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FULL PAPER

Synthesis and characterization of a new three-dimensional aluminophosphate $[\mathrm{Al_{11}P_{12}O_{48}}][\mathrm{C_4H_{12}N_2}][\mathrm{C_4H_{11}N_2}]$ with an Al/P ratio of 11 : 12

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Employing piperazine as a template, a new three-dimensional aluminophosphate $[\mathrm{Al_{11}P_{12}O_{48}}][\mathrm{C_4H_{12}N_2}][\mathrm{C_4H_{11}N_2}]$ (denoted AlPO-CJ11) has been prepared hydrothermally. The as-synthesized product has been characterized by X-ray powder diffraction, inductively coupled plasma, thermogravimetric and differential thermal analyses. Single crystal X-ray diffraction analysis shows that AlPO-CJ11 crystallizes in the trigonal space group $R\bar{3}c$ (no. 167) with $a = 14.045(2)$ Å, $c = 42.091(6)$ Å, $V = 7191.0(16)$ Å^3, and $Z = 6$. The framework structure of AlPO-CJ11 is constructed from two new types of chiral cage and has a new stoichiometry with an Al/P ratio of 11 : 12. The possible locations of the templates in the cages have been investigated by molecular modeling.

Introduction

Since the first discovery of microporous aluminophosphates ($\mathrm{AlPO_4}$-n) in 1982,[1] great attention has been paid to the exploration of new microporous aluminophosphate materials because they have potential applications in the fields of catalysis, ion-exchange, adsorption and host–guest assembly.[2–4] The structures of $\mathrm{AlPO_4}$-n are built up from strict alternation of $\mathrm{AlO_4}$ and $\mathrm{PO_4}$ tetrahedra through corner-sharing vertex oxygen atoms, which defines a neutral framework.

In contrast to $\mathrm{AlPO_4}$-n, with an Al/P ratio of unity, a large number of 1-dimensional (1-D), 2-D and 3-D anionic aluminophosphate compounds with Al/P ratios less than unity, have recently been successfully synthesized under hydrothermal or solvothermal conditions.[5] These materials greatly enrich the compositional and structural chemistry of aluminophosphate materials, and give further insight into the formation of microporous materials. There are Al/P ratios of 1 : 2,[6–8] 2 : 3,[9–12] 3 : 4,[13–24] 3 : 5,[25] 4 : 5,[26,27] 5 : 6[28] and 12 : 13.[29] Their frameworks or networks are constructed from alternation of Al units including $\mathrm{AlO_4}$, $\mathrm{AlO_5}$ and $\mathrm{AlO_6}$, and P units including tetrahedral $\mathrm{PO_4}$ with one, two, three or four oxygen atoms being shared by adjacent Al atoms. By combination of various structural building units, it is possible that aluminophosphates with other Al/P ratios, such as 6 : 7, 7 : 8, 8 : 9, 10 : 11, 11 : 12 and so forth, exist.

In this work, we report a new compound $[\mathrm{Al_{11}P_{12}O_{48}}][\mathrm{C_4H_{12}N_2}][\mathrm{C_4H_{11}N_2}]$, denoted AlPO-CJ11 (CJ11: China, Jilin University, Number 11), which has a new stoichiometry with an Al/P ratio of 11 : 12. The possible locations of the templates have been investigated by molecular modeling.

Results and discussion

Using piperazine as a template, AlPO-CJ11 has been crystallized in an aqueous system with a gel composition of $2.0\mathrm{Al}(^i\mathrm{PrO})_3 : 4.0\mathrm{H_3PO_4} : 1.5\mathrm{C_4H_{10}N_2} : 227\mathrm{H_2O}$ at 180 °C for 5 days. It is noted that the pH value of the starting mixture has a big influence on the resulting products (Table 1). When the pH value is lower than 5.0, the dense phase of cristobalite is crystallized. The crystals of AlPO-CJ11 can only be prepared in a system with pH values ranging from 5.0 to 6.0. If the pH value is in the region between 6.0 and 8.0, an unidentified phase is obtained, while at pH higher than 8.0, a new phase $[\mathrm{C_4H_{12}N_2}][\mathrm{Al_2P_2O_8(OH)_2}]$ (AlPO-CJ9) is formed. The changes in pH are achieved by varying the molar ratios of $\mathrm{H_3PO_4}$ or piperazine in the reaction mixture.

Table 1 Synthesis conditions of AlPO-CJ11[a]

	Gel composition (molar ratio)				
Runs	$\mathrm{Al_2O_3}$	$\mathrm{P_2O_5}$	Piperazine	pH	Product
1	1.0	2.0	0.5–1.0	3–5	Cristobalite
2	1.0	2.0	1.5–2.0	5–6	AlPO-CJ11
3	1.0	2.0	2.5–3.5	6–8	Unidentified phase
4	1.0	2.0	4.0–6.0	8–9	AlPO-CJ9
5	1.0	2.5	2.0	5.8	AlPO-CJ11
6	1.0	1.5	1.0	5.6	AlPO-CJ11
7	1.0	3.0	2.0	5.2	AlPO-CJ11

[a] Solvent = $227\mathrm{H_2O}$; reaction temperature = 180 °C; reaction time = 5 days.

The type of solvent is also an important factor influencing the crystallization of AlPO-CJ11. When ethylene glycol, tetraethylene glycol or 2-butanol is used as the solvent, keeping other conditions unchanged, no AlPO-CJ11 is formed, whereas when triethylene glycol is used as a solvent, $\mathrm{AlPO_4}$-5 is produced.

The experimental and simulated powder X-ray diffraction (XRD) patterns are in good agreement with each other, suggesting the phase purity of the as-synthesized product (Fig. 1). The slight differences in reflection intensity are probably due to the preferred orientation effect in the powder sample.

Inductively coupled plasma (ICP) analysis gives the Al and P contents as 17.0 and 21.5 wt%, respectively, indicating that the crystallites have an Al/P ratio of 11 : 12. Elemental analysis gives C, H and N compositions of 5.69, 1.52 and 3.5 wt%, respectively, suggesting that in the structure of AlPO-CJ11 there are two piperazine molecules corresponding to one $[\mathrm{Al_{11}P_{12}O_{48}}]^{3+}$ unit. In order to keep charge neutrality, one of the piperazine molecules must be diprotonated and the other mono-

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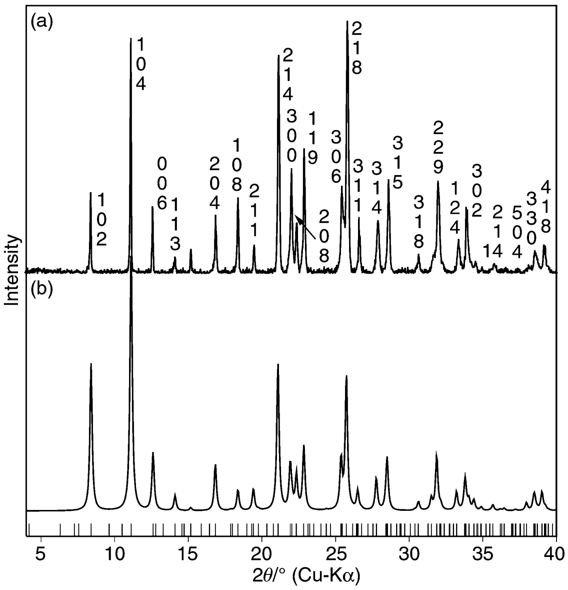

Fig. 1 (a) Experimental and (b) simulated X-ray powder diffraction patterns of AlPO-CJ11.

protonated. Thus, it can be concluded that AlPO-CJ11 has an empirical formula of $[Al_{11}P_{12}O_{48}]^{3-}[C_4H_{12}N_2]^{2+}[C_4H_{11}N_2]^{+}$.

AlPO-CJ11 crystallizes in the trigonal space group $R\bar{3}c$ (no. 167) with lattice paramters $a = 14.045(2)$ Å and $c = 42.091(6)$ Å. The selected bond distances and angles are presented in Table 2. Fig. 2 shows one asymmetric unit of APO-CJ11. It contains three crystallographically distinct Al atoms. Al(1) is octahedrally coordinated to oxygen atoms (Al–O$_{av}$ = 1.880 Å), while Al(2) and Al(3) are tetrahedrally coordinated (Al–O$_{av}$ = 1.720 Å, O–Al–O$_{av}$ = 109.5°). There are two crystallographically distinct PO_4 units. The P–O distances (1.486–1.538 Å) and the O–P–O angles (105.6–113.2°) are all typical for aluminophosphate materials.[13–28] The alternation of Al- and P-centered polyhedra gives a three-dimensional anionic framework with stoichiometry $[Al_{11}P_{12}O_{48}]^{3-}$. Differently from most anionic networks or frameworks that usually contain terminal oxygen atoms,[6–28] all the vertex oxygen atoms of AlPO-CJ11 are shared by adjacent Al and P atoms as in the case of AlPO-CJB1.[29]

The framework of AlPO-CJ11 features two new types of cage, as shown in Fig. 3; that is, cage 1, which is composed of three 4-membered rings (4-MRs), six 6-MRs and six 8-MRs (denoted $4^36^68^6$ cage), and cage 2, which is composed of twelve 6-MRs (denoted 6^{12} cage). Both of them exhibit an interesting chiral character. A column is formed through alternation of cages 1 and 2 that share a common chiral motif along the *c* direction (Fig. 4). The chiral motif is composed of Al(1)-centered six 4-MRs. Such columns connect with each other and form the 3-D framework of AlPO-CJ11 (Fig. 5). Compared with known microporous materials including aluminophosphates and aluminophosphate-based compounds, AlPO-CJ11 exhibits unique structural features, constructed from two novel types of cage. Considering the compositional analysis result, each cage should accommodate one template molecule with a total of 12 template molecules in 12 cages in one unit cell.

Thermogravimetric (TG) analysis shows a weight loss of about 8.64 wt% at 560–750 °C, which is attributed to the decomposition of piperazinium cations (calc. 10.97 wt% based on the empirical formula $[Al_{11}P_{12}O_{48}][C_4H_{12}N_2][C_4H_{11}N_2]$). That the observed weight loss is lower than that calculated is due to the existence of a certain amount of carbon residue in the product. The slight weight loss at temperatures lower than 120 °C is due to the release of physically adsorbed water molecules.

Table 2 Selected bond lengths (Å) and bond angles (°) for AlPO-CJ11

P(1)–O(3)	1.486(4)	P(1)–O(1)	1.526(5)
P(1)–O(2)	1.553(5)	P(1)–O(4)	1.538(4)
P(2)–O(5)	1.503(4)	P(2)–O(6)	1.526(4)
P(2)–O(8)	1.527(4)	P(2)–O(7)	1.530(4)
Al(1)–O(3)	1.858(4)	Al(1)–O(3)#1	1.858(4)
Al(1)–O(3)#2	1.858(4)	Al(1)–O(5)#2	1.902(4)
Al(1)–O(5)	1.902(4)	Al(1)–O(5)#1	1.902(4)
Al(2)–O(2)#3	1.700(4)	Al(2)–O(6)	1.719(4)
Al(2)–O(8)#4	1.732(4)	Al(2)–O(4)	1.740(4)
Al(3)–O(1)#5	1.711(5)	Al(3)–O(1)#1	1.711(5)
Al(3)–O(7)	1.733(4)	Al(3)–O(7)#6	1.733(4)
O(1)–Al(3)#2	1.711(5)	O(2)–Al(2)#7	1.700(4)
O(8)–Al(2)#4	1.732(4)		
O(3)–P(1)–O(1)	113.2(3)	O(3)–P(1)–O(2)	107.9(2)
O(1)–P(1)–O(2)	110.7(3)	O(3)–P(1)–O(4)	111.2(2)
O(1)–P(1)–O(4)	105.6(3)	O(2)–P(1)–O(4)	108.3(2)
O(5)–P(2)–O(6)	112.6(2)	O(5)–P(2)–O(8)	108.1(2)
O(6)–P(2)–O(8)	109.8(2)	O(5)–P(2)–O(7)	111.4(2)
O(6)–P(2)–O(7)	107.3(2)	O(8)–P(2)–O(7)	107.6(2)
O(3)–Al(1)–O(3)#1	89.12(19)	O(3)–Al(1)–O(3)#2	89.12(19)
O(3)#1–Al(1)–O(3)#2	89.12(19)	O(3)–Al(1)–O(5)#2	91.06(18)
O(3)#1–Al(1)–O(5)#2	178.3(2)	O(3)#2–Al(1)–O(5)#2	92.56(17)
O(3)–Al(1)–O(5)	92.56(17)	O(3)#1–Al(1)–O(5)	91.06(18)
O(3)#2–Al(1)–O(5)	178.3(2)	O(5)#2–Al(1)–O(5)	87.26(19)
O(3)–Al(1)–O(5)#1	178.3(2)	O(3)#1–Al(1)–O(5)#1	92.56(17)
O(3)#2–Al(1)–O(5)#1	91.06(18)	O(5)#2–Al(1)–O(5)#1	87.26(19)
O(5)–Al(1)–O(5)#1	87.26(19)	O(2)#3–Al(2)–O(6)	112.3(2)
O(2)#3–Al(2)–O(8)#4	108.5(2)	O(6)–Al(2)–O(8)#4	109.2(2)
O(2)#3–Al(2)–O(4)	108.9(2)	O(6)–Al(2)–O(4)	108.9(2)
O(8)#4–Al(2)–O(4)	108.9(2)	O(1)#5–Al(3)–O(1)#1	111.2(4)
O(1)#5–Al(3)–O(7)	109.5(2)	O(1)#1–Al(3)–O(7)	107.5(2)
O(1)#5–Al(3)–O(7)#6	107.5(2)	O(1)#1–Al(3)–O(7)#6	109.5(2)
O(7)–Al(3)–O(7)#6	111.8(3)	P(1)–O(1)–Al(3)#2	157.8(4)
P(1)–O(2)–Al(2)#7	152.2(3)	P(1)–O(3)–Al(1)	151.6(3)
P(1)–O(4)–Al(2)	128.7(3)	P(2)–O(5)–Al(1)	151.6(3)
P(2)–O(6)–Al(2)	152.9(3)	P(2)–O(7)–Al(3)	138.2(3)
P(2)–O(8)–Al(2)#4	149.8(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-y + 1, x - y + 1, z$; #2 $-x + y, -x + 1, z$; #3 $y - 1, -x + y, -z$; #4 $y - 2/3, x + 2/3, -z + 1/6$; #5 $-x + 1/3, -x + y - 1/3, -z + 1/6$; #6 $x - y + 1/3, -y + 2/3, -z + 1/6$; #7 $x - y + 1, x + 1, -z$.

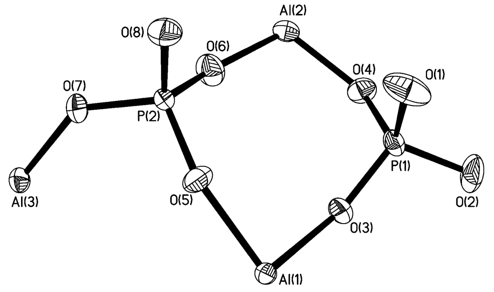

Fig. 2 Thermal ellipsoid plot (50% probability) and atomic labeling scheme for an asymmetric unit of AlPO-CJ11.

Powder XRD studies on the samples calcined at different temperature are shown in Fig. 6. It shows that the structure of as-synthesized AlPO-CJ11 is retained on heating the sample at 660 °C, and that it becomes amorphous above 770 °C. Efforts to remove the occluded organic templates from the crystal without destroying the framework failed. Compared with previously reported aluminophosphate materials, AlPO-CJ11 shows higher thermal stability because there are no terminal P–OH or P=O groups in the structure.

In the structural refinement, the residual electron density peaks of the guest species within the cage regions are due to C and N atoms of the template molecules. However, the position or identity of the guest species is not unambiguously determined by single-crystal structure determination. Molecular modeling is feasible in predicting the possible positions of the guest species in terms of the non-bonding interaction energies.

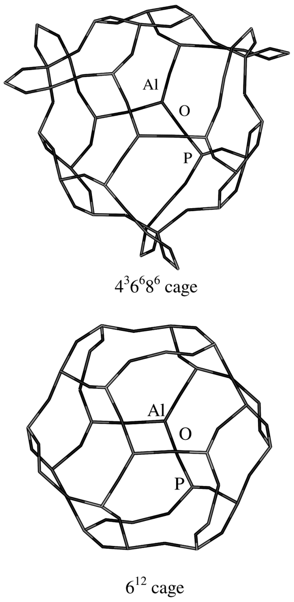

Fig. 3 View of cage 1 ($4^36^68^6$ cage) and cage 2 (6^{12} cage).

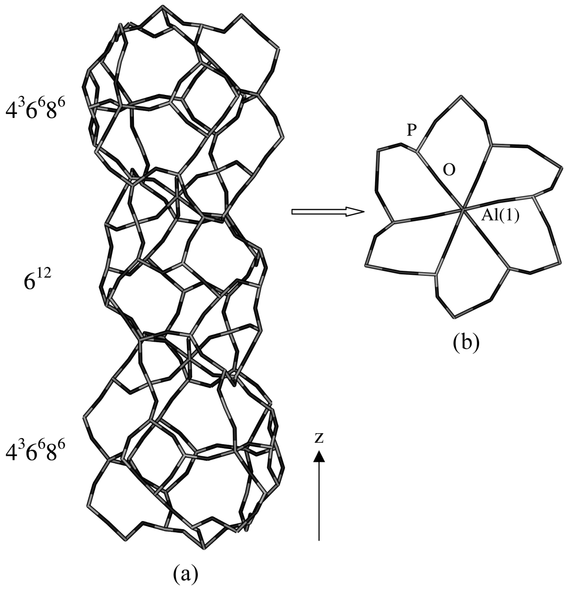

Fig. 4 (a) A column formed by alternation of cage 1 and cage 2 along the *c* direction *via* sharing. (b) A chiral motif which is composed of Al(1)-centered six 4-MRs.

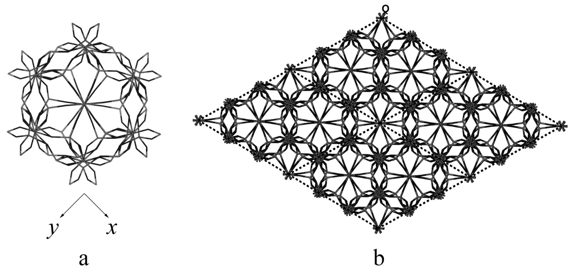

Fig. 5 (a) Column (a) in Fig. 4 viewed along the *c* direction and (b) the framework of AlPO-CJ11 viewed along the *c* direction, formed from connections of the columns with each other.

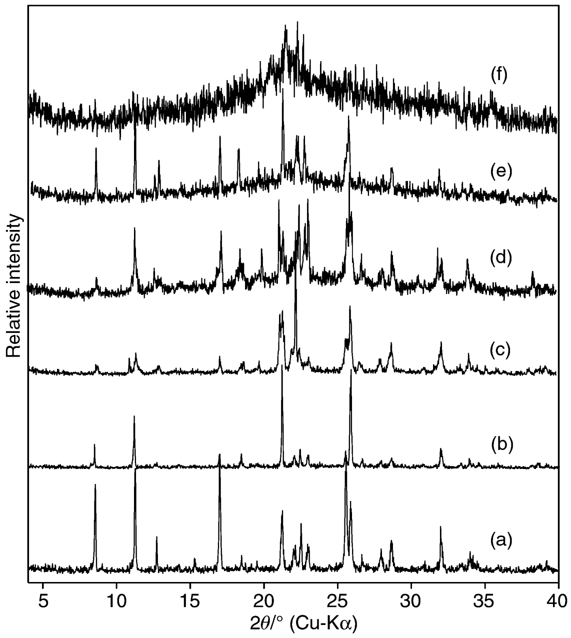

Fig. 6 XRD patterns of samples calcined at (a) 240, (b) 340, (c) 440, (d) 550, (e) 660, and (f) 770 °C.

Table 3 Minimized non-bonding interaction energies (kcal mol^{-1} per unit cell of AlPO-CJ11) in cases **I**–**IV**[a]

	Contents				
No.	6^{12} cage	$4^36^68^6$ cage	van der Waals	Coulombic energy	E_{inter}
I	$PipH^+$	$PipH_2^{2+}$	−172.61	−256.71	−429.32
II	$PipH_2^{2+}$	$PipH^+$	−169.84	−255.26	−425.10
III	$PipH_2^{2+}$	H_3O^+	−137.26	−46.28	−183.54
IV	H_3O^+	$PipH_2^{2+}$	−75.08	−78.43	−153.51

[a] $PipH^+$: monoprotonated piperazine. $PipH_2^{2+}$: diprotonated piperazine.

We investigated four cases: (**I**) one monoprotonated piperazine molecule located in each 6^{12} cage and one diprotonated piperaazine molecule in each $4^36^68^6$ cage; (**II**) one monoprotonated piperazine molecule located in each $4^36^68^6$ cage and one diprotonated piperazine molecule in each 6^{12} cage; (**III**) one diprotonated piperazine molecule located in each 6^{12} cage and one protonated water molecule in each $4^36^68^6$ cage and (**IV**) one diprotonated piperazine molecule located in each $4^36^68^6$ cage and one protonated water molecule in each 6^{12} cage for comparison. The non-bonding interaction energies between the guest species within the cages and the anionic framework are listed in Table 3. The calculated interaction energies suggest that each cage with one piperazine molecule, as in cases **I** and **II**, is strikingly energetically favorable. This is consistent with our compositional analysis results. It is worth noting that the non-bonding interaction energies in cases **I** and **II** are similar. This is because the two types of cage have a similar size. However, on the other hand, it is noted that the non-bonding interaction energies in cases **III** and **IV** are rather higher compared to cases **I** and **II**. This indicates that it is not likely that the template molecules exist in the case of **III** or **IV**. This is also consistent with our compositional analysis.

Experimental

Synthesis and characterization

Single crystals of AlPO-CJ11 were prepared under hydrothermal conditions. 1.0 g of aluminium triisopropoxide was first dispersed into 10 mL of distilled water, followed by addition of 0.32 g of piperazine. The mixture was stirred for 30 min and then 0.67 mL of orthophosphoric acid (85 wt%) was added to give a gel with overall composition of $2.0Al(^iPrO)_3 : 4.0H_3PO_4 : 1.5C_4H_{10}N_2 : 227H_2O$. The gel was stirred until it was homogeneous, sealed in a Teflon-lined stainless steel autoclave, and heated at 180 °C for 5 days under static conditions. The resulting product, consisting of large colorless

Table 4 Crystal data and structure refinement for AlPO-CJ11

Empirical formula	$[Al_{11}P_{12}O_{48}][C_4H_{12}N_2][C_4H_{11}N_2]$
Formula weight	1611.72
Temperature/K	293(2)
λ/Å	0.71073
Crystal system	Trigonal
Space group	$R\bar{3}c$
a/Å	14.045(2)
b/Å	14.045(2)
c/Å	42.091(6)
γ/°	120
V/Å^3	7191.0(16)
Z	6
μ/mm^{-1}	0.766
Reflections collected/unique	8009/2210 [R(int) = 0.0637]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0696$, $wR_2 = 0.1908$
R indices (all data)	$R_1 = 0.1139$, $wR_2 = 0.2117$

rhombic single crystals was collected by filtration, washed with distilled water, and dried in air at 80 °C.

The X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with Cu-Kα ($\lambda = 1.5418$ Å) radiation. Thermogravimetric analysis was performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of 10 °C min^{-1}. The elemental analysis was carried out on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Perkin-Elmer Optima 3300DV spectrometer.

Crystallography

A suitable single crystal with size dimensions 0.16 × 0.16 × 0.16 mm was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program.[30] The structure was solved in the space group $R\bar{3}c$ by direct methods and refined on F^2 by full-matrix least squares with the SHELXTL crystallographic software package.[31] All the non-hydrogen framework atoms were easily located from difference Fourier maps. However, attempts to locate C and N atoms for an ordered piperazinium cation that was suggested to be occluded in the extra-framework region by TG, and C, H and N analyses, failed. It was not possible to identify template molecules unambiguously from the difference Fourier synthesis, because they will necessarily be disordered, as the symmetry of the template is lower than that of the framework. Electron density peaks in the cages were attributed to disordered positions for the carbons and nitrogens of the template. Crystal data and details of the data collection are given in Table 4.

CCDC reference number 154045.

See http://www.rsc.org/suppdata/dt/b1/b102327f/ for crystallographic data in CIF or other electronic format.

Molecular modeling

A computational approach combining Monte Carlo and an energy minimization technique was used to model the likely positions of the piperazine molecules within the cages in the structure of AlPO-CJ11. Calculations were carried out using the Burchart 1.01–Dreiding 2.21 force field that combines the Burchart force field,[32] which was used to treat the frameworks of zeolites, and the Dreiding II force field,[33] that was used to treat the intra- and inter-molecular interactions. In order to ensure the charge neutrality in the calculation, we distributed the charge of +3 to two piperazine molecules or to one piperazine molecule and one water molecule. In the calculation, the non-bonding interaction energies (E_{inter}) including van der Waals and coulombic interactions were considered. We assume $E_{\text{inter}} = E - E_f - E_R$, where E is the total energy of the whole structure, E_f is the energy of the framework, and E_R is the energy of the encapsulated organic template.

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