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Solid-state NMR studies of the aluminophosphate molecular sieve VPI-5

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Abstract

MAS ^{27}Al, ^{31}P, and ^{27}Al nutation NMR spectra show that at 294 K fully hydrated VPI-5 contains three Al and P crystallographic sites in an 1:1:1 occupancy ratio and one-third of Al is 6-coordinate. The results are consistent with the P6$_3$ space group. Above 353 K two ^{31}P MAS resonances in a 2:1 intensity ratio are found, and quadrupole nutation spectrum gives only one line from 4-coordinate Al, indicating that fully hydrated VPI-5 undergoes a structural transformation to a higher framework symmetry P6$_3$cm space group. The preparation of partially hydrated VPI-5 can be monitored by ^{2}H NMR and by ^{27}Al and ^{31}P MAS NMR. Both partially and fully hydrated VPI-5 undergo a symmetry change from P6$_3$ space group at 294 K to P6$_3$cm above 353 K, which indicates that the breakdown of hydrogen-bonded water structure inside the pores is not a factor in the process.

Keywords: VPI-5; Aluminophosphate; Molecular sieves; NMR

1. Introduction

VPI-5 is an AlPO$_4$ molecular sieve containing 18-membered ring unidimensional channels [1]. The large channel diameter of ca. 12 Å gives the material potential for the separation of large molecules and for catalytic cracking of heavy fractions of petroleum. From the powder XRD pattern Rudolf and Crowder [2] refined the structure of the fully hydrated VPI-5 to P6$_3$cm space group (see Fig. 1a) which contains two Al and P crystallographic sites and all Al atoms are 4-coordinate. However, this result is difficult to reconcile with the ^{27}Al and ^{31}P MAS NMR spectra [3,4]. The ^{31}P spectrum contains three resonances with the intensity ratio 1:1:1, and the ^{27}Al spectrum lines from 4- and 6-coordinate Al with the intensity ratio 2:1. McCusker et al. [5] obtained a significantly better refinement in the lower P6$_3$ space group (see Fig. 1b), which is fully consistent with the NMR results. In their model there are three P and Al crystallographic sites in fully hydrated VPI-5. The refinement locates all the water molecules inside the large pores: two molecules (referred to as 'framework' water) link the Al atoms between the fused 4-membered rings, thus making one-third of Al atoms 6-coordinate; the remaining water molecules (referred to as 'free' water) form a triple helix.

^{31}P MAS NMR studies of VPI-5 in the range 294–423 K [6–11] show that VPI-5 undergoes a symmetrical change from P6$_3$ space group at

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ambient temperature to P6$_3$cm above 353 K. However, the cause of this structural change was not widely studied. Here we report variable-temperature MAS ^{27}Al, ^{31}P and ^{27}Al nutation NMR measurements in the range 294–373 K for the fully and partially hydrated VPI-5. Partially hydrated VPI-5 is the sample containing only 'framework' water and 'free' water selectively removed from the channels.

2. Experimental

VPI-5 was synthesized with DPA and TBA as templates according to the optimized compositions established in Ref. [12]. The samples synthesized in DPA and TBA systems have very similar NMR results. Fully hydrated samples were prepared over a saturated solution of NH_4Cl for 12 h. To prepare a partially hydrated sample, VPI-5 was evacuated at 10^{-4} torr for 2 days and rehydrated for 24 h with 10% D_2O + 90% H_2O. The sample was then heated in situ for ca. 15 min in a NMR rotor with a hole in the cap at 373 K until no intensity change was observed in the ^{2}H NMR spectrum. The principle of the technique is discussed below. The sample was then transferred to a tightly closed rotor in a dry box for NMR experiments.

^{2}H, ^{27}Al, and ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer at 61.4, 104.3 and 162.0 MHz, respectively. ^{2}H spectra were recorded using a quadrupole echo pulse sequence with a 20 μs echo delay and a 2 s recycle delay. ^{27}Al spectra were recorded with 0.6 μs ($< 10°$) radiofrequency pulses and 0.3 s recycle delays with MAS at 10–12 kHz. ^{27}Al nutation spectra were recorded with $\omega_{rf}/2\pi$ of 115 ± 5 kHz and with MAS at 8–12 kHz. ^{31}P spectra were recorded with 1 μs (30°) pulses and 30 s recycle delays with MAS at 7–12 kHz. Chemical shifts of ^{2}H, ^{27}Al and ^{31}P are given in ppm from external D_2O, $Al(H_2O)_6^{3+}$ and 85% H_3PO_4, respectively.

3. Results

3.1. Fully hydrated VPI-5

^{31}P MAS NMR spectra of fully hydrated VPI-5 in the range 294–353 K are shown in Fig. 2a. In agreement with the results reported by Houckgeest et al. [7], the spectra change considerably above room temperature. Changes are observed already at 338 K and become prominent at 343 K. The resonance at -27 ppm grows at the expense of that at -23 ppm. The two peaks do not coalesce and the growing peak only shifts slightly from -27.3 ppm at 294 K to -26.7 ppm at 348 K, while the resonance

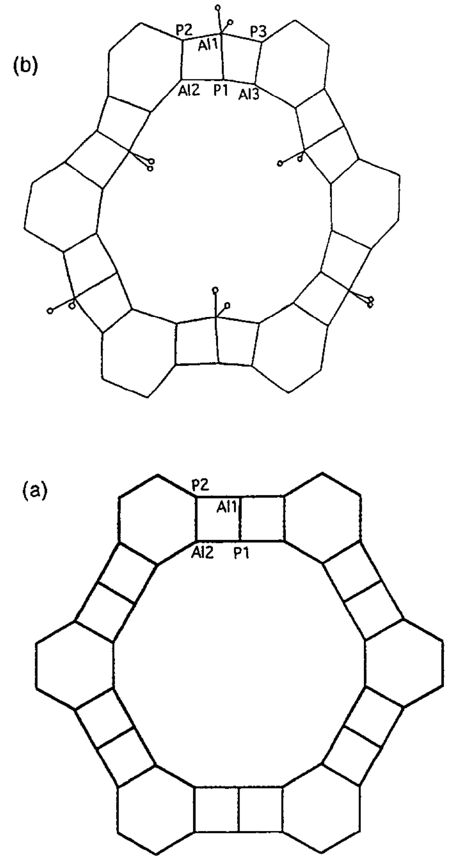

Fig. 1. One layer of framework structure of VPI-5 along the [001] direction (a) according to Rudolf et al. [2] showing P6$_3$cm symmetry; (b) according to McCusker et al. [5] showing the P6$_3$ symmetry. Intracrystalline water is not shown, except for the 'framework' water.

decreasing in intensity shifts gradually from −23.4 to ca. −25 ppm. The transformation is complete at 353 K and the final spectral intensity ratio is 2:1. The transformation is fully reversible. A considerable decrease of the intensity of ^{1}H-^{31}P CP/MAS line was found when the temperature is increased from 294 to 330 K.

The ^{27}Al MAS NMR spectrum of fully hydrated VPI-5 at 294 K in Fig. 3a shows 4- and 6-coordinate Al lines in the 2:1 intensity ratio centred at 40 and −18 ppm, respectively, the latter displaying a characteristic second-order quadrupole powder pattern. The line at 40 ppm is composed of two overlapping resonances from 4-coordinate Al in a 1:1 intensity ratio. Between 294 and 370 K the intensity ratio of 4-coordinate/6-coordinate Al lines is ca. 2:1. The shape and width of the line at 40 ppm also does not change significantly. By contrast, the second-order quadrupole powder pattern at −18 ppm changes significantly with temperature, and can be simulated to yield the quadrupole coupling constant, C_Q, the asymmetry parameter, η, and the isotropic chemical shift, δ (Fig. 3b). In parallel with the ^{31}P evidence, a considerable loss of the ^{1}H-^{27}Al CP/MAS line is observed when the temperature is increased from 294 K to 330 K.

^{27}Al MAS nutation spectra in the 4-coordinate Al region (shown in Fig. 4) provide further insights into the structural change. At 294 K the spectrum has one line at $\omega_{rf}/2\pi$ and two lines between $\omega_{rf}/2\pi$ and ca. 3 $\omega_{rf}/2\pi$. This shows that the two 4-coordinate Al lines, which over-

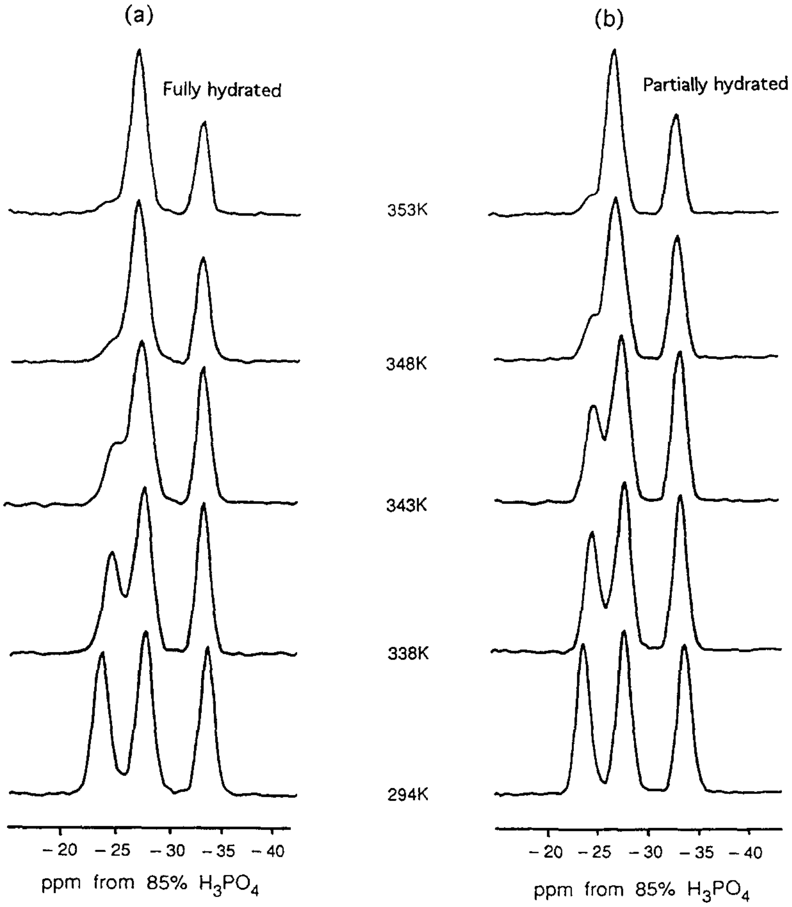

Fig. 2. Variable-temperature ^{31}P MAS NMR spectra of (a) fully hydrated VPI-5 and (b) partially hydrated VPI-5.

lap in the ordinary MAS NMR spectrum and can only be observed using double-rotation (DOR) [13], have slightly different quadrupole interaction parameters. These two lines come from 4-coordinate Al. When the temperature is increased from 294 to 343 K, the resolution of the two peaks from 4-coordinate Al decreases considerably, and above 343 K only one line is detected. In parallel with the ^{31}P NMR evidence, this suggests that above 343 K the two kinds Al sites between 4- and 6-membered rings become identical. If these two Al sites are still present, they must have very similar quadrupole interaction parameters and very similar isotropic chemical shifts. In addition, in the range 294–353 K the line width of ^{1}H MAS line from the

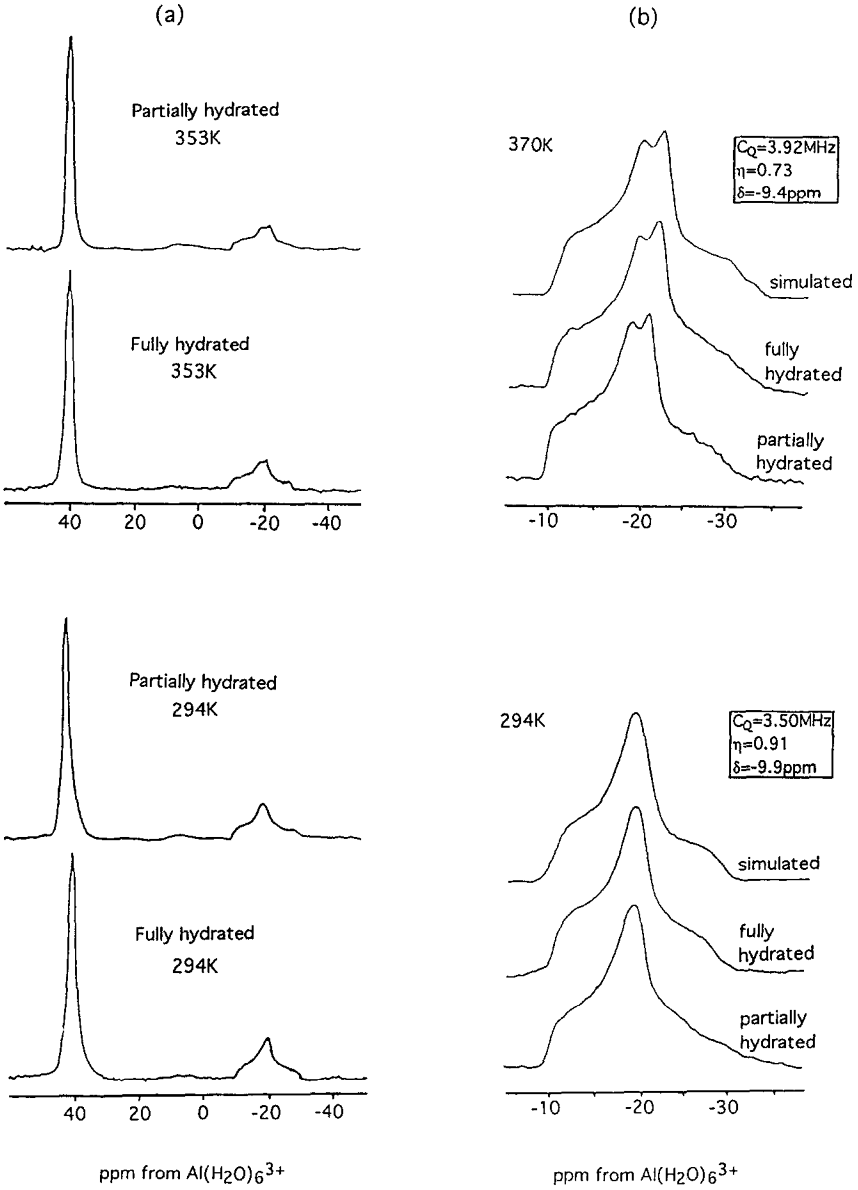

Fig. 3. (a) ^{27}Al MAS NMR spectra measured at 294 and 353 K of fully and partially hydrated VPI-5. (b) The comparison of the experimental and simulated 6-coordinate Al second-order quadrupole line shapes of fully and partially hydrated VPI-5 at 294 and 370 K.

water in fully hydrated VPI-5 narrows from 1220 to 300 Hz, which means that the motion of water molecules becomes faster and the triple helix of water molecules is less ordered at increased temperatures.

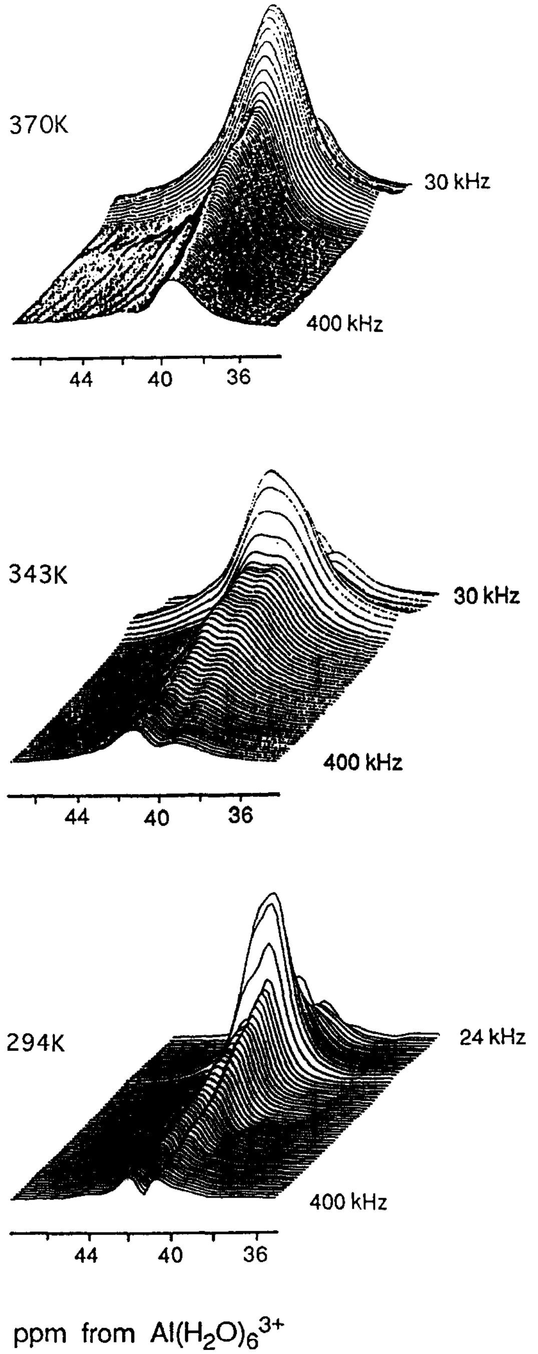

Fig. 4. Variable-temperature ^{27}Al MAS nutation spectra in the region of 4-coordinate Al of fully hydrated VPI-5 measured with $\omega_{rf}/2\pi = 115 \pm 5$ kHz radiofrequency field.

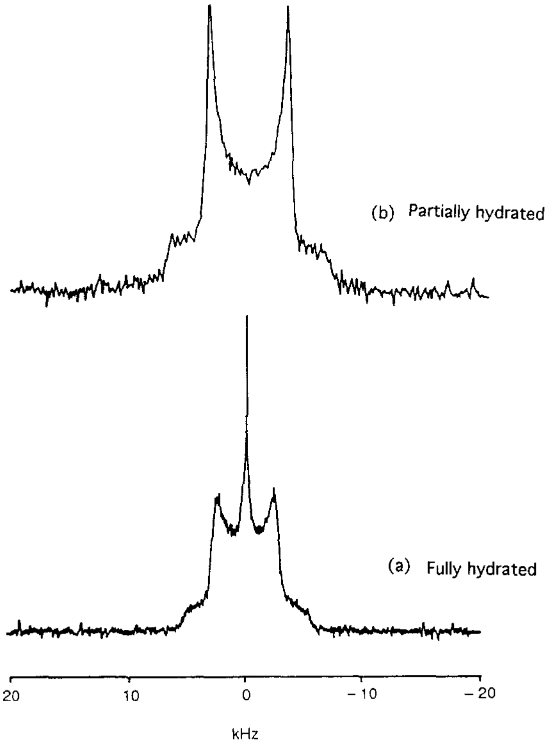

Fig. 5. ^2H NMR spectra measured at 373 K of (a) fully hydrated and (b) partially hydrated VPI-5.

3.2. Partially hydrated VPI-5

The preparation of partially hydrated VPI-5 was monitored by ^2H NMR and by ^{27}Al and ^{31}P MAS NMR. Fig. 5a shows that the ^2H NMR spectrum of fully hydrated (10% D_2O + 90% H_2O) VPI-5 heated to 373 K in a closed rotor has a narrow central peak and a characteristic spin-1 powder pattern. After heating the sample to 373 K for 15 min in an open-cap rotor (until there is no change of lineshape), only the powder pattern remains (Fig. 5b). A comparison with the results of Goldfarb et al. [14] indicates that the sharp line probably comes from D_2O adsorbed on the crystal surface. The ^2H NMR simulations suggest that the powder pattern in Fig. 5b comes from the rotation of two 'framework' water molecules around their C_2 axes, although at higher water contents the 'free' water molecules may also contribute. Thus the sample prepared as shown in Fig. 5b contains only 'framework' water. Correct preparation of partially hydrated VPI-5 was further proved by ^{27}Al and ^{31}P MAS NMR. Fig. 3a shows that both fully and partially hydrated VPI-5 have very similar ^{27}Al MAS NMR spectra at different temperatures. That means that only the 'free' water was removed. It is also clear that for this particular sample dehydration was taken marginally too far: a very small amount of water was detached from 6-coordinate Al atoms producing very small amount of 5-coordinate Al responsible for the line at ca. 6 ppm (see the 294 K spectrum in Fig. 3a). Perez et al. [15] who measured ^{31}P MAS NMR spectra of VPI-5 with different water contents found that the spectrum of a partially hydrated sample, such as that described here or dehydrated further, should contains an additional small line at -30.8 ppm. However, we did not find this to be the case, even in excessively dehydrated samples (see Fig. 2b). ^{2}H NMR and ^{27}Al and ^{31}P MAS NMR shows that the 'free' water in fully hydrated VPI-5 channels can be selectively removed, so that only the 'framework' water bonded to Al remains. It follows that partially hydrated VPI-5 was correctly prepared.

The ^{31}P MAS NMR spectra (Fig. 2b) show that from 294 to 353 K both fully and partially hydrated VPI-5 undergo the same symmetry change, and the chemical shifts of both samples are almost identical. Considering the intensity ratio of the peaks at -23 and -27 ppm, the temperature of symmetry change of partially hydrated VPI-5 is only slightly higher than that of fully hydrated VPI-5.

^{27}Al MAS NMR spectra of partially hydrated VPI-5 shown in Fig. 3a also contain lines from 4- and 6-coordinate Al with the intensity ratio of ca. 2:1 at all temperatures. The line shapes of the second-order quadrupole powder pattern from 6-coordinate Al of both samples (Fig. 3b) are almost the same at the same temperature. This means that the quadrupole parameters and the isotropic chemical shift for both samples are identical. With increasing temperature, the change of the line width of the line from 4-coordinate Al is similar to that of fully hydrated VPI-5, except that the line width is slightly smaller than that of fully hydrated VPI-5. ^{27}Al MAS NMR indicates that only the environment of 4-coordinate Al atoms is slightly changed by removal of 'free' water molecules from VPI-5 channels.

In view of the smaller dipolar interactions at low concentrations of water, the line width of ^{1}H MAS line from the water in partially hydrated VPI-5 is smaller than that of fully hydrated VPI-5 between 294 and 353 K. The line is narrow above room temperature.

4. Discussion

MAS ^{27}Al, ^{31}P, and ^{27}Al nutation NMR spectra show that VPI-5 has three crystallographic sites at 294 K, thus supporting the XRD structure of fully hydrated VPI-5 proposed by McCusker et al. [5] Fully hydrated VPI-5 completes a transformation from $P6_3$ space group at 294 K to the higher $P6_3cm$ space group above 353 K. Indeed, the loss of both ^{1}H-^{27}Al and ^{1}H-^{31}P CP/MAS lines with increasing temperature indicates that dipolar interactions with water molecules are greatly reduced by an increased water motion. Line simulations of the second-order quadrupole powder pattern of 6-coordinate Al indicate that the higher framework symmetry above 353 K is obtained at the expense of a larger local distortion (larger C_Q) of the Al sites.

The combined results of ^{2}H NMR, ^{27}Al and ^{31}P MAS NMR clearly show that the 'free' water is completely removed from the VPI-5 channels and only the 'framework' water bonded to Al sites remains. NMR is thus capable of monitoring the preparation of partially hydrated VPI-5.

Houckgeest et al. [7] suggested that the symmetry change from $P6_3$ space group to $P6_3cm$

in fully hydrated VPI-5 is due to a breakdown of the triple-helix structure of water inside VPI-5 channels. It would follow that a sample without 'free' water molecules should have the $P6_3cm$ space group at room temperature. This is not consistent with our results. At room temperature the ^{31}P MAS NMR spectrum of partially hydrated VPI-5 contains three resonances with the intensity ratio 1:1:1 corresponding to three crystallographic sites. Variable-temperature ^{31}P MAS NMR spectra show further that both the fully and the partially hydrated VPI-5 undergo the same reversible symmetry change at very similar temperatures. The environment of the 6-coordinate Al atom in partially hydrated VPI-5 is not influenced by 'free' water molecules since their quadrupole parameters and isotropic chemical shifts are very similar to those of the fully hydrated sample at the same temperature, while the environment of the 4-coordinate Al atoms changes slightly. Thus, this symmetry change does not involve the 'free' water molecules. It strongly depends on either the 'framework' water molecules, on the framework itself or both.

In view of the gradual changes of peak intensities and chemical shifts in variable-temperature ^{31}P MAS NMR spectra, the structural change would appear to be a second-order phase transformation. Since the chemical shift of one P site between 4- and 6-membered rings changes much less than that of the other, we believe that the structural environment of one P site between 4- and 6-membered rings in the $P6_3$ structure is similar to the P sites between 4- and 6-membered rings in the $P6_3cm$ structure, although the structure of VPI-5 with $P6_3cm$ space group above 353 K has not yet been reported.

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