthesis. We report that the isolated 18-crown-6 ether molecule is involved in the assembly of zeolite RHO, and for zeolite ZK-5 it is the K⁺ coordinated macrocation. In both cases the relevant additive is disordered in the framework, suggesting that they behave as space-filling species that stabilise the formation of the α -cage.

Introduction

Zeolites are crystalline aluminosilicate minerals, known for their microporosity and pervasive use as molecular sieves, adsorbents and catalysts.¹ One of their most renowned uses is as catalysts for hydrocracking in the petrochemical industry,² however there is ongoing research into using zeolites for hydrogen fuel storage,³ carbon dioxide capture⁴ and selective extraction of radionuclides.⁵ Their structure consists of a three-dimensional framework built from silica and alumina TO₄ tetrahedra (T = Si or Al) that are connected via a shared apical oxygen atom. Within the structure, it can be recognised that the TO₄ tetrahedra arrange themselves into regular geometric subunits, which are referred to as secondary building units (SBUs).⁶

Energetically, zeolites are recognised as being metastable and it is the stabilisation of the open framework cavities that is an integral factor dictating the crystallisation process. Species that provide such a structure stabilising effect are known as structure directing agents (SDAs).^{7,8} In natural occurring zeolite formation this stabilisation is achieved by metal cations which use electrostatic interactions to stabilise the voids and guide the assembly of certain SBUs.⁹ For the preparation of synthetic zeolites, we can employ the use of organic additives that use a mixture of electrostatic, van der Waals and hydrogen bonding interactions to direct structure.¹⁰⁻¹² Although the available non-bonding interactions between organic additives and the growing zeolite framework are known there is little clarity on how exactly this impacts the zeolite crystallisation process. This is particularly important if we are to rationally traverse the metastable zeolite synthesis landscape and prepare new zeolite architectures for intended applications. The prevalent use of organic additives is best illustrated by the fact that less than 30 of the 255 zeolitic frameworks recognised by the International Zeolite Association can be synthesised in the absence of an organic additive.^{13, 14}

Davis and Lobo^{15, 16} suggest that the potential behaviour of organic additives can be divided into three classifications: true templates, organic structure directing agents (OSDAs) and space-filling species. True templates are seen to employ strong interactions and imprint their symmetry onto the growing framework. The discrepancy between OSDAs and templates is unclear, but the former is attributed by weaker interactions and an absence of symmetric or geometric matchup. Lastly, space-filling species are recognised by weak interactions and occupy the framework void spaces rather than being forthrightly involved in directing assembly. Despite these recognised categories, additional additive roles such as “structure-blocking”^{17, 18} and influence on the free-energy landscape of crystallisation^{19, 20} have been suggested but have received little research. Currently, computational calculations and synthetic approaches only consider the templating roles of organic species to rationally predict the ideal additives to prepare new zeolites.²¹⁻²³ However, a much wider appreciation of the structure directing capabilities of organic additives is required to take full advantage of their use in zeolite design.

18-crown-6 ether (18C6) is an example of an organic additive that can be used in the synthesis of multiple zeolites with a variety of topologies.²⁴⁻²⁷ Previously, it has been observed that 18C6 can undertake differing roles in the synthesis of the polymorphic EMT and FAU-type zeolites.^{20, 28} Although in both the 18C6 exists as a [(18C6)Na⁺] macrocation, it is a true geometric template for the synthesis of EMT-type zeolites and a space-filling species in the synthesis of FAU-type zeolites.²⁹⁻³³ This is important, as it demonstrates the integral role of 18C6 in the synthesis mechanism to differentiate between the two polymorphs. Zeolites RHO and ZK-5 (KFI) are two zeolites that can also be prepared using 18C6,^{24, 26} however the role, identity and location of the 18C6 species has not been determined. Figure 1 shows the framework structure of these two zeolites, in addition to the constituent SBUs. Both zeolites consist of α -cages in a body centred cubic arrangement and it is these α -cages that the 18C6 is believed to occupy,^{33, 34} however it has not been explicitly proven. Due to the lack of structural information, there is currently no understanding of how the 18C6 molecule is involved in the synthesis of these two zeolites in comparison to the FAU and EMT-type zeolites.

For the first time, we report the crystal structure of zeolites RHO and ZK-5 with the 18C6 species occluded within their zeolite frameworks. We present experimental evidence that the 18C6 molecule occupies the α -cage cavities in both zeolites, in addition to what cations the molecule is coordinated to. Using these structures, we have gleaned the role of the 18C6 organic additive throughout the crystallisation of both zeolites.

Figure 1. Structure of the RHO and KFI framework types. Included are the constituent SBUs: the α -cage, the double 8-ring (D8R), *t-pau* unit and the double 6-ring (D6R). For the latter three the code in parenthesis indicates the framework that this SBU belongs to exclusively. The framework structures are shown with the α -cages and D8Rs as solid polyhedra.

Methods

Sample Preparation

The zeolite RHO and ZK-5 samples were synthesised using the verified procedures reported by Chatelain *et al.*^{24, 26, 27, 34} using 18-crown-6 ether (18C6) as organic additive. The molar batch compositions used in the synthesis of each zeolite is shown in table 1. The materials used for sample preparation were sodium hydroxide (NaOH), potassium hydroxide (KOH), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), caesium hydroxide solution (50 wt% CsOH in water), 18-crown-6 ether ($\text{C}_{12}\text{H}_{24}\text{O}_6$, 18C6), sodium aluminate (NaAlO_2), aluminium hydroxide ($\text{Al}(\text{OH})_3$), colloidal silica (LUDOX® HS-40, 40 wt% SiO_2 in water) and deionised water. Aside from the deionised water, all the materials used were purchased from Sigma-Aldrich.

Table 1. Hydrogel batch compositions used to prepare zeolites RHO and ZK-5.

Zeolite	Al_2O_3	Na_2O	K_2O	SrO	Cs_2O	SiO_2	18C6	H_2O
RHO	1	1.8			0.3	10	0.50	100
ZK-5	1		2.7	0.1		10	1.0	220

Zeolite RHO

Zeolite RHO was prepared as follows. First the sodium and caesium hydroxide were added to the deionised water, followed by the addition of the 18C6. Upon complete dissolution the sodium

aluminate was added, and the mixture permitted to stir until it was homogeneous. Next the colloidal silica was slowly poured into the solution under stirring, to negate any rapid gelation. The produced hydrogel was then aged under stirring at ambient conditions for 24 hours. After aging, the hydrogel was transferred to a Teflon cup within a stainless-steel autoclave and heated at 110°C for 8 days. Following heating, the autoclave was removed from the oven and left to cool to the ambient temperature. The crystallised zeolite product was subsequently separated from the mother liquor via Buchner filtration, and washed with distilled water until the pH of the filtrate was neutral. The product was then dried at 90°C, before being ground prior to further calcination and dehydration.

Zeolite ZK-5

The zeolite ZK-5 precursor hydrogel was prepared by first dissolving the potassium hydroxide in a portion of the distilled water. To this solution the aluminium hydroxide was added, and then dissolved under stirring and heating to near 110°C. After dissolution, the solution was cooled to ambient temperature and replenished with any water loss via evaporation during heating. In a separate vessel the 18C6 and strontium nitrate were dissolved in the second portion of distilled water. The colloidal silica was then poured into this solution and stirred until homogeneous. Next the previously prepared alumina solution was rapidly poured into the silica solution under stirring, to produce the hydrogel which was aged under stirring for 30 minutes. After aging, the hydrogel was transferred to a Teflon cup within a stainless-steel autoclave and heated at 150°C for 5 days. Following heating, the autoclave was removed from the oven and cooled to ambient temperatures. To retrieve the as-synthesised zeolite ZK-5 sample the same process of separation, washing and drying performed for zeolite RHO was used.

Calcination and Dehydration

The as-synthesised sample of each zeolite was divided into two halves, to produce the filled and empty analogues. The filled analogue being as-synthesised with the 18C6 intact, and the empty analogue having been calcined so as to remove occluded 18C6.

Calcination was achieved by heating the relevant analogue in a tube furnace under air to 450°C for 6 hours at a ramp rate of 1 Kmin⁻¹. Throughout this heating cycle the temperature was held static at 100°C, 200°C and 300°C for 1 hour each. After calcination the sample was cooled at a rate of 1 Kmin⁻¹ to ambient conditions, including a static stage at 200°C for 1 hour.

Based on sample conditions on the respective diffractometers, only the zeolite RHO empty and filled samples were dehydrated in preparation for measurements. This was performed by heating the samples in a tube furnace under vacuum. The heating cycle consisted of a ramp rate of 1 Kmin⁻¹, with static temperatures stages of 100°C for 1 hour and 200°C for 6 hours. Following this, the sample was then cooled at a rate of 1 Kmin⁻¹ to ambient conditions, including a static stage at 100°C for 1 hour during this cooling cycle. The dehydrated sample was then transferred under vacuum to a dry argon glove box and sealed into a glass vial under argon gas.

High Resolution Powder X-ray Diffraction

Both the empty and filled analogues of zeolites RHO and ZK-5 were analysed using high resolution powder X-ray diffraction. The diffraction patterns for the dehydrated zeolite RHO samples were

recorded on the ID22 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The detector parameters were calibrated with silicon and the incident X-ray radiation had a wavelength of 0.49598 Å. The samples were loaded into 1 mm diameter borosilicate capillaries within an inert nitrogen atmosphere to prevent any sample hydration. The capillaries were subsequently sealed with vacuum grease and wax, before being mounted onto the diffractometer and cooled to 100 K using a liquid-helium-cooled cryostat. A scan range of $2\theta = 0.5\text{--}45.0^\circ$ and step size of 0.002° were used, equating to a scan length of approximately 22 minutes. Throughout scanning the capillaries were spun perpendicular to the X-ray beam to reduce preferred orientation effects.

The hydrated zeolite ZK-5 samples were analysed using a STOE STADI MP diffractometer, equipped with a MYTHEN2 1K silicon strip detector. The incident X-ray radiation was pure Cu K α 1, of wavelength 1.5406 Å, obtained using a Cu X-ray tube and a Ge(111) monochromator. A scan range of $2\theta = 3\text{--}100^\circ$, step size of 0.015° and scan length of 13.6 hours were used. The diffraction measurements were obtained in the Debye-Scherrer mode, using a transmission sample holder between two foil insets with 3 mm masks. The diffraction patterns were recorded at ambient temperature.

The patterns obtained from both diffractometers were used for structure determination, using the Rietveld method in the TOPAS Academic software.³⁵ The starting structures used were the crystal structures of zeolite RHO in the $I\bar{4}3m$ symmetry and the synthetic (Cs, K)-ZK5 zeolite, both reported by Parise *et al.*^{36, 37} For the latter ZK5 zeolite structure, the Cs sites were substituted with K sites prior to the refinement process. First the structure of the empty analogues of zeolites RHO and ZK-5 were determined, and these models used as the starting structures for the respective filled analogues.

The Rietveld refinements were performed using the $2\theta = 5.0\text{--}25.0^\circ$ and $2\theta = 14.0\text{--}69.0^\circ$ data ranges for the zeolite RHO and ZK-5 samples accordingly. During the refinement process 100,000 iterations were used, in addition to a χ^2 convergence criteria of 0.001. The quality of the Rietveld fit was evaluated using the goodness of fit factor G , equal to R_{wp}/R_{exp} .³⁸ The average mean-square displacement in all directions B_{eq} , was used to assess the degree of atomic displacement.³⁹ A summary of the refinement process and profile functions are included in the Supplementary Information (SI).

Results

Zeolite RHO

The powder X-ray diffraction patterns and final Rietveld fits for both the empty and filled zeolite RHO samples are shown in figures 2 and 3 respectively. These figures also include the goodness of fit G value for the Rietveld fits, as well as the difference between the experimental data and the fit. Tables 2 and 3 contain the final refined unit cell parameters and crystallographic data for the empty and filled zeolites accordingly. Both zeolites were fit using the $I\bar{4}3m$ space group as opposed to the ambient higher symmetry $Im\bar{3}m$ space group that zeolite RHO is typically reported in,^{40, 41} as shown in figure 1. However, there is substantial evidence in the literature where the symmetry is lowered due to certain stimuli, such as dehydration³⁶ and low temperatures⁴² which are relevant here, as well as applying mechanical pressure.^{43, 44} The $I\bar{4}3m$ symmetry is characterised by elliptical deformations in the 8-ring apertures, as illustrated in figure 4.

Figure 2. Powder X-ray diffraction patterns for the empty zeolite RHO sample. The experimental data is shown in blue, the Rietveld fit in red and the difference between the two in grey.

Figure 3. Powder X-ray diffraction patterns for the filled zeolite RHO sample. The experimental data is shown in blue, the Rietveld fit in red and the difference between the two in grey.

Table 2. Final refined unit cell parameters and crystallographic sites for the empty zeolite RHO sample. ‘Occ.’ refers to the fractional occupancy of the relevant crystallographic site.

Symmetry		Unit Cell		Refinement	
Cubic $I\bar{4}3m$		$a / \text{\AA}$	14.5457(1)	G	3.3112
				R _{wp}	6.4640
				R _{exp}	1.9522
Atom	x	y	z	Occ.	B _{eq}
Si	0.2691(1)	0.1216(1)	0.4225(1)	0.860(28)	0.64(3)
Al	0.2691(1)	0.1216(1)	0.4225(1)	0.140(28)	0.64(3)
O(1)	0.2181(1)	0.2181(1)	0.4046(1)	1	0.54(5)
O(2)	0.1261(1)	0.1261(1)	0.6182(1)	1	0.54(5)
O(3)	0.0345(2)	0.2085(2)	0.3870(2)	1	0.54(5)
Cs	0	0	0.5	0.648(1)	11.45(5)
Na	0.3333	0.3333	0.3333	0.170(6)	0.15(64)

Table 3. Final refined unit cell parameters and crystallographic sites for the filled zeolite RHO sample. ‘Occ.’ refers to the fractional occupancy of the relevant crystallographic site.

Symmetry		Unit Cell		Refinement	
Cubic $I\bar{4}3m$		$a / \text{\AA}$	14.59248(7)	G	3.6137
				R_{wp}	6.4237
				R_{exp}	1.7776
Atom	x	y	z	Occ.	B_{eq}
Si	0.2706(1)	0.1202(1)	0.4220(1)	0.859(29)	-0.34(3)
Al	0.2706(1)	0.1202(1)	0.4220(1)	0.141(29)	-0.34(3)
O(1)	0.2181(1)	0.2181(1)	0.4046(1)	1	-0.49(5)
O(2)	0.1261(1)	0.1261(1)	0.6182(1)	1	-0.49(5)
O(3)	0.0316(2)	0.2133(2)	0.3905(2)	1	-0.49(5)
Cs	0	0	0.5	0.923(1)	5.49(4)
Na	0.3333	0.3333	0.3333	0.306(9)	11.4(11)
C(1)	0.3333	0.6667	0.5	1.000(26)	20.0(5)
C(2)	0.4501(13)	0.4501(13)	0.6992(24)	0.727(26)	20.0(7)
Oc(1)	0.4552(7)	0.4552(7)	0.3598(11)	0.540(22)	17.2(7)
Oc(2)	0.6667	0.3333	0.3333	1.000(30)	19.2(8)

Metal Cations

Two crystallographic metal cation sites were determined in both zeolite RHO structures – these being a Cs^+ and a Na^+ site. Both cation sites were seen to occupy special positions in the structure and are shown in figure 4 for the empty zeolite. The Cs site is positioned at the centre of the distorted double 8-ring (D8R) units, between the elliptical 8-ring apertures. Alternatively, the Na site is associated with the single 6-ring (S6R) faces of the α -cage. The Na sites are located within the interior of an α -cage if the associated S6R face is connected to the minor axis of the elliptical 8-ring aperture. Both cation sites are comparable to those reported by Robson *et al.*⁴¹ in the ambient $Im\bar{3}m$ space group, despite the difference in symmetry. The only distinctions are that in the Robson structure the Cs site is located in the centre of each 8-ring aperture, and a Na site is observed on either side of the S6R faces.

Figure 4. Location of the Cs and Na cation sites determined in the empty zeolite RHO. The framework is shown as a stick model, the caesium cations as pink spheres and the sodium cations in yellow. Also included is the fractional occupancy (Occ.) of each site.

The 18C6 Species

For the occluded 18C6 species four crystallographic sites were determined, consisting of the carbon C(1) C(2) sites and the oxygen Oc(1) Oc(2) sites. The atomic identity of the sites was assessed based on the goodness of fit, interatomic distances and the rationale that there should be approximately twice as many carbons present compared to oxygen based on the chemical formula of 18C6. Figure 5 illustrates the location of these four crystallographic sites in the filled zeolite RHO structure. It was observed that the sites are best described as a cluster within the interior of the α -cage. This contrasts the structure of 18C6 within zeolite EMC-2 reported by Baerlocher *et al.*²⁹ where a discrete planar molecule is seen within the framework structure. We expect that the disorder seen in zeolite RHO is likely due to the cubic symmetry of the framework, meaning that the 18C6 molecule is not aligned along a single crystallographic axis as it is in the hexagonal zeolite EMC-2. Consequently, the periodic structure is an average of the different 18C6 orientations between adjacent unit cells.

Figure 5. Location of the C(1), C(2), Oc(1) and Oc(2) sites of the 18C6 oxyethylene chain in the filled zeolite RHO. The framework is shown as a stick model, the carbon sites as black spheres and the oxygen sites as red spheres. Also included is the fractional occupancy (Occ.) of each site.

The structure of the 18C6 cluster consists of a central core of twelve Oc(1) oxygen sites, each with an occupancy of approximately 54%. This core is then surrounded by a shell of twelve C(1) and twelve C(2) sites, having occupancies of 100% and 73% respectively. Lastly, the cluster possesses an outer shell of four Oc(2) sites in a tetrahedral arrangement and an occupancy of 100% each. This results in a higher population of carbon atoms compared to oxygen, as anticipated for the 18C6 oxyethylene chain. The observed fractional occupancies suggest that there is more than a single 18C6 molecule per α -cage, however based on the disorder of the cluster itself this cannot be confirmed. It is worth noting that there is an absence of a coordinated metal cation in the centre of the 18C6 cluster, as is seen in zeolite EMC-2.²⁹ This suggests that it is the isolated 18C6 molecule, as opposed to a macrocation complex, that is involved in assembly of the RHO framework.

Zeolite ZK-5

Figures 6 and 7 show the powder X-ray diffraction patterns and final Rietveld fits for the hydrated empty and filled zeolite ZK-5 samples accordingly. Included is a plot of the difference between the experimental data and the fit, in addition to the model's goodness of fit G value. The final refined crystallographic coordinates and unit cell parameters for the empty and filled samples are displayed in tables 4 and 5 respectively. Both zeolites were fit using the $Im\bar{3}m$ space group, which is the ambient symmetry anticipated for zeolite ZK-5.^{37, 43, 45}

Figure 6. Powder X-ray diffraction patterns for the empty zeolite ZK-5 sample. The experimental data is shown in blue, the Rietveld fit in red and the difference between the two in grey.

Figure 7. Powder X-ray diffraction patterns for the filled zeolite ZK-5 sample. The experimental data is shown in blue, the Rietveld fit in red and the difference between the two in grey.

Table 4. Final refined unit cell parameters and crystallographic sites for the empty zeolite ZK-5 sample. ‘Occ.’ refers to the fractional occupancy of the relevant crystallographic site.

Symmetry		Unit Cell		Refinement	
Cubic $Im\bar{3}m$		$a / \text{\AA}$	18.6833(1)	G	4.4678
				R_{wp}	7.1047
				R_{exp}	1.5902
Atom	x	y	z	Occ.	B_{eq}
Si	0.0837(1)	0.2026(1)	0.3193(1)	0.820(34)	-1.08(6)
Al	0.0837(1)	0.2026(1)	0.3193(1)	0.180(34)	-1.08(6)
O(1)	0.1280(1)	0.1280(1)	0.3145(1)	1	0.14(10)
O(2)	0.2522(1)	0.2522(1)	0.4081(1)	1	0.14(10)
O(3)	0.0000(1)	0.1783(1)	0.3369(1)	1	0.14(10)
O(4)	0.2500(1)	0.1085(1)	0.3915(1)	1	0.14(10)
K(1)	0	0.25	0.5	0.963(5)	2.14(17)
K(2)	0.15	0.15	0.15	0.363(6)	2.14(17)
K(3)	0	0	0.3474(8)	0.445(7)	2.14(17)

Ow(1)	0.1031(6)	0	0.5	0.952(15)	8.79(46)
Ow(2)	0.3333	0.4	0.5	0.237(8)	8.79(46)
Ow(3)	0.1273(14)	0.1273(14)	0.1273(14)	0.637(6)	8.79(46)
Ow(4)	0	0	0.2258(15)	0.461(15)	8.79(46)

Table 5. Final refined unit cell parameters and crystallographic sites for the filled zeolite ZK-5 sample. ‘Occ.’ refers to the fractional occupancy of the relevant crystallographic site.

Symmetry		Unit Cell		Refinement	
Cubic $Im\bar{3}m$		$a / \text{\AA}$	18.6900(1)	G	6.1289
				R _{wp}	9.9383
				R _{exp}	1.6216
Atom	x	y	z	Occ.	B _{eq}
Si	0.0825(1)	0.2029(2)	0.3190(1)	0.840(43)	-1.00(6)
Al	0.0825(1)	0.2029(2)	0.3190(1)	0.160(43)	-1.00(6)
O(1)	0.1280(2)	0.1280(2)	0.3145(2)	1	-0.03(11)
O(2)	0.2522(2)	0.2522(2)	0.4081(2)	1	-0.03(11)
O(3)	0.0000(2)	0.1783(2)	0.3369(2)	1	-0.03(11)
O(4)	0.2500(2)	0.1085(2)	0.3915(2)	1	-0.03(11)
K(1)	0	0.25	0.5	1.000(7)	3.65(19)
K(2)	0.15	0.15	0.15	0.299(9)	3.65(19)
K(3)	0	0	0.3642(6)	0.610(11)	3.65(19)
K(4)	0.5	0.5	0.5	0.365(18)	3.65(19)
C(1)	0.3234(18)	0.4236(17)	0.5	0.243(12)	20.0(25)
C(2)	0.3735(11)	0.4468(9)	0.5532(9)	0.360(28)	20.0(25)
Oc(1)	0.3830(30)	0.5	0.5	0.207(25)	9.44(18)
Oc(2)	0.4	0.4	0.4	0.357(31)	9.44(18)
Ow(1)	0.0868(10)	0	0.5	0.833(20)	15.1(8)
Ow(3)	0.1286(17)	0.1286(17)	0.1286(17)	0.135(8)	15.1(8)
Ow(4)	0	0	0.2340(25)	0.547(20)	15.1(8)

Metal Cations

Three crystallographic K⁺ cation sites were determined in the structure of the empty zeolite ZK-5 and are shown in figure 8. The first of these is the K(1) site located in the puckered 8-ring opening that links two adjoining orthogonal *t-pau* units. The site has an occupancy of 96%, which the literature has shown to be consistently the most energetically favourable and highest population cation site in KFI-type zeolites.^{37, 46, 47} It is this observation that strongly suggests that the K⁺ cations play an active role in directing these puckered 8-ring openings, and consequently the KFI framework, during crystallisation. The second cation site determined is the K(2) site, which is located in the interior of the α -cage adjacent to the S6R faces, which adjoin the double 6-ring (D6R) units between α -cages. Lastly there is the K(3) site positioned within the *t-pau* units but associated with the 8-ring apertures that connect to the α -cage. All three of these cation sites are congruent with those observed for the (Cs,K)-ZK5 zeolite by Parise *et al.*³⁷ with the distinction that the Cs site is occupied by the K(3) site herein. The sites also agree with the crystal structure reported by Lievens *et al.*⁴⁶ for zeolite ZK-5. It is also worth noting that the D6R units in our structure are vacant from occupancy of a K⁺ cation, consistent with calculations by Lievens *et al.* that this site has a high energy in the KFI framework and is unfavourable to occupy.

All three cation sites are also seen in the filled zeolite ZK-5 structure, in addition to the K(1) cation site having the greatest occupancy. However, there is the addition of a fourth cation site which is associated with the occluded oxyethylene species. This K(4) site is located at the centre of the α -cage, and is shown alongside the 18C6 species sites in figure 10.

Figure 8. Location of the K(1)-K(3) cations sites determined in the empty zeolite ZK-5. The framework is shown as a stick model and the potassium cations as purple spheres. Also included is the fractional occupancy (Occ.) of each site.

Water Molecules

As the zeolite ZK-5 samples were hydrated when analysed, crystallographic sites for the oxygen atoms in extra-framework water molecules (Ow) were determined. In the empty zeolite four water molecule sites were observed, as shown in figure 9. Site Ow(1) is positioned within the *t-pau* unit, in the same plane as the K(1) cation site. Based on its location, it is anticipated that the Ow(1) water molecules are coordinated to the K(1) and K(3) sites that are likewise in the *t-pau* unit. The occupancy of the Ow(1) site is 95%, comparable to the occupancy of the K(1) site further supporting that this water molecular is coordinated to the K(1) cation.

The three remaining Ow sites are all positioned within the α -cage. The Ow(2) site is represented by a larger cluster in a β -cage arrangement, with the single 4-rings being parallel to the 8-ring apertures of the α -cage. Although there is a large number of positions in the structure, the site only has an occupancy of 24%, averaging as right Ow(2) water molecules per α -cage. It is anticipated that the Ow(2) water molecules are coordinated to the K(2) cations due to their proximity. The Ow(3) site is seen to occupy a comparable position to the K(2) site, to the extent that the sites overlap in the average unit cell structure as shown in the Supplementary Information (SI). Therefore, this position is either occupied by a K⁺ cation (36%) or a water molecule (64%). Lastly, the Ow(4) was observed to be adjacent to the centre of the 8-ring apertures of the α -cage, meaning it is likely coordinated to the K(3) site. According to this structural model each cation site is potentially hydrated by a water molecule.

Concerning the filled zeolite ZK-5 structure, all of the water molecule sites are observed aside from the Ow(2) site. Instead, the Ow(2) is replaced by the C(1) carbon site associated with the 18C6 oxyethylene chain. There are also subtle changes to the occupancy of the remaining water molecule sites. However, such adjustments to the water molecules in the structure are anticipated, as the open framework is instead occupied by the 18C6 species macromolecule.

Figure 9. Location of the Ow(1)-Ow(4) water molecule oxygen sites determined in the empty zeolite ZK-5. The framework is shown as a stick model and the water oxygen sites as red spheres. Included is the fractional occupancy (Occ.) of each site.

18C6 Species

A total of five crystallographic sites were determined for the occluded 18C6 species in the filled zeolite ZK-5, including the central K(4) cation site. The remaining four sites belong to the oxyethylene chain, consisting of two carbon and two oxygen sites. As with zeolite RHO, the atomic identity of the four sites were determining by assessing a mixture of the model's goodness of fit, interatomic distances and the chemical formula of 18C6. Figure 10 shows the location of all five of the 18C6 species crystallographic sites which are situated within the interior of the α -cage. The presence of the K(4) site in the centre of the cluster demonstrates that the occluded 18C6 species exists as a $[(18C6)K^+]$ macrocation. This is analogous to FAU and EMT-type zeolites where the $[(18C6)Na^+]$ macrocation exists within the framework supercages.²⁹

Figure 10. Location of the C(1), C(2), Oc(1) and Oc(2) sites of the 18C6 oxyethylene chain in the filled zeolite ZK-5. Included is the position of the K(4) cation site, as shown by a purple sphere. The framework is shown as a stick model, the carbon sites as black spheres and the oxygen sites as red spheres. Also noted is the fractional occupancy (Occ.) of each site.

As seen in zeolite RHO, the structure of the occluded 18C6 species in zeolite ZK-5 is best described as a cluster. Again, this is likely due to the cubic symmetry of the zeolite, and that 18C6 species can be aligned along different orientations between adjacent α -cages. Moving outwards from the central K(4) site, there is first a surrounding shell of oxygen Oc(1) sites that each possess an occupancy of 21%. These sites are positioned in an octahedral arrangement and are likely coordinated to the central cation. The next shell consists of the carbon C(2) sites, which have an occupancy of 36% and are arrayed as vertices of a rhombicuboctahedron. These carbon sites are subsequently surrounded by a shell of Oc(2) oxygen sites in a cubic arrangement, also with an occupancy of 36%. Lastly, the cluster consists of the outer shell of C(1) sites with an occupancy of 24%. Considering the occupancies of each of the crystallographic sites there is less than one macrocation per α -cage.

Within the 18C6 species cluster potential covalent bonds can be evaluated using the expected 1.4 and 1.5 Å lengths for C-O and C-C bonds in organic ether molecules accordingly.⁴⁸ The interatomic distances between the crystallographic sites that could form possible C-C and C-O connections are shown in table 6. With the aforementioned threshold, it is clear that the C(2)-Oc(2), C(2)-Oc(1) and C(1)-C(2) sites may form respective covalent bonds between them. All other distances between carbon and oxygen sites are greater than 1.8 Å, meaning it is increasingly less likely that a covalent bond could exist between the sites.

Table 6. The interatomic distances between atoms associated with the oxyethylene chain of the [(18C6)K⁺] macrocation cluster in the filled zeolite ZK-5. Listed in ascending order.

Interatomic Distance /Å	
C(2)-Oc(2)	1.331(18)
C(2)-Oc(1)	1.418(11)
C(1)-C(2)	1.434(18)
C(1)-Oc(1)	1.811(30)
C(2)-C(2)	1.935(11)
C(1)-C(1)	2.019(18)
C(1)-Oc(2)	2.396(18)

Discussion

In zeolites RHO and ZK-5 it is seen that the occluded 18C6 species occupies the α -cage, as has been expected^{33, 34} but not explicitly proven. We observe that the 18C6 species is disordered in both zeolites, and hence the structure has been described as a cluster. The reason for this being based on the inherent symmetry of the cubic system, whereby all three crystallographic axes are indistinguishable and the 18C6 species can be orientated along different directions between unit cells. Consequently, the periodic structure is an average of all these possible orientations, producing the disordered cluster. Furthermore, the absence of a coherent molecule with symmetry match-up with the framework, as seen in zeolite EMC-2,²⁹ suggests that the 18C6 species does not behave as a geometric template in the crystallisation of zeolites RHO and ZK-5.

Interestingly, both zeolites RHO and ZK-5 can be prepared without the need for 18C6.^{27, 49-51} For zeolite RHO it is the Cs⁺ cations that direct the assembly of the D8Rs,⁵² and in zeolite ZK-5 the K⁺ cations are thought to be involved in the formation of the *t-pau* units.⁴⁶ In both cases, this behaviour must be sufficient to assemble the relevant framework structure. Therefore, we believe that the 18C6 species must play a role in stabilising the formation of the α -cage, which is supported by its presence in this cavity in both crystal structures. For zeolite RHO it is the non-complexed 18C6 molecule and in zeolite ZK-5 it is the [(18C6)K⁺] macrocation that performs this stabilisation role. The influence of this stabilisation on the actual synthesis of zeolite RHO is that it becomes increasingly facile and expands the crystallisation field.⁵³⁻⁵⁶ Therefore, we anticipate a similar impact on the synthesis of zeolite ZK-5. Such behaviour would suggest that it influences the free-energy of crystallisation, as we have seen for FAU and EMT-type zeolites.²⁰

Conclusions

Herein, we present the crystal structure of the as-synthesised, 18C6 containing and calcined analogues of zeolites RHO and ZK-5. We have successfully identified the identity of the occluded 18C6 species, which in zeolite RHO is an isolated 18C6 molecule, and in zeolite ZK-5 is a coordinated [(18C6)K⁺] macrocation. In both zeolites, we observe that the relevant 18C6 species occupies the α -cage cavities. According to the fractional occupancies we predict that there are potentially 2 molecules per cage in the former, and less than one macrocation per cage in the latter. Furthermore, the occluded 18C6 species are disordered in both periodic frameworks, so we have described the 18C6 species as a cluster of atomic sites. We believe that this is due to the 18C6 species being orientated along different directions between adjacent unit cells, which in the cubic symmetry averages to the disordered cluster seen.

Due to the lack of symmetry matchup between the 18C6 species and the zeolite framework it is deemed that in both cases the relevant 18C6 species does not behave as a true geometric template. Instead, we believe that the role of the 18C6 species is better described as a structure directing or space-filling agent. Rather than imprinting symmetry during crystallisation, the 18C6 species stabilise the open void of the α -cage as it is being assembled.

Using these crystal structures, a more coherent understanding of the role of 18C6 as an organic additive in the synthesis of zeolites can be made. This presents the need for greater appreciation of the multiple available behaviours of organic additives that can be applied to prepare new zeolites.

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Author Contributions

The original manuscript was prepared and written by A.N. with input from all the co-authors. Synthesis of the samples was performed by A.N. The high resolution X-ray diffraction data for the zeolite RHO samples were collected by A.N., C.D. and A.S. on the ID22 beamline at the ESRF. The high resolution X-ray diffraction data for the zeolite ZK-5 samples were performed by Gabriele Kociok-Kohn (of the University of Bath) and Sascha Corell (of STOE & CIE GmbH). A.N. performed the Rietveld refinements using TOPAS Academic and with the assistance of C.D. and A.S. Interpretation of the data and editing of the manuscript was performed by all the authors: A.N., C.D., P.R.R. and A.S.

Data Availability

All data created during this study is available free of charge from the University of Bath data archive at [\[URL to be added on acceptance\]](#).

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