

The ambient hydration of the aluminophosphate JDF-2 to AIPO-53(A): insights from NMR crystallography

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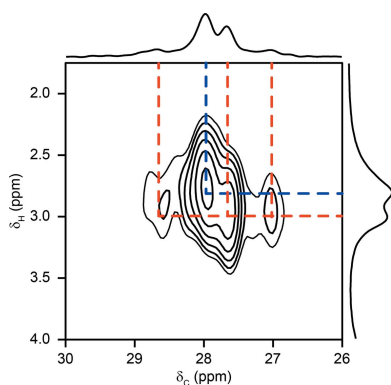
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The aluminophosphate (AIPO) JDF-2 is prepared hydrothermally with methylammonium hydroxide (MAH⁺·HO⁻, MAH⁺ = CH₃NH₃⁺), giving rise to a microporous AEN-type framework with occluded MAH⁺ cations and extra-framework (Al-bound) HO⁻ anions. Despite the presence of these species within its pores, JDF-2 can hydrate upon exposure to atmospheric moisture to give AIPO-53(A), an isostructural material whose crystal structure contains one molecule of H₂O per formula unit. This hydration can be reversed by mild heating (such as the frictional heating from magic angle spinning). Previous work has shown good agreement between the NMR parameters obtained experimentally and those calculated from the (optimized) crystal structure of JDF-2. However, several discrepancies are apparent between the experimental NMR parameters for AIPO-53(A) and those calculated from the (optimized) crystal structure (*e.g.* four ¹³C resonances are observed, rather than the expected two). The unexpected resonances appear and disappear reversibly with the respective addition and removal of H₂O, so clearly arise from AIPO-53(A). We investigate the ambient hydration of JDF-2 using quantitative ³¹P MAS NMR to follow the transformation over the course of ~3 months. The structures of JDF-2 and AIPO-53(A) are also investigated using a combination of multinuclear solid-state NMR spectroscopy to characterize the samples, and first-principles density functional theory (DFT) calculations to evaluate a range of possible structural models in terms of calculated NMR parameters and energetics. The published structure of JDF-2 is shown to be a good representation of the dehydrated material, but modification of the published structure of AIPO-53(A) is required to provide calculated NMR parameters that are in better agreement with experiment. This modification includes reorientation of all the MAH⁺ cations and partial occupancy of the H₂O sites.

1. Introduction

Microporous aluminophosphate molecular sieves (AIPOs) and their metal- and silicon-substituted analogues (MeAPOs and SAPOs, respectively) are of great interest in industry, medicine and the environment, owing to the number of zeotypic frameworks accessible by these materials and (through iso- or aliovalent substitution) their versatile chemistry (Wilson *et al.*, 1982; Wright, 2008). During the synthesis of AIPOs, Al and P sources are combined with the required structure-directing agent (SDA) or ‘template’ – typically an organic ammonium-based species and, in some cases, a mineralizer (*e.g.* HF). The role of the SDA is to direct the crystallization of the AIPO₄ framework, giving the desired framework connectivity, although the precise mechanism by



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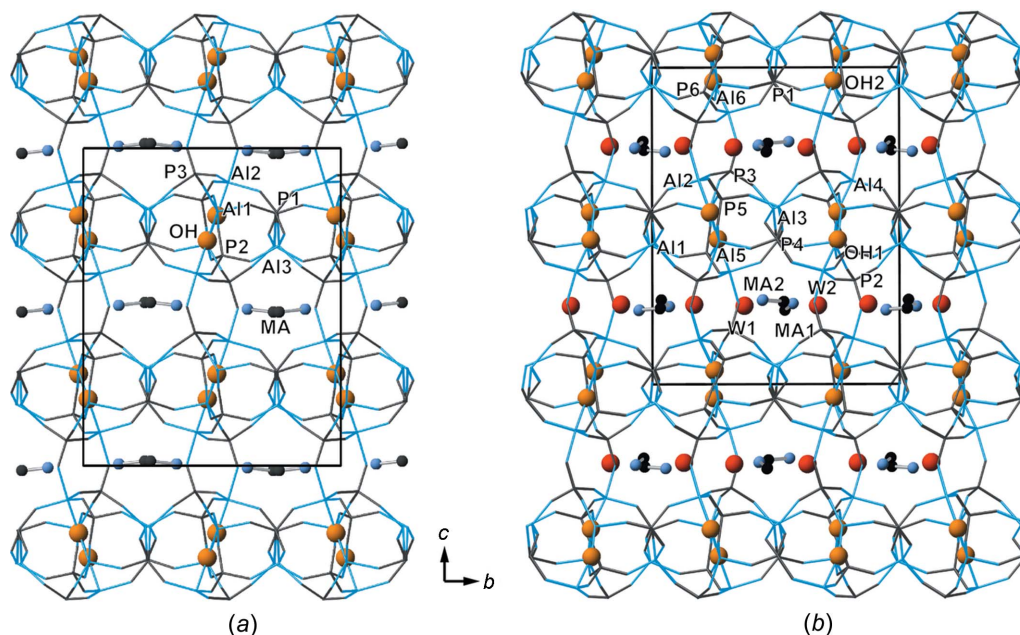


Figure 1
The crystal structures of (a) JDF-2 (Chippindale *et al.*, 1994) and (b) AIPO-53(A) (Kirchner *et al.*, 2000). The solid lines indicate the unit cell. Crystallographically distinct Al (blue sticks), P (dark-grey sticks), MAH⁺ (blue and grey spheres), OH⁻ (orange spheres) and H₂O (red spheres) are indicated and H atoms have been omitted for clarity.

which this occurs is not generally well understood. The material crystallizes as a network of corner-sharing AlO₄ and PO₄ tetrahedra (with strict alternation of Al and P). Voids in the network (pores and channels) are typically occupied by the cationic SDA and, in many cases, occluded water molecules. As the AlPO₄ framework has an overall neutral charge, the positive charge of the SDA is balanced by anionic species (HO⁻ and/or F⁻), which bind to the framework, forming five- or six-coordinate Al in addition to the four-coordinate species of the neutral framework. In many cases, the exact locations of the SDA, extra-framework anions and any water molecules present are poorly defined in reported crystal structures, owing to factors such as orientational or motional disorder of the SDA and/or H₂O, and mixed or fractional anion occupancies (Antonijevic *et al.*, 2006; Ashbrook *et al.*, 2009; Martineau *et al.*, 2011). Given the insensitivity of Bragg diffraction techniques to these features, solid-state NMR is often used as a complementary characterization method, owing to its sensitivity to structure on the local scale (rather than the bulk crystal scale) and dynamics occurring on time-scales spanning ~12 orders of magnitude (Ashbrook *et al.*, 2014). Owing to the different structural features observable by solid-state NMR and Bragg diffraction, it is unsurprising that combining results from the two techniques is often challenging, particularly when assigning the resonances observed in NMR spectra to the atomic sites present in the crystal structure. In recent years, periodic first-principles density functional theory (DFT) calculations have greatly eased this task and, consequently, gained great popularity (Charpentier, 2011; Bonhomme *et al.*, 2012; Ashbrook & Dawson, 2013; Ashbrook & McKay, 2016). Often the excellent agreement between calculated and experimental NMR parameters enables

immediate assignment and, in cases where discrepancies are apparent, these can often be explained by more detailed investigation (often by DFT and NMR spectroscopy) of the dynamics and disorder present (Ashbrook & McKay, 2016). One of the key advantages of DFT calculations is the ease with which the structural model can be manipulated, allowing the validation of many possible models with respect to experimental observables (*e.g.* NMR parameters). However, care must be taken in obtaining the atomic positions in the structural models to be investigated. While these are typically based on structures obtained by Bragg diffraction, any changes to the diffraction-based structure must initially be made either manually, based on ‘chemical intuition’, idealized bond geometries and, ultimately, (educated) guesswork, or automatically, based on random structure generation [*e.g.* in the *ab initio* random structure searching (AIRSS) approach of Pickard & Needs (2006)]. It is, therefore, common to optimize such structural models, such that the forces acting on the atoms are minimized to within a reasonable tolerance, leading to minimum-energy structures. In addition to providing more reliable structures for the calculation of NMR parameters, the calculated energies of the optimized structures may allow an evaluation of the likelihood of such structures occurring in reality (Ashbrook & McKay, 2016). Common periodic plane-wave pseudopotential DFT methods often unrealistically expand the unit cell by *ca* 10%, owing to an inherently poor description of the long-range electron-electron correlations (*i.e.* van der Waals and other ‘dispersion’ interactions). When optimizing the published crystal structure, this expansion can be overcome by constraining the unit-cell parameters to those determined (generally with a high precision) by Bragg diffraction experiments. However, when modifications are

made to this starting structure, the unit-cell parameters must also be varied, *i.e.* the structure is no longer that for which the average unit-cell parameters were determined and such constraints are not, therefore, necessarily realistic. Recently, schemes correcting for the underestimation of dispersion forces have been introduced to periodic planewave DFT codes (Grimme, 2006; Tkatchenko & Scheffler, 2009; McNellis *et al.*, 2009), allowing for the variation of unit-cell parameters without the artificial expansion otherwise observed. Sneddon *et al.* (2014) recently showed that such semi-empirical dispersion correction (SEDC) schemes provided a means of optimizing the structures of AlPOs without constraining the unit-cell parameters. The resulting calculated unit-cell parameters were typically in better agreement with the experimentally determined values, while the NMR parameters obtained from the optimized structures were in much better agreement with the experimental parameters than those calculated from the initial structures. Therefore, it appears that such SEDC schemes present the best current approach for determining the minimum-energy configuration of any structural models for disorder in AlPOs, whilst imposing the minimum number of constraints on the calculation. This is an important consideration when the structures to be calculated are theoretical models that include defects or disorder, for which experimental unit-cell data will represent only a bulk average, rather than accurately describing the cell containing the defect.

JDF-2 has the formula $\text{Al}_3\text{P}_3\text{O}_{12}(\text{CH}_3\text{NH}_3\text{OH})$ (Chippindale *et al.*, 1994; Gai-Boyes *et al.*, 1992). Its structure comprises an AlPO_4 framework with the AEN topology, with HO^- bridging Al1 and Al2 (which are, consequently, five-coordinate) and methylammonium (MAH^+) located within the two-dimensional network of pores. Despite the presence of the MAH^+ , JDF-2 can hydrate reversibly under ambient conditions (Ashbrook *et al.*, 2009), giving the isostructural AlPO-53(A) , with formula $\text{Al}_6\text{P}_6\text{O}_{24}(\text{CH}_3\text{NH}_3\text{OH})_2(\text{H}_2\text{O})_2$, where the presence of H_2O causes a lowering of the crystallographic symmetry (from $Pbca$ to $P2_12_12_1$), giving rise to six crystallographically distinct Al and P species, two inequivalent MAH^+ and HO^- species, and two inequivalent H_2O molecules (Kirchner *et al.*, 2000). The crystal structures of JDF-2 and AlPO-53(A) are shown in Fig. 1, with the crystallographically distinct Al, P, MAH^+ , HO^- and H_2O species identified. Reports of such hydration are uncommon for as-prepared AlPOs, whose pores are already occupied by guest species, and its occurrence in this case warrants further investigation, (i) in order to understand why both JDF-2 and AlPO-53(A) are stable, and (ii) as a model for the interaction of guest species in the confined spaces present in microporous materials. Ashbrook *et al.* (2009) previously observed that the hydration was facile, but relatively slow (on the timescale of weeks) under ambient conditions. In this work, a more detailed investigation of the hydration process is reported, using quantitative ^{31}P magic angle spinning (MAS) NMR spectroscopy to follow the transformation of JDF-2 to AlPO-53(A) under ambient conditions. The discrepancy between the observed and expected number of resonances in the NMR spectra

[particularly ^{13}C , as noted earlier by Ashbrook *et al.* (2009), and ^{15}N] is also investigated using a combination of high-resolution multinuclear solid-state NMR and first-principles DFT calculations. A number of possible models for defects within AlPO-53(A) , based around MAH^+ reorientations and/or H_2O vacancies, are considered, with the ultimate conclusion that all MAH^+ cations must be reoriented and the H_2O partially occupied in order to provide a structure consistent with other observations.

2. Experimental

2.1. Synthesis

The samples studied in the present work are the same as those prepared for the earlier work of Ashbrook *et al.* (2009), who reported the full synthetic procedure, based on that of Kirchner *et al.* (2000). Samples of AlPO-53(A) were dehydrated at 383 K for between 16 and 72 h to afford JDF-2, and samples of JDF-2 were hydrated under ambient conditions or by immersion in distilled water to afford AlPO-53(A) . The sample used in the ambient hydration study was stored in a sample vial covered with punctured sealing film (to minimize contamination by dust particles, *etc.*) between NMR experiments. The room temperature and relative humidity were recorded using an ETI Thermo-hydrometer and had ranges of 291.8–292.2 K and 20–46%, respectively.

2.2. Solid-state NMR spectroscopy

Solid-state NMR spectra were recorded using Bruker Avance III spectrometers equipped with 9.4 or 14.1 T wide-bore superconducting magnets. For ^1H NMR spectra, samples were packed into 1.3 mm zirconia rotors and rotated at a MAS rate of 60 kHz. ^1H MAS NMR spectra were acquired with signal averaging for 8 transients and a repeat interval of 3 s. Two-dimensional ^1H homonuclear double-quantum (DQ) MAS correlation experiments were carried out with one rotor period of BABA pulses (Sommer *et al.*, 1995; Feike *et al.*, 1996) used to excite and reconvert double-quantum coherences. Signal averaging was carried out over 16 transients for each of 300 t_1 increments of 33.33 μs .

For ^{31}P , ^{27}Al and ^{13}C NMR spectra, the samples were packed into 4 mm zirconia rotors and rotated at a MAS rate of 8–12.5 kHz. ^{13}C NMR spectra were recorded with cross polarization (CP) from ^1H . A spin lock of 1 ms was used, with a ramped pulse (90–100%) applied to ^1H . The room-temperature spectra of JDF-2 and AlPO-53(A) were recorded with signal averaging for 512 transients and a repeat interval of 3 s. The variable-temperature ^{13}C NMR spectra of AlPO-53(A) were recorded with a 1 ms spin lock, a 3 s repeat interval and signal averaging for 2048 transients. The sample temperature was controlled using a Bruker BCU-II chiller and a Bruker BVT/BVTB-3000 temperature controller and heater booster. The sample temperature (including frictional heating effects arising from sample spinning) was calibrated using the isotropic ^{87}Rb shift of solid RbCl (Skibsted & Jakobsen, 1999). For all ^{13}C spectra, high-power ($\nu_1 = 100$ kHz) TPPM-15 ^1H

decoupling was applied during acquisition. The ^1H – ^{13}C correlation spectrum of AIPO-53(A) was recorded using a through-bond J -transferred refocused INEPT pulse sequence (Elena *et al.*, 2005). Signal averaging was carried out for 224 transients for each of 80 t_1 increments of 63 μs . Homonuclear decoupling of ^1H during t_1 was achieved using the eDUMBO-1₂₂ scheme (Elena *et al.*, 2004) and heteronuclear decoupling of ^1H during acquisition was achieved using TPPM-15. ^{27}Al MAS NMR spectra were recorded with signal averaging for 32 transients and a repeat interval of 5 s. The ^{27}Al multiple-quantum (MQ) MAS NMR spectrum of JDF-2 was recorded using a shifted-echo split- t_1 pulse sequence (Brown & Wimperis, 1997), with the signal enhanced using a SPAM composite conversion pulse (Gan & Kwak, 2004). Signal averaging was carried out for 288 transients with a 1 s repeat interval for each of 120 t_1 increments of 142.8 μs . The delay used to allow acquisition of a whole echo was 6.5 ms. The indirect dimension was referenced according to Pike *et al.* (2000). The ^{27}Al MQMAS NMR spectrum of AIPO-53(A) was recorded using a z -filtered pulse sequence, and then sheared and referenced according to Pike *et al.* (2000). Signal averaging was carried out for 192 transients with a repeat interval of 1.5 s for each of 144 t_1 increments of 71.43 μs . ^{31}P MAS NMR spectra were recorded with signal averaging for 2 transients and a repeat interval of 1200 s.

For ^{15}N NMR spectra, samples were packed into 7 mm zirconia rotors and rotated at a MAS rate of 5 kHz. The spectra were recorded with cross polarization (CP) from ^1H . A spin lock of 3 ms was used, with a ramped pulse (90–100%) applied to ^1H . The spectrum was recorded with signal averaging for 29696 transients and a repeat interval of 3 s [for AIPO-53(A)] or 1600 transients and a repeat interval of 90 s (for JDF-2). TPPM-15 ^1H decoupling ($\nu_1 \sim 45$ kHz) was applied during acquisition. Note that the ^{15}N resonances for both materials are very sharp (<14 Hz) and, therefore, the FIDs were truncated at 60–80 ms to prevent probe arcing. In order to minimize truncation artefacts while retaining the relevant spectral features, the FIDs were processed with 5 Hz (for JDF-2) or 2.5 Hz [for AIPO-53(A)] exponential weighting.

Chemical shifts are reported in ppm relative to $(\text{CH}_3)_4\text{Si}$ (^1H and ^{13}C), CH_3NO_2 (^{15}N), 1 M $\text{Al}(\text{NO}_3)_3$ or 85% H_3PO_4 using L-alanine (NH_3 $\delta_{\text{iso}} = 8.5$ ppm, CH_3 $\delta_{\text{iso}} = 20.5$ ppm), ^{15}N -enriched glycine ($\delta_{\text{iso}} = -347.4$ ppm), $\text{Al}(\text{acac})_3$ ($\delta_{\text{iso}} = 0.0$ ppm, $C_Q = 3.0$ MHz, $\eta_Q = 0.17$) and BPO_4 ($\delta_{\text{iso}} = -29.6$ ppm) as secondary solid references.

2.3. Computational details

Geometry optimizations and calculation of NMR parameters were carried out using the CASTEP DFT code (Versions 8 and 16) (Clark *et al.*, 2005), employing the GIPAW algorithm (Pickard & Mauri, 2001), to reconstruct the all-electron wavefunction in the presence of a magnetic field. The initial crystal structures were taken from the literature, and additional models were constructed from these as discussed below. Calculations were performed using the GGA PBE

Table 1

Reference shieldings, σ_{ref} , and scaling factors, m , used to convert calculated isotropic shieldings to isotropic chemical shifts as described in equation (1).

Nucleus	σ_{ref} (ppm)	m	Nucleus	σ_{ref} (ppm)	m
^1H	27.53	0.90	^{27}Al	554.40	0.94
^{13}C	173.94	1.00	^{31}P	281.31	1.14
^{15}N	−155.60	1.00			

functional, with core-valence interactions described by ultrasoft pseudopotentials (Yates *et al.*, 2007). A planewave energy cut-off of 60 Ry was used, and integrals over the Brillouin zone were performed using a Monkhorst–Pack grid with a k -point spacing of $0.04\ 2\pi\ \text{\AA}^{-1}$. Dispersive interactions were reintroduced using the scheme of Grimme (2006), as implemented by McNellis *et al.* (2009). Calculations were performed on either a 198-node (2376-core) Intel Westmere cluster with 2 GB memory per core and QDR Infiniband interconnects, or a 54-node (1728-core) Intel Broadwell cluster with 4 GB memory per core and FDR Infiniband interconnects at the University of St Andrews.

The calculated isotropic magnetic shielding, $\sigma_{\text{iso}}^{\text{calc}}$, was converted to a calculated isotropic chemical shift using the relationship

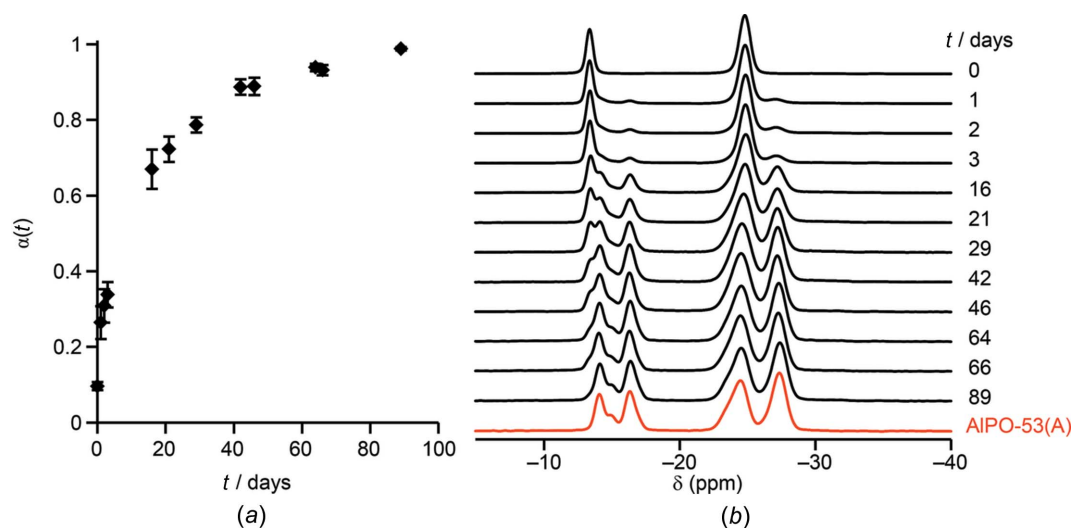
$$\delta_{\text{iso}}^{\text{calc}} \approx \frac{\sigma_{\text{ref}} - \sigma_{\text{iso}}^{\text{calc}}}{m}, \quad (1)$$

where σ_{ref} and m are the reference shielding and scaling factor, respectively, for a given nucleus. Ideally, $m = 1$, but it is sometimes the case that, in reality, non-unity scaling factors are required (Ashbrook & McKay, 2016). The values used in this work are summarized in Table 1. The magnitude of the quadrupolar coupling constant is given by $C_Q = eQV_{zz}/h$, where Q is the nuclear quadrupole moment (for which a value of 146.6 mb was used for ^{27}Al) (Pyykko, 2008). The asymmetry parameter is given by $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$.

3. Results and discussion

3.1. The ambient hydration of JDF-2 to AIPO-53(A)

The transformation from JDF-2 to AIPO-53(A) was followed by quantitative ^{31}P MAS NMR spectroscopy (*i.e.* ensuring full relaxation before repeating the experiment). Using the spectral assignments reported previously (Ashbrook *et al.*, 2009), the integrated intensities of the resonances can be used to determine the proportions of JDF-2 to AIPO-53(A) within the sample. It is important to note that at no point in the investigation were any resonances observed that did not correspond to either JDF-2 or AIPO-53(A), suggesting that, upon contact with H_2O , the transformation of one unit cell of JDF-2 to AIPO-53(A) occurs directly and not *via* any intermediate phase. The limiting factor for the overall bulk transformation must, therefore, be a combination of the availability of atmospheric water, and the transport of water through the pores of the material. Consequently, the compo-


Figure 2

(a) Plot of the degree of transformation $\alpha(t)$ for JDF-2 to AIPO-53(A) as a function of time. Error bars indicate the standard deviation in α , obtained as described in the *Supporting information* (§S1). (b) ^{31}P (14.1 T, 12.5 kHz MAS) NMR spectra of JDF-2 exposed to ambient conditions for the time indicated. The ^{31}P NMR spectrum of a sample prepared as AIPO-53(A), acquired under the same conditions, is shown in red.

sition of the sample may be expressed in terms of the degree of transformation, $\alpha(t)$ (Boldyreva & Boldyrev, 1999)

$$\alpha(t) = 1 - \phi_{\text{JDF-2}}(t), \quad (2)$$

where $\phi_{\text{JDF-2}}(t)$ is the fraction of the sample that remains as JDF-2 at time, t , after the start of the hydration. The degree of transformation can also be expressed as the proportion of the sample that has been converted to AIPO-53(A) after a time, t . A plot of $\alpha(t)$ against t is shown in Fig. 2, along with the ^{31}P MAS NMR spectra used to determine $\alpha(t)$. The error bars indicate the standard deviation of values of $\alpha(t)$ determined from the integrated intensities of different spectral resonances, as described in the *Supporting information* (§S1).

The data fit well to a first-order kinetic model,

$$\alpha(t) = e^{-kt}, \quad (3)$$

where k is the first-order rate constant and $\alpha(t)$ describes the degree of hydration of the material,

$$\alpha(t) = 1 - \frac{\phi_{\text{J}}(t)}{\phi_{\text{J}}(0)}, \quad (4)$$

with $\phi_{\text{J}}(t)$ representing the fraction of the material that remains as JDF-2 at time t . However, the straight-line form of the model, $-\ln(1 - \alpha) = -\ln(1 - \alpha_0) + kt$ has an intercept of 0.2645, indicating an initial rapid hydration of *ca* 23% of the material within the first day. It can be assumed that this represents hydration of the surface layers of the crystallites, with further diffusion of water into the cores of the crystallites proceeding with a rate constant, k , of $1.8 \times 10^{-3} \text{ h}^{-1}$. This value is clearly much slower than the ‘overnight’ hydration typically observed for many calcined AIPOs [see the *Supporting information* (§S2) for examples]. However, to our knowledge, there are no other studies on the ambient hydration of as-prepared AIPOs for direct comparison, so we are unable to say with certainty whether the hydration of as-made

JDF-2 is unusually rapid. Further kinetic analysis was not carried out as, although the room temperature was maintained at 292 (1) K, the relative humidity varied between 23 and 43%, depending on fluctuations in the weather.

3.2. Multinuclear solid-state NMR spectra of AIPO-53(A)

While it was noted above that no intermediate species were observed in the transformation of JDF-2 to AIPO-53(A), several resonances in the multinuclear NMR spectra of AIPO-53(A) cannot immediately be assigned to species in the published crystal structure (Kirchner *et al.*, 2000). This was first noted by Ashbrook *et al.* (2009), who reported four resonances in the ^{13}C NMR spectrum of AIPO-53(A), despite the structure containing only two crystallographically distinct C-atom sites. Here, we investigate this discrepancy further using multinuclear one- and two-dimensional NMR spectra to gain insight into the origins of the unexpected resonances.

The ^1H MAS NMR spectra shown in Fig. 3(a) contain the expected number of resonances, according to the published crystal structures. The use of 60 kHz MAS and a repeat interval of 3 s affords high-resolution quantitative spectra. The

Table 2

Chemical shifts and relative integrated intensities of resonances observed in the ^1H NMR spectra of AIPO-53(A) and JDF-2.

Species	δ_{iso} (ppm)	Relative intensity	Species	δ_{iso} (ppm)	Relative intensity
JDF-2			AIPO-53(A)		
CH_3	3.1	3.0	CH_3	2.9, 3.1	6.0 ^a
OH	5.3	1.1	H_2O	4.1	1.1
NH_3	6.16, 6.34	3.1 ^a	OH	4.8, 5.3	1.2, 1.1
			NH_3	6.3–6.8	5.9 ^a

Note: (a) accurate decomposition was not possible and only the combined integrated intensity for these resonances is reported.

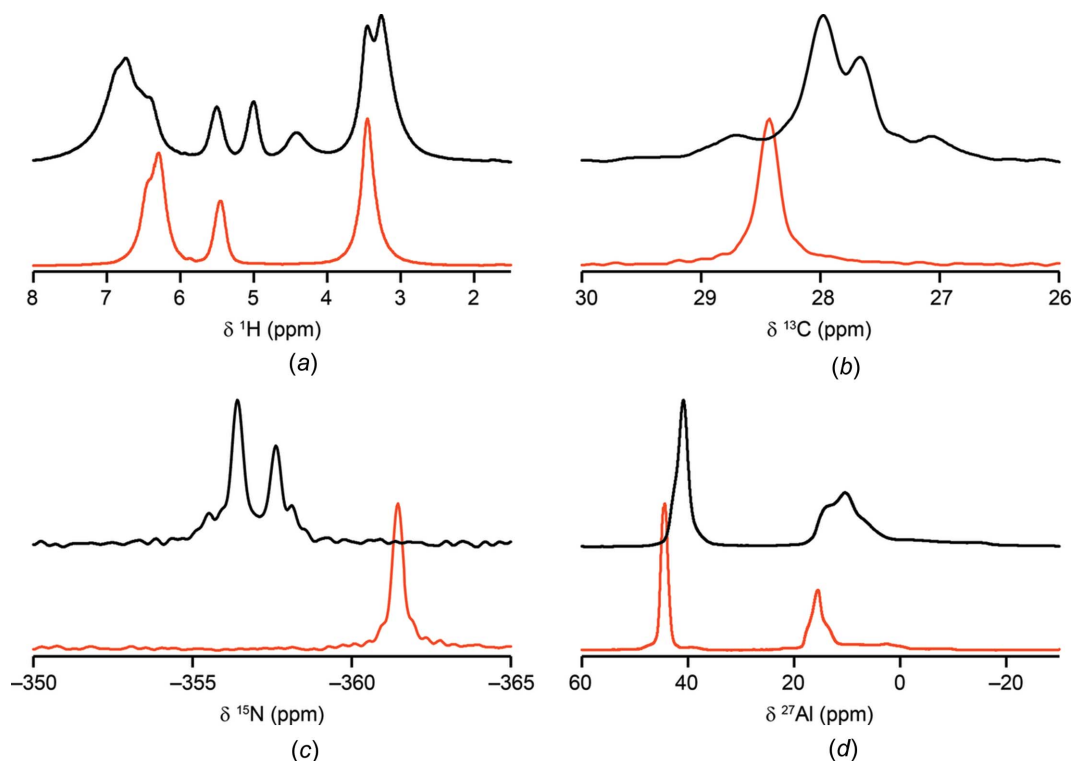


Figure 3 (a) ^1H (14.1 T, 60 kHz MAS), (b) ^{13}C (14.1 T, 12.5 kHz CP MAS), (c) ^{15}N (9.4 T, 5 kHz CP MAS) and (d) ^{27}Al (14.1 T, 12.5 kHz MAS) NMR spectra of AIPO-53(A) (black) and JDF-2 (red).

chemical shifts, integrated intensities and assignments of all ^1H resonances observed for JDF-2 and AIPO-53(A) are provided in Table 2. As shown in the *Supporting information* (§S3), two-dimensional ^1H double-quantum (DQ) MAS experiments confirm all assignments. From both spectra, it can be seen that the relative proportions of CH_3 and NH_x is 1:1, confirming that only protonated methylammonium (MAH^+) is present in both materials. However, the relative intensity of the H_2O resonance indicates a stoichiometry closer to $\text{Al}_6\text{P}_6\text{O}_{24}(\text{CH}_3\text{NH}_3\text{-OH})_2(\text{H}_2\text{O})_{0.5}$, *i.e.* with only 25% occupancy of each of the two

H_2O sites. This differs significantly from the thermogravimetric analysis reported by Ashbrook *et al.* (2009), which indicated that the H_2O sites were fully occupied [for a freshly-prepared sample of AIPO-53(A) dried under air at 303 K]. However, the variable hydration state of the material and the frictional heating of the sample in MAS experiments (especially 60 kHz MAS) is likely responsible for this discrepancy, especially as any surface-bound water is likely to be easily removed with only gentle heating, and we note that the NMR spectra recorded for this work are consistent with those recorded earlier (Ashbrook *et al.*, 2009).

The ^{13}C CP MAS NMR spectrum of JDF-2 in Fig. 3(b) contains a single sharp resonance at 28.5 ppm, as expected from the single crystallographic MAH^+ . However, as observed previously by Ashbrook *et al.* (2009), the equivalent spectrum for AIPO-53(A), also shown in Fig. 3(b), contains four, rather than the expected two, resonances at 27.1, 27.7, 28.0 and 28.7 ppm. The relative intensity ratio of these four resonances is 1.0:2.4:5.3:1.0, which does not fit unambiguously to a simple stoichiometric ratio. However, it is worth noting that the sum of the integrated intensities of the three least intense resonances is close to that of the most intense resonance. This suggests that one of the crystallographic MAH^+ species may be responsible for the most intense resonance, while the other three arise from the second MAH^+ species, in a range of magnetically inequivalent environments [*i.e.* there is some nonperiodic feature of the system that affects exclusively (or predominantly) one of the two crystallographic MAH^+ species within the published structure]. The two-dimensional ^1H - ^{13}C

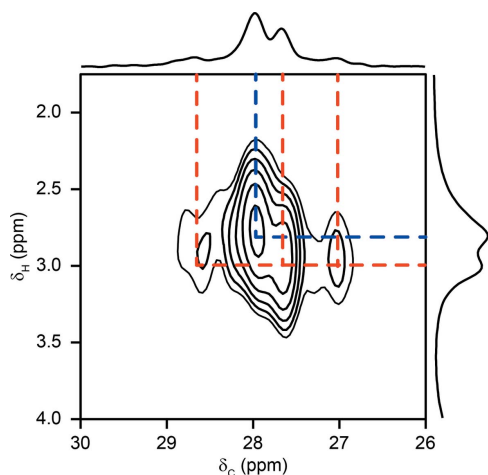


Figure 4 ^1H - ^{13}C (14.1 T, 12.5 kHz MAS) *J*-transfered INEPT spectrum of AIPO-53(A).

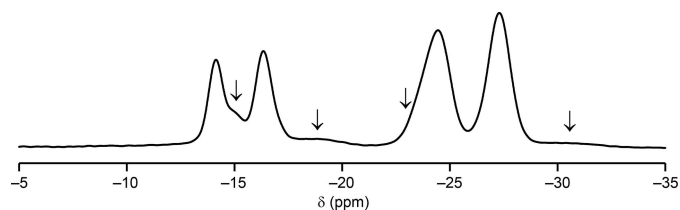


Figure 5
 ^{31}P (14.1 T, 12.5 kHz MAS) NMR spectrum of as-prepared AIPO-53(A). Resonances not expected from the given crystal structure of AIPO-53(A) are indicated.

Table 3
 Chemical shifts and relative integrated intensities of resonances observed in the ^{13}C and ^{15}N NMR spectra of AIPO-53(A) and JDF-2.

^{13}C δ_{iso} (ppm)	Relative intensity	^{15}N δ_{iso} (ppm)	Relative intensity
JDF-2			
28.5	1.0	-361.3	1.0
AIPO-53(A)			
27.1	1.0	-356.4	1.0
27.7	2.4	-355.5	4.1
28.0	5.3	-357.6	2.1
28.7	1.0	-358.2	1.1

correlation spectrum shown in Fig. 4 demonstrates that the ^1H resonance at 3.1 ppm correlates to the three ^{13}C resonances at 27.1, 27.7 and 28.0 ppm, whereas the remaining ^{13}C resonance (at 28.0 ppm) correlates to the ^1H resonance at 2.9 ppm. Therefore, it seems that the most likely explanation for the differences between the number of CH_3 resonances observed in the ^1H and ^{13}C NMR spectra is that one of the two crystallographic MAH^+ species in AIPO-53(A) is disordered, whereas the other is fully ordered. This disorder appears to give rise to a small change in the local environment of the CH_3 group, which is too small to be detected in the (relatively low-resolution) ^1H NMR spectrum, but yields a measurable chemical-shift difference for ^{13}C .

The ^{15}N CP MAS NMR spectra of the two materials (Fig. 3c) are similar in appearance to the ^{13}C spectra, in that a single sharp resonance is observed for JDF-2 ($\delta = -361.3$ ppm) and four resonances are observed for AIPO-53(A), at -356.4, -355.5, -357.6 and -358.2 ppm. This is consistent with the presence of four distinct MAH^+ species within AIPO-53(A) and the relative intensities of the ^{15}N and ^{13}C resonances are summarized in Table 3. As was indicated by the ^1H NMR spectra discussed above, no resonances from neutral CH_3NH_2 are observed in the ^{15}N NMR spectra. It can, therefore, be concluded from a combination of the integrated intensities of the ^1H NMR spectrum and ^{15}N chemical shifts, that there are no OH^- vacancies (*i.e.* giving rise to neutral MA) within AIPO-53(A).

The ^{31}P MAS NMR spectrum of JDF-2, shown in Fig. 2(b), contains resonances at -13.4 and -24.8 ppm, with a 1:2 integrated intensity ratio. These have been assigned previously by Ashbrook *et al.* (2009) as summarized in Table 4. The ^{31}P MAS NMR spectrum of AIPO-53(A), shown in red in

Table 4
 Chemical shifts and assignments of the ^{31}P and ^{27}Al resonances of AIPO-53(A) and JDF-2. For ^{27}Al (spin $I = 5/2$), the magnitude of the quadrupolar coupling constant, $|C_Q|$, and asymmetry, η_Q , are also reported.

Assignment ^a	δ_{iso} (ppm)	$ C_Q $ (MHz)	η_Q
JDF-2			
P2	-13.4		
P1+P3	-24.8		
Al1	18 (1)	6.6 (1)	0.2 (1)
Al2	18 (1)	2.8 (1)	0.8 (1)
Al3	45 (1)	1.7 (1)	0.5 (1)
AIPO-53(A)			
P6	-14.2		
P5	-16.3		
P1, P4	-24.3		
P2, P3	-27.3		
Al2+Al4	16 (1)	4.3 (2)	0.4 (1)
Al5	17 (1)	5.6 (2)	0.9 (1)
Al6	19 (2)	9.7 (2)	0.1 (1)
Al3	42 (1)	1.9 (1) ^b	
Al1	44 (1)	2.6 (1) ^b	

Notes: (a) using the numbering schemes of Chippindale *et al.* (1994) (for JDF-2) and Kirchner *et al.* (2000) [for AIPO-53(A)]; (b) only the quadrupolar product, $P_Q (= C_Q[1 + (\eta_Q^2/3)]^{1/2})$ could be determined for these resonances. See §S4 of the *Supporting information* for details.

Fig. 2(b), contains four intense resonances at -14.2, -16.3, -24.3 and -27.3 ppm, with approximate intensity ratios of 1:1:2:2. These correspond to the six crystallographically distinct P species, as summarized in Table 4. However, as shown in Fig. 5, there is also some signal intensity at -15, -19, -23 and -31 ppm, accounting for *ca* 15% of the total spectral intensity, which cannot be assigned directly to any of the crystallographic P species. This spectral intensity disappears on dehydration of the AIPO-53(A) sample to JDF-2, and returns upon rehydration of JDF-2 to AIPO-53(A), confirming that this signal must be assigned to AIPO-53(A), rather than an impurity phase. It should be noted that the intensity of this unassigned ^{31}P signal is similar to the sum of the integrated intensities of the two lowest-intensity resonances in both the ^{13}C and ^{15}N CP MAS NMR spectra (21 and 25%, respectively). This suggests that whatever structural modification affects the NMR spectra of the MAH^+ species may also affect the NMR parameters of the AlPO_4 framework.

It was previously shown by Ashbrook *et al.* (2009) that the experimental ^{27}Al NMR parameters of AIPO-53(A), summarized in Table 4, are broadly consistent with those calculated from the (optimized) structure of Kirchner *et al.* (2000), suggesting that any disorder present within AIPO-53(A) does not affect the ^{27}Al NMR parameters as significantly as those of ^{31}P . Spectra recorded for this work, shown in Fig. 3(d) and the *Supporting information* (§S4), confirmed this observation, and the ^{27}Al MAS NMR spectrum of JDF-2 is also consistent with both the earlier work and the published crystal structure (Chippindale *et al.*, 1994; Gai-Boyes *et al.*, 1992). However, it is possible that any effects of the disorder apparent in the NMR spectra of the other nuclei present within AIPO-53(A) are masked by the second-order quadrupolar broadening of the ^{27}Al ($I = 5/2$) resonances.

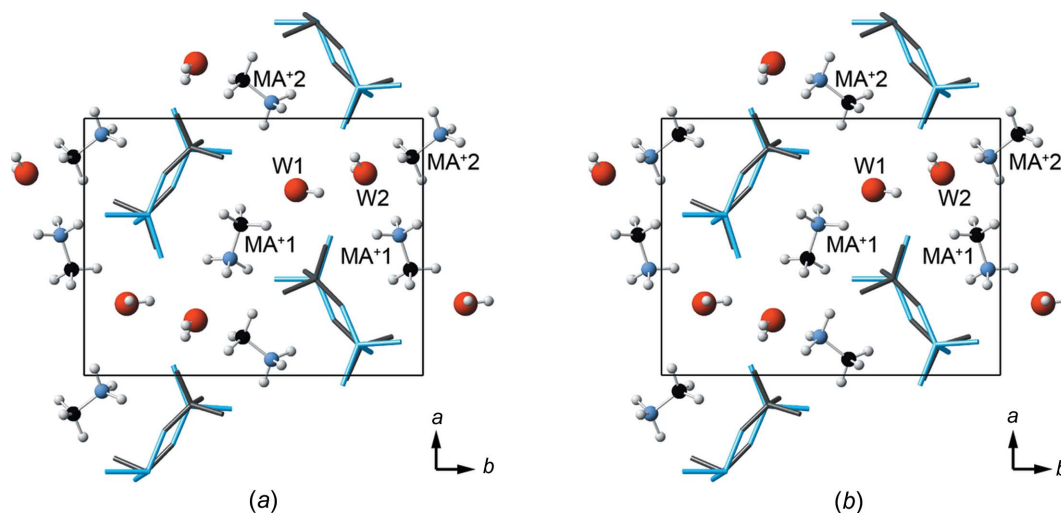


Figure 6

One of the methylammonium hydrate layers of (a) the published structure of AIPO-53(A), model A1, and (b) model A4, where the C and N atoms of each MAH⁺ cation have been reversed. See the text and *Supporting information* (§S5) for details.

3.3. DFT-based investigation of the local structure of AIPO-53(A)

In the present case, it can be assumed that the AIPO₄ framework itself is not significantly altered upon hydration of JDF-2 to AIPO-53(A), as the hydration and dehydration processes involved occur at very low temperatures relative to the temperature of 673 K required to calcine either material to the ordered AIPO-53(B), and even higher temperatures (*ca* 973 K) are required to break and reform Al–O and P–O bonds to give first AIPO-53(C) and then dense AIPO₄ tridymite (Kirchner *et al.*, 2000). It is, therefore, reasonable to consider that any disorder within AIPO-53(A) must arise from the hydrated methylammonium hydroxide sublattice. As can be seen in Fig. 1, the hydroxide anions are trapped within the ‘layers’ of AIPO₄, with the methylammonium hydrates occupying the spaces between successive aluminophosphate hydroxide ‘layers’. The hydroxide anions are, therefore, also excluded from consideration in the following discussion, since their position is essentially restricted by the surrounding AIPO₄ framework, which does not vary between AIPO-53(A) and JDF-2. Therefore, the methylammonium hydrate layers in the structure must contain the disorder responsible for the observed NMR spectra. This is, perhaps, unsurprising, given that this layer contains predominantly discrete molecules and ions, rather than an infinitely connected framework, so it may be expected to have more degrees of freedom. In addition, the atoms of the methylammonium hydrate layers have low atomic numbers and will be challenging to locate by Bragg powder diffraction techniques (the original structure was determined using synchrotron powder X-ray diffraction; Kirchner *et al.*, 2000), especially in the presence of the higher electron density of the AIPO₄ framework, which is generally of more interest to the materials science community, as it is this framework that will remain in the calcined material.

Within the unit cell of AIPO-53(A), there are two crystallographically-identical methylammonium hydrate layers, con-

taining two crystallographically-distinct methylammonium species, MAH⁺1 and MAH⁺2, and two crystallographically-distinct water molecules, W1 and W2. As shown in Fig. 6, these species are organized into MAH⁺1...W2 W1...MAH⁺2 motifs, where ‘...’ represents the O...H–N hydrogen bonds between the water molecules and methylammonium cations. Several chemically and physically plausible structures can be generated from this starting point, based either on reversal of the C/N coordinates of MAH⁺ [*i.e.* assuming that the location of the MAH⁺ was identified correctly by Kirchner *et al.* (2000), but its orientation was not], or on the absence of one or more water molecules [*i.e.* assuming that the published structure of AIPO-53(A) is the idealized fully hydrated end point of hydration of JDF-2, whereas a partially hydrated material is the stable equilibrium state under ambient conditions].

The most obvious constraint on any structural models of AIPO-53(A) is that, when dehydrated, they must yield JDF-2. When optimized, JDF-2 (model J1) has a dispersion-corrected total enthalpy of -58257.298 eV, which is 0.856 eV more stable than the optimized structure of AIPO-53(A), where the water molecules have been removed prior to optimization (model A2). However, after optimization, a structural model of dehydrated AIPO-53(A), where the C- and N-atom coordinates were swapped (model A3), has a total enthalpy of -58257.290 eV, *i.e.* very close to that of the optimized JDF-2. Upon optimization, a structural model for JDF-2, in which the C- and N-atom coordinates were swapped (model J2), had a total enthalpy of -58256.335 eV, which is 0.963 eV less stable than model J1. This suggests that the orientation of the MAH⁺ cations in AIPO-53(A) is the opposite of that reported by Kirchner *et al.* (2000), whereas the cation orientation in the published structure of JDF-2 (Chippindale *et al.*, 1994) is correct. Further details and all optimized structures discussed are provided in the *Supporting information* (§S5) and underpinning data.

Fig. 6(b) shows the arrangement of the methylammonium hydrate layers in the structural model of AIPO-53(A) with the

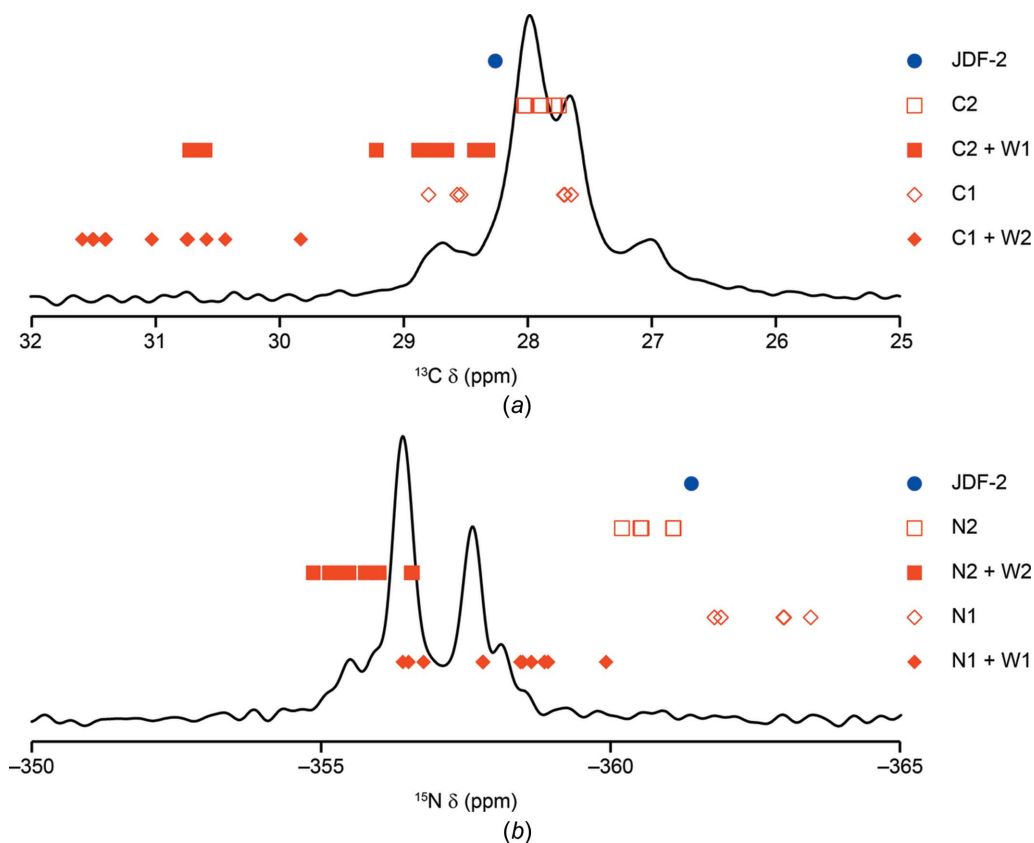


Figure 7

Experimental (a) ^{13}C and (b) ^{15}N CP MAS NMR spectra of AIPO-53(A), overlaid with the calculated isotropic chemical shifts for the different types of C and N species in the structural models J1 and those based on A4 [see the *Supporting information* (§S5) for details]. Filled red shapes indicate that the water site (W1 or W2) adjacent to the C or N site is occupied and empty shapes indicate that the water site is vacant.

MAH^+ cations reversed. It can be seen that there is still potential for hydrogen bonding similar to that in the parent structure (Fig. 6a), but now in an $\text{MAH}^+\cdots\text{W1}\cdots\text{W2}\cdots\text{MAH}^+$ motif. After optimization, the enthalpies of the two fully hydrated structural models (A1 and A4) shown in Fig. 6 are very similar, with model A1 only 0.034 eV less stable than A4, as opposed to the 0.844 eV difference between the dehydrated models A2 and A3. The greater similarity of the energies of the hydrated structural models likely arises from the potential to stabilize an unfavourable arrangement of cations within the pores by hydrogen bonding to H_2O , which is not possible in the dehydrated structures discussed above. However, the cation arrangement in the published structure remains energetically disfavoured relative to reversal of the cation orientations.

The quantitative ^1H MAS NMR spectra, discussed above, indicated that the H_2O sites were only 25% occupied. To investigate which water site is most energetically favourable to occupy, a series of structures with W1 and W2 vacancies was considered. Removal of a single W2 (model A6) is (after optimization) 0.040 eV more favourable than removal of a single W1 (model A5). However, for model A4, removal of W1 (model A7) is 0.379 eV more favourable than removal of W2 (model A8). When all W1 are removed from model A1 (before optimization, model A9), this arrangement is 0.186 eV more stable than when all W2 sites are vacant (model A10),

i.e. 0.047 eV more stable per H_2O removed. However, when all W1 are removed from model A4 (before optimization, model A11), this arrangement is just 0.035 eV more stable per H_2O removed, *i.e.* around one-tenth of the value observed when a single W1 is removed (model A12). This suggests that the removal of W1 from this more likely parent structure is actually less favoured as more W1 is removed. In all cases investigated, loss of W1 was energetically favoured to some extent but, in order to achieve a total of 25% occupancy of the H_2O sites, 50% of W2 sites would also have to be vacant.

The ^{13}C and ^{15}N chemical shifts calculated for models J1 and those based on A4 are plotted in Fig. 7, overlaid with the experimental NMR spectra of AIPO-53(A). It can be seen that the calculated ^{13}C shifts agree best for the more dehydrated structures (*i.e.* ^{13}C next to a water vacancy). The most intense resonance agrees well with the predicted shifts for C2 adjacent to a W1 vacancy (proposed above to be the more energetically favourable water vacancy), which is consistent with the high relative intensity of this resonance. The resonances at 28.7 and 27.7 ppm can be assigned to C1 adjacent to a W2 vacancy, but the resonance at 27.1 ppm remains unassigned by these calculations. On the other hand, the calculated ^{15}N chemical shifts appear to indicate a much more hydrated structure, with the most intense resonance at -355.5 ppm assigned to N2 adjacent to an occupied W2 site (*i.e.* the most energetically favourable water location). However, there is a considerably

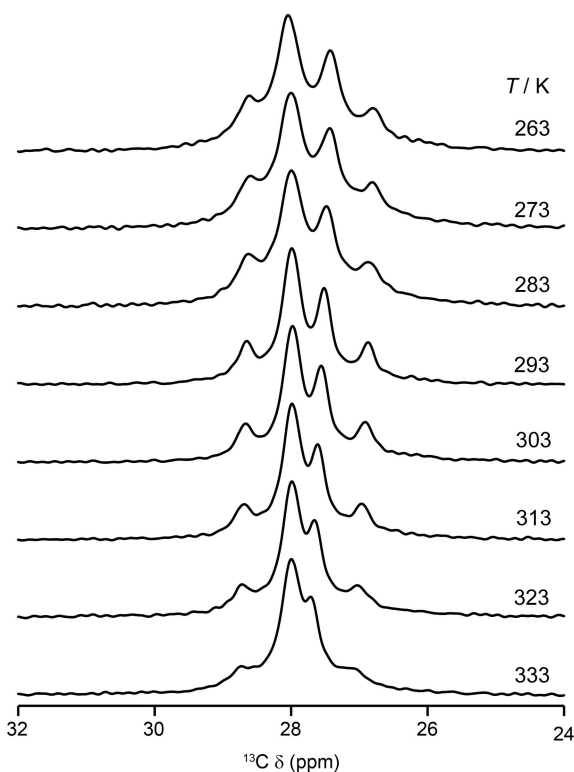


Figure 8
Variable-temperature ^{13}C (14.1 T, 12.5 kHz CP MAS) NMR spectra of AlPO-53(A).

greater spread of the calculated ^{15}N shifts than was observed for ^{13}C , meaning that assignment of the other three resonances is more challenging. In general, however, from the calculated ^{13}C and ^{15}N chemical shifts, it can be concluded that the water appears to be preferentially associated with the hydrophilic NH_3^+ groups, while the water vacancies are preferentially associated with the hydrophobic CH_3 groups.

As shown in Fig. 8, the ^{13}C NMR spectrum of AlPO-53(A) changes with temperature, with the peak positions and relative intensities of the resonances varying significantly between 263 and 333 K. Such temperature dependence of the spectrum is indicative of dynamics, which means that static snapshots of possible models of disorder considered above are unlikely to provide good agreement with the experimental spectra. A full investigation of the dynamics present would require molecular-dynamics (MD) calculations and further in-depth NMR experiments, such as probing variation in the ^{27}Al and ^2H quadrupolar broadening as a function of temperature. However, to a first approximation, assuming an almost instantaneous ‘hopping’ motion between two structures, the calculated NMR parameters for these two structures can simply be averaged (see, for example, Griffin *et al.*, 2009). In AlPO-53(A), it is reasonable to assume that, since the water sites are only 25% occupied, the water molecules can hop between the W1 and W2 sites with relatively little hindrance. Two calculations (models A13 and A14) were carried out with a single water molecule placed in either the W1 or W2 position of a $\text{MAH}^+1 \cdots \text{W2}$ $\text{W1} \cdots \text{MAH}^+2$ motif and the isotropic ^{13}C and ^{15}N shifts for $\text{MAH}^+1 \cdots \square$ $\text{W1} \cdots \text{MAH}^+2$ and

$\text{MAH}^+1 \cdots \text{W2}$ $\square \cdots \text{MAH}^+2$ (where \square represents a water vacancy) were averaged. This gave values of δ_{iso} for C1 and C2 of 30.0 and 29.7 ppm, and for N1 and N2 of -358.6 and -359.7 ppm. These still do not agree perfectly with the experimental spectra, but this is perhaps not surprising as the model takes into account only one type of motion and does not allow for any more complicated or longer-range water motion (which must occur as part of the hydration/dehydration process).

The ^{31}P NMR spectrum of AlPO-53(A) also displayed unexpected resonances, as highlighted in Fig. 5. However, as shown in the *Supporting information* (§S6), no one model provides agreement with the experimental shifts sufficient to allow a more detailed assignment. Again, this is not particularly surprising, as we have demonstrated the presence of dynamics, which were not included in any of the models considered for ^{31}P .

4. Conclusions

Using quantitative ^{31}P MAS NMR spectroscopy, we have demonstrated that the ambient hydration of JDF-2 to AlPO-53(A) proceeds slowly, with the hydration complete after ~ 3 months under the conditions employed. However, the endpoint of this hydration (when studied by solid-state NMR spectroscopy) is not consistent with the published structure of AlPO-53(A) reported by Kirchner *et al.* (2000). The structure obtained by ambient hydration is evidently significantly more disordered than refined by Kirchner *et al.*, and a combination of multinuclear solid-state NMR spectroscopy and periodic density functional theory calculations were used to evaluate possible models for modifications to the published crystal structure. The DFT calculations suggested that reversal of the C- and N-atom positions of the MAH^+ cations was energetically favourable and gave a structure comparable to JDF-2. Quantitative ^1H MAS NMR spectra showed $\sim 25\%$ occupancy of the H_2O sites. However, it should be noted that the JDF-2/AlPO-53(A) system clearly has a variable hydration capacity, meaning that the published crystal structure may have been determined for a more completely hydrated material (although attempts to force the hydration to occur by submerging the material in water – results not shown – did not lead to a noticeably more hydrated material). While no one structural model considered here could adequately explain all of the spectral data, DFT calculations indicate that water vacancies on the W1 site would be most energetically favourable. Calculated ^{13}C and ^{15}N chemical shifts indicate that the more hydrophobic CH_3 end of the MAH^+ cations are, generally, near an environment closer to a water vacancy than a water molecule, whereas the water is more associated with the hydrophilic NH_3^+ group. However, variable-temperature ^{13}C NMR spectroscopy indicated that dynamics are present, probably including some bulk water motion, which is an integral part of the hydration and dehydration process.

Ultimately, we propose a model of AlPO-53(A) in which all MAH^+ cations have their C- and N-atom positions swapped compared to the crystal structure previously reported and with

the overall formula $\text{Al}_6\text{P}_6\text{O}_{24}(\text{CH}_3\text{NH}_3\text{OH})_2(\text{H}_2\text{O})_{0.5}$. The water molecules are likely to be more closely associated with the polar NH_3^+ groups of MAH^+ than the hydrophobic CH_3 groups, but the water (and possibly the SDA) are dynamic. These results demonstrate the power of the NMR crystallography approach to provide structural detail beyond that available from either NMR spectroscopy or crystallography alone.

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