

## Oxyfluorinated Microporous Compounds. II. Solid State NMR of $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}$

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Received May 11, 1992; accepted January 5, 1993

The compound  $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}$  (AlPO4-CJ2) has been studied by solid state NMR. Using the different observable nuclei,  $^{27}\text{Al}$ ,  $^{31}\text{P}$ ,  $^{19}\text{F}$ ,  $^{15}\text{N}$ , and  $^1\text{H}$ , the crystallographic nonequivalences have been established and agree with the previous crystal structure analysis. Furthermore, the  $^{15}\text{N}$  has allowed us to confirm the presence of ammonium in the structure and to determine its population ratio. Some  $\text{H}_3\text{O}^+$  are present in the structure and their number is calculated using  $^1\text{H}$  and  $^{15}\text{N}$  NMR. The number of bridging OH proposed in the structure has also been quantified by NMR. Both determinations are in agreement. © 1993 Academic Press, Inc.

### Introduction

The recently discovered compound  $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}$  (AlPO4-CJ2 (1)) has been synthesized and its structure has been reexamined (2). The main interest of this compound lies in its applicability to catalysis. It belongs to a more general family of three-dimensional aluminophosphates prepared, as is well known for zeolites, by the use of quaternary ammonium salts as templates.

Once reevaluated, the structure appears (Fig. 1) as a three-dimensional network of  $\text{PO}_4$  tetrahedra, of  $\text{AlX}_5$  ( $X = \text{O}^{2-}$ ,  $\text{OH}^-$ ,  $\text{F}^-$ ) trigonal bipyramids, and of  $\text{AlX}_6$  octahedra sharing vertices. The anion shared between aluminum coordination polyhedra is either a fluorine or a hydroxyl group.

The aluminums are in two different environments: a pentacoordinated  $\text{Al}(\text{OP})_4(X)$  site and a hexacoordinated  $\text{Al}(\text{OP})_4(\text{F})(X)$  site. The two  $\text{PO}_4$  tetrahedra have their four oxygens connected to aluminums, two to the five-coordinated aluminums and two

to the six-coordinated aluminums of  $\text{P}(\text{OAl}^{\text{V}})_2(\text{OAl}^{\text{VI}})_2$ .

Most of the problems left unresolved by the first structure determination have been solved during its reexamination (2). Among them, two oxygens O(10) and O(11) of the work of Yu have been reassigned to nitrogens (N(1) and N(1)) of ammonium ions. Furthermore, the two aluminum polyhedra are linked by an ion, O(9) in Yu, which has been reassigned to be OH or F, with an occupation probability of 0.66 and 0.34. Among these reassignments, the occupation probability has still to be proved; the presence of the ammoniums should be confirmed and its possible substitution by  $\text{H}_3\text{O}^+$  checked.

This is why a solid state NMR study was undertaken. It used  $^{31}\text{P}$ ,  $^{27}\text{Al}$ ,  $^{19}\text{F}$ ,  $^{15}\text{N}$ , and  $^1\text{H}$  NMR.

### Experimental

The NMR experiments have been run on a MSL 400 Bruker instrument for  $^{31}\text{P}$ ,  $^{27}\text{Al}$ ,

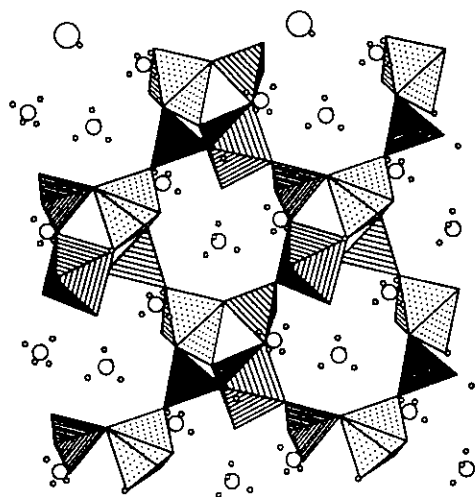


FIG. 1. 001 projection of the  $\text{AlPO}_4\text{-CJ2}$  structure.

$^{19}\text{F}$ , and  $^1\text{H}$  nuclei. A high speed probe head spinning at up to 15 kHz with 4-mm rotors has been used.  $^{15}\text{N}$  has been acquired on a AMX 300 equipped with a solid state accessory, a 7-mm rotor spinning at 5 kHz. NMR experimental acquisition conditions are given in Tables I and II.

## Results and Discussion

### $^{27}\text{Al}$

In  $^{27}\text{Al}$  MAS NMR two sites have been observed, as can be seen in Fig. 2. Their

TABLE II  
 $^{15}\text{N}$  CPMAS NMR ACQUISITION CONDITIONS ON  
THE BRUKER AMX 300 SPECTROMETER

H-1 and N-15 $t_{90}$	6.5 $\mu\text{sec}$
Contact time	2 msec
Decoupling time	100 msec
Dead time	10 $\mu\text{sec}$
Recycle time	5 sec
Resonance frequency	30 MHz
MAS spinning speed	5 kHz
Number of scans	10,000
Number of digitized points	8 kwords
Referencing	0 ppm on $\text{CH}_3\text{NO}_2$
Test sample	$\text{NH}_4\text{NO}_3$

chemical shifts are respectively 20 and  $-5$  ppm. They are respectively characteristic of a pentacoordinated (Al(1)) and a hexacoordinated (Al(2)) aluminum site (3,4). This result agrees completely with the non-equivalent aluminum sites proposed in the structure determination. The quadrupolar interaction is  $\nu_Q = 450$  kHz and  $\eta = 0.6$  for the pentacoordinated site and for the hexacoordinated one  $\nu_Q = 280$  kHz and  $\eta = 0.3$ . Their population ratio is  $1 (\pm 5\%)$ , which confirms an occupancy of 1 for each of them. The line broadening that must be added to the simulation to get a reasonable lineshape indicates some site distribution. The origin of the distribution is certainly due to OH and F occupying statistically the

TABLE I  
MAS NMR ONE PULSE ACQUISITION CONDITIONS ON THE BRUKER MSL 400 SPECTROMETER

	$^{27}\text{Al}$	$^{31}\text{P}$	$^1\text{H}$	$^{19}\text{F}$
Pulse length	1 $\mu\text{sec}$	1 $\mu\text{sec}$	1 $\mu\text{sec}$	1 $\mu\text{sec}$
Dead time	4 $\mu\text{sec}$	4 $\mu\text{sec}$	4 $\mu\text{sec}$	4 $\mu\text{sec}$
Recycle time				4 sec
Resonance frequency	104 MHz	162 MHz	400 MHz	376 MHz
Spectral width	125 kHz	125 kHz	125 kHz	125 kHz
MAS spinning speed	15 kHz	15 kHz	15 kHz	15.2 kHz
Number of scans	256	204	3000	198
Number of digitized points	2048	4096	2048	4096
Referencing 0 ppm	$\text{Al}(\text{NO}_3)_3$ , $\text{HNO}_3$ , $\text{H}_2\text{O}$	$\text{H}_3\text{PO}_4$ 85%	TMS	$\text{CFCl}_3$
Solid test sample	Yttrium-aluminum garnet	$\text{NH}_4(\text{H}_2\text{PO}_4)$	Adamantane	$\text{CaF}_2$

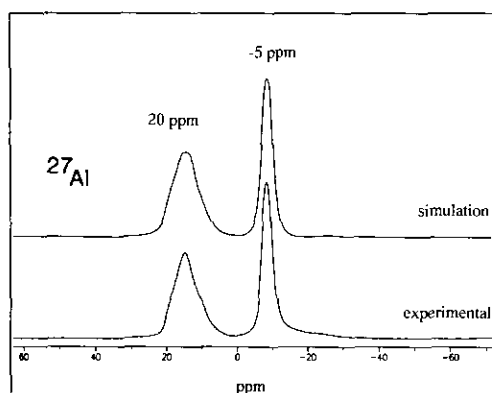


FIG. 2.  $^{27}\text{Al}$  NMR. At 20 ppm the site is a pentacoordinated aluminium, Al(1), at -5 ppm it is a hexacoordinated aluminium, Al(2), with a mixed first sphere of  $\text{AlO}_5\text{F}$ .

same position. Locally the aluminum does not see exactly the same electric field gradient (EFG). However, the long distance constraints make the local site only slightly distorted.

### $^{31}\text{P}$

The  $^{31}\text{P}$  MAS spectrum in Fig. 3 exhibits two well resolved lines at -10.6 and -21.4 ppm corresponding to two different crystallographic phosphorous sites. These results agree equally well with the structure findings. In order to assign the NMR peaks to

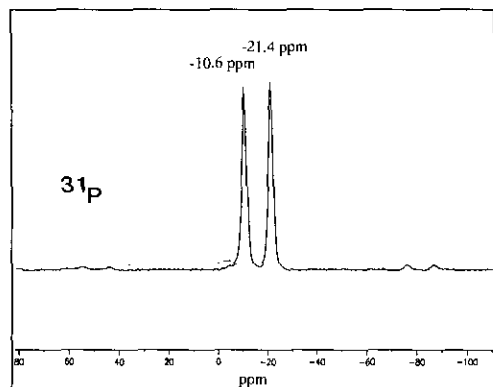


FIG. 3.  $^{31}\text{P}$  NMR. P(1) resonates at -10.6 ppm, P(2) at -21.4 ppm. P(1)/P(2) is 1.

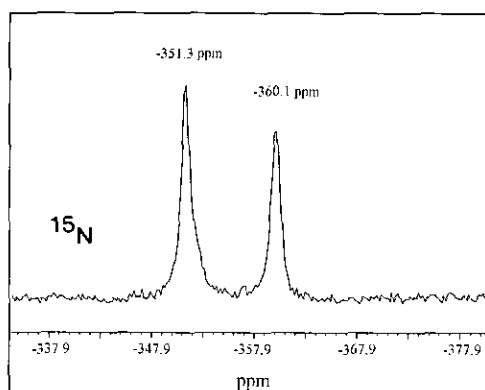


FIG. 4.  $^{15}\text{N}$  NMR. N(1) resonates at -351.3 ppm, N(2) at -360.1 ppm. N(1)/N(2) is 1.30.

the nonequivalent structure sites, an empirical relationship (5) between the mean  $d(\text{P}-\text{O})$  distance and the isotropic chemical shift has been used:

$$d(\text{P}-\text{O}) = 1.27 \cdot 10^{-3} \cdot \delta + 1.569 \text{ \AA}.$$

P(1) has a mean P-O distance of 1.531 Å and P(2) has a 1.536 Å mean distance, both measured on the structure. Using the above formula, distances of 1.542 Å and 1.556 Å are found. They are close enough to the actual distances to attribute the lines. Therefore, P(1) resonates at -21.4 ppm and P(2) resonates at -10.6 ppm. Their area ratio is 1 as expected for occupancy of 1 for each of them. Their linewidths are equal, with a value of 1.8 ppm for both sites. This leads to a statistical distance distribution of less than  $1.6 \times 10^{-3}$  Å for the mean  $d(\text{P}-\text{O})$  around each site.

### $^{15}\text{N}$

The CPMAS result for  $^{15}\text{N}$  gives rise to two peaks at -351.3 and -360.1 ppm relative to  $\text{CH}_3\text{NO}_2$ , as seen in Fig. 4. They are very close to the  $\text{NH}_4^+$  observed in the reference sample,  $\text{NH}_4\text{NO}_3$ , in agreement with the assumed two nonequivalent  $\text{NH}_4$  sites. Their area ratio is  $1.30 \pm 0.05$  for the sites at -351.3 and -360.1 ppm, respectively. This indicates that some  $\text{H}_3\text{O}^+$  is present in the structure replacing some  $\text{NH}_4^+$

at the  $-360.1$  ppm site. The sites differ regarding the nature of the anion they are connected to. The site N(1)H<sub>4</sub> is hydrogen bonded to a fluorine (F(1)), while the N(2)H<sub>4</sub> is connected to a bridging oxygen O(1). In the latter case, two hydrogens are close to oxygen O(1) while in the former case, only one hydrogen is close to the fluorine. The mean N–H distances found by Fourier difference analysis are  $0.83$  Å for N(1) and  $0.75$  Å for N(2). This is a part of the structural analysis fraught with difficulties and uncertainties. Actually the N–H distances lie around  $1.03$  Å, and values of  $0.75$  Å and  $0.83$  Å are far too short.

However, their relative position should be sufficient to attempt an attribution of the two observed <sup>15</sup>N peaks. The chemical shift is a function of the electronic density. The chemical shift convention gives positive values to high frequencies versus a known reference. For a positive gyromagnetic ratio the electronic density decreases with frequency. For a negative gyromagnetic ratio it increases. <sup>15</sup>N has a negative gyromagnetic ratio, so the line at  $-351.3$  ppm corresponds to a more negatively charged nitrogen than the line at  $-360.1$  ppm. Therefore, the sites may be attributed by using the mean distance value. The electronic density is shared between nitrogen and hydrogen; for two given mean N–H distances, the net electronic density carried by nitrogen is weaker for the shorter mean distance. The site at  $-351.3$  ppm is therefore more charged on nitrogen. This corresponds to a longer mean distance, i.e., N(1), with one hydrogen pointing towards a fluorine. The site at  $-360.1$  ppm is less charged on nitrogen with a shorter mean N–H distance. It corresponds to N(2), with two hydrogens close to a bridging oxygen.

Once this attribution has been qualitatively done, an empirical relation can be drawn out between the chemical shifts of <sup>15</sup>N and the mean N–H distance in the NH<sub>4</sub> environment. The chemical shift is, approximately, a linear function of the mean distance N–H. Three values are known, 0 ppm

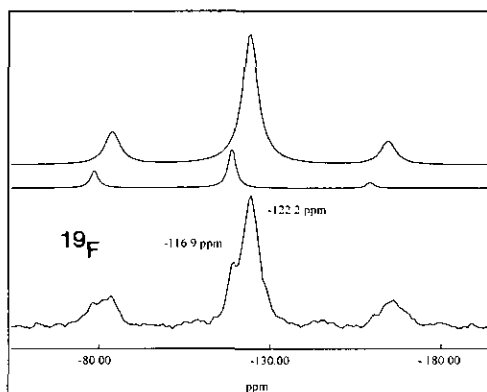


Fig. 5. <sup>19</sup>F NMR. F(1) resonates at  $-116.9$  ppm. F(2) resonates at  $-122.2$  ppm.

for the NH<sub>4</sub>NO<sub>3</sub> and the two values for N(1) and N(2) in this structure. The distance N–H for NH<sub>4</sub>NO<sub>3</sub> known to be  $1.03$  Å. The distance difference found in the Fourier difference analysis is considered to be a good approximation of the distance difference. Therefore the relation between mean distance and chemical shift become

$$d(\text{N-H}) = 9.1 \cdot 10^{-3} \text{ \AA } \delta (\text{ppm}) + 1.030 \text{ \AA }.$$

Mean N–H distances of  $1.09$  Å and  $1.01$  Å are then obtained for N(1)H<sub>4</sub> and N(2)H<sub>4</sub>.

In the process of condensation the presence of a strong H–F hydrogen bond may well be responsible for the lack of condensation through this fluorinated site, and also may well explain the geometry of the cavity around this central ammonium. Actually the Al–F—H–N(1) association may have a more molecular behavior than the other bonds. This “molecular” behavior could lead to a local repulsion of a “hydrophobic” type. N(2)H<sub>4</sub> has a different interaction with the network. It behaves with a more polar character, as a local charge compensator, and therefore must be more exchangeable with water.

#### <sup>19</sup>F

At  $15.2$  kHz in <sup>19</sup>F, two signals are resolved with  $\pm 1$  spinning sidebands (Fig. 5). The positions are  $-116.9$  ppm and  $-122.2$

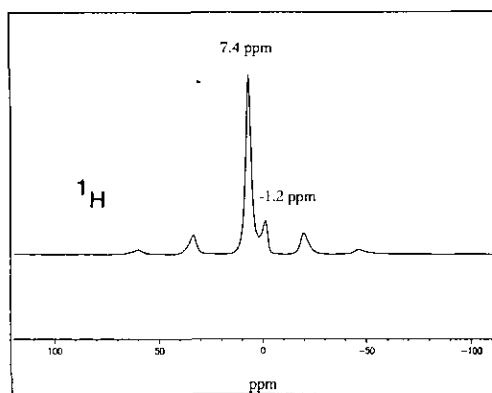


FIG. 6.  $^1\text{H}$  NMR. OH groups resonate at  $-1.2$  ppm,  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  are not resolved and resonate at  $7.4$  ppm.

ppm relative to  $\text{CFCl}_3$ . The spectrum is decomposed as a sum of the lorentzian-gaussian lines. In order to get a realistic decomposition, the position of the sidebands are fixed at  $\pm 15.2$  kHz from the isotropic components, and the linewidths of the sidebands are fixed to the linewidth of the isotropic line. In such conditions integration is performed over the isotropic line as well as the sidebands. If we attribute the more intense line to the nonbridging fluorine, F(1) and the small component to F(2), the bridging fluorine, a ratio of  $\text{F}(1)/\text{F}(2) = 1/0.33$  is found. This is in agreement with the value of  $1/0.34$  proposed from the X-ray analysis, hence confirming the NMR attribution  $\text{Al}(2)\text{-F}(2)\text{-Al}(1)$  at  $-116.9$  ppm and  $\text{Al}(1)\text{-F}(1)$  at  $-122.2$  ppm.

### $^1\text{H}$

At  $15$  kHz, two  $^1\text{H}$  signals have been observed resonating at  $7.4$  and  $-1.2$  ppm (Fig. 6). The signal at  $7.4$  ppm has about three spinning sidebands, indicating a strong dipolar coupling. In contrast the site at  $-1.2$  ppm does not exhibit any such sideband. The site at  $7.4$  ppm can therefore be attributed to the ammoniums, with strong dipolar coupling due to the short H-H distances in  $\text{NH}_4^+$  (ca.  $2.52$  Å), and the site at  $-1.2$  ppm to the bridging OH group. No other peak is resolved. Under the peak at  $7.4$  ppm a  $\text{H}_3\text{O}^+$

signal could be present and not resolved from the  $\text{NH}_4\text{s}$ .

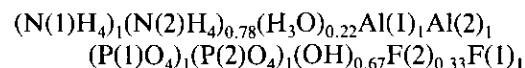
So, in order to test the presence of such a possibility, integration of the two sites has been performed. The site at  $7.4$  ppm has been integrated with all its sidebands. The site at  $-1.2$  ppm is integrated without sidebands.

The ratio found,  $r_{\text{H}} = \text{OH}/\text{H}_{\text{total}}$ , is  $0.088$ . If the global formula of the compound can be written as  $(\text{N}(1)\text{H}_4)_1(\text{N}(2)\text{H}_4)_{1-y}(\text{H}_3\text{O})_y(\text{AlPO}_4)_2(\text{OH})_{1-2x}(\text{F})_{1-2x}$  the above ratio has the expression

$$r_{\text{H}} = \frac{(1 - 2x)/[4 \times (2 - y) + 3 \times y + 1 - 2x]}{1}$$

The value "y" is obtained from the  $^{15}\text{N}$  spectrum as being  $0.22 \pm 0.02$  ( $\text{N}(1)/\text{N}(2) = 1/1 - y = 1.30 \pm 0.05$ ). The value of x obtained from  $^{19}\text{F}$  is  $0.165$ . Therefore,  $r_{\text{H}}$  is equal to  $0.080$ , which is quite close to the  $0.088$  experimentally observed. Both values are well within experimental error and provide some confidence in the assumption that only the N(2) site is substituted by  $\text{H}_3\text{O}^+$ . As  $0.080$  is measured from more accurate data than the direct  $^1\text{H}$  determination, it will be used for the chemical composition analysis.

From the above NMR results the chemical composition can be set to



or in a reduced form, losing the details of the site occupancies:



This NMR analysis is in overall agreement with the chemical analysis,



but it presents more details (2).

### Conclusion

This structure has exemplified how NMR and X-ray analysis can be complementary techniques, as has been recently shown

(6,7). It has been possible to show that non-equivalent sites are easily detected by NMR on a powder on all the nuclei observed,  $^{27}\text{Al}$ ,  $^{31}\text{P}$ ,  $^{19}\text{F}$ ,  $^{15}\text{N}$ , and  $^1\text{H}$ . It has also been shown that not only the nonequivalence but also the occupancy of each site could be measured by NMR. It has been also shown that, from  $^1\text{H}$  NMR, the localization of hydrogens could be determined, as well as their quantification. Their acidity determination would bring a large wealth of information in this field. The complementary aspect of X-ray analysis and NMR lies in the fact that properties which are usually measured on single crystals can be measured by NMR on powders.

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