Synthesis, Crystal Structure, and Solid-State NMR Spectroscopy of $(4\text{-HAP})_2[Ga_4O(PO_4)_4(H_2O)_4]$ (AP = Aminopyridine), a Gallophosphate Containing Discrete Double-Four-Ring Units

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A new gallophosphate, $(4\text{-HAP})_2[Ga_4O(PO_4)_4(H_2O)_4]$ (designated NCUGa-1), has been synthesized in the presence of 4-aminopyridine as the structure-directing agent. The structure consists of discrete $Ga_4(PO_4)_4(H_2O)_4$ double-four-ring (D4R) units hosting O^{2-} anions. Charge compensation is achieved by the monoprotonated amine. Each D4R unit is linked to adjacent units and the organic cations via hydrogen bonding. Crystal data: $(C_5H_7N_2)_2[Ga_4O(PO_4)_4(H_2O)_4]$, orthorhombic, space group *Aba*2 (no. 41), $a = 18.879(4)$ Å, $b = 18.481(4)$ Å, $c = 7.469(1)$ Å, $V = 2606.1(9)$ Å^3, $Z = 4$, R1 = 0.025, and wR2 = 0.062. ^1H MAS NMR confirms that protonation is on the pyridine nitrogen in aminopyridine. The proton-decoupled ^{31}P MAS NMR spectrum exhibits two resonances at 3.8 and 3.4 ppm with an intensity ratio of 1:1, corresponding to two distinct crystallographic ^{31}P sites. The information obtained from $^1H \rightarrow {}^{31}P$ CP/MAS NMR experiments provides insight into the interaction between the hydrogen atoms of the water molecules and/or the amine and the ^{31}P spins, and can be used to correlate ^{31}P resonances with crystallographic sites. In addition, ^{71}Ga MAS NMR confirms the presence of two Ga sites.

Introduction

In 1985, Parise reported several microporous gallophosphates.[1] Since then, a large number of other gallophosphates have been synthesized, particularly by using the fluoride route.[2,3] These gallophosphates are of particular interest since they show a wide structural diversity and potential applications in catalysis. Many have framework topologies analogous to those of zeolites, while others have unique structures. One of the most interesting gallophosphates is cloverite.[4] The cages of cloverite have body diagonals of ∼29−30 Å, the openings to which are comprised of 20 tetrahedra arranged in the form of a four-leaf clover. The structure can be described solely in terms of Ga−O−P double four rings (D4Rs) having fluoride ions in the center. D4R units are apparently versatile and have been observed in alumino- or gallophosphates as well as in phosphates of vanadium, iron, or cobalt.[5−15] The unit can be represented as a cube, the corners of which are occupied by gallium and phosphorus atoms alternately. A fluorine or oxygen atom is occluded in the D4R cage. The metal atoms are often five-coordinate in a geometry of trigonal bipyramid. D4R units without an ion at the center also exist in group 13 phosphonates.[16,17] Most gallium compounds which consist of D4R units adopt 3-D framework or 2-D sheet structures, while only three contain discrete units. One of them, named Mu-1, uses bis(cyclopentadienyl)cobalt ion $(Cp_2Co)^+$ in the synthesis,[18] and one contains protonated diazabicyclo(2.2.2)octane (DABCO).[19] However, both structures were not fully determined, and some problems remain with the locations of the cations. In both compounds the D4R unit has a fluoride ion occluded at its center. Very recently a

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(1) Parise, J. B. *J. Chem. Soc., Chem. Commun.* **1985**, 606.
(2) Férey, G. *J. Fluorine Chem.* **1995**, *72*, 187 and references therein.
(3) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268 and references therein.
(4) Estermann, M.; McCusker, L. B.; Baerlocher, Ch.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.
(5) Schreyeck, L.; Caullet, P.; Mougenel, J. C.; Patarin, J.; Paillaud, J. L. *Microporous Mater.* **1997**, *11*, 161.
(6) Loiseau, T.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 403.
(7) Simmen, A.; Patarin, J.; Baerlocher, Ch. In *Proceedings from the 9th International Zeolite Conference;* Von Ballmoos, R., et al., Eds.; Butterworth-Heinemann: Boston, 1993; Vol. 1, p 433.
(8) Reinert, P.; Marler, B.; Patarin, J. *Chem. Commun.* **1998**, 1769.
(9) Reinert, P.; Patarin, J.; Loiseau, T.; Férey, G.; Kessler, H. *Microporous Mesoporous Mater.* **1998**, *22*, 43.
(10) Wessels, T.; McCusker, L. B.; Baerlocher, Ch.; Reinert, P.; Patarin, J. *Microporous Mesoporous Mater.* **1998**, *23*, 67.
(11) Matijasic, A.; Paillaud, J.-L.; Patarin, J. *J. Mater. Chem.* **2000**, *10*, 1345.
(12) Taulelle, F.; Samoson, A.; Loiseau, T.; Férey, G. *J. Phys. Chem. B* **1998**, *102*, 8588.
(13) Riou, D.; Taulelle, F.; Férey, G. *Inorg. Chem.* **1996**, *35*, 6392.
(14) Huang, C.-Y.; Wang, S.-L.; Lii, K.-H. *J. Porous Mater.* **1998**, *5*, 147.
(15) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735.
(16) Mason, M. R. *J. Cluster Sci.* **1998**, *9*, 1.
(17) Walawalkar, M. G.; Roesky, H. W. *Acc. Chem. Res.* **1999**, *32*, 117.
(18) Kallus, S.; Patarin, J.; Marler, B. *Microporous Mater.* **1996**, *7*, 89.
(19) Kessler, H.; Patarin, J.; Schott-Darie, C. *Stud. Surf. Sci. Catal.* **1994**, *85*, 75.

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Table 1. Crystallographic Data for $(4\text{-HAP})[Ga_4O(PO_4)_4(H_2O)_4]$ (AP = aminopyridine)

empirical formula	$C_{10}H_{22}N_4O_{21}P_4Ga_4$	Z	4
fw	937.07	D_{calcd}, g•cm^{-3}	2.388
color, habit	colorless, column	T, °C	23
size, mm	0.41 × 0.21 × 0.20	λ(Mo Kα), Å	0.71073
cryst syst	orthorhombic	μ(Mo Kα), cm^{-1}	44.4
space group	*Aba*2 (no. 41)	$T_{min,max}$	0.673, 0.942
a, Å	18.879(4)	no. of unique data [$I > 2\sigma(I)$]	2765
b, Å	18.481(4)	no. of variables	196
c, Å	7.469(1)	R1,[a] wR2[b]	0.0250 (0.0258), 0.0619
V, Å^3	2606.1(9)		

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. The value in parentheses is for all data. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 5.74P]$ with $P = (\max F_o^2 + 2F_c^2)/3$.

discrete gallium phosphate D4R unit containing occluded oxygen was synthesized in the presence of pyridinium ion as the structure-directing agent.[20] ULM-17 is a vanadium fluorophosphate whose structure consists of two kinds of discrete D4R units built up from the tetrahedral arrangement of VO_5F octahedra sharing edges and vertexes.[13] In the present work, we report the synthesis, crystal structure, and solid-state NMR spectroscopy of a new gallophosphate which contains discrete D4R units. This material, named NCUGa-1, was prepared in a fluoride-free medium in the presence of 2-aminopyridine, and characterized by single-crystal X-ray diffraction and solid-state NMR spectroscopy.

Experimental Section

Synthesis and Initial Characterization. Hydrothermal reaction of $Ga(NO_3)_3{\cdot}4H_2O$, H_3PO_4, 4-aminopyridine, tetrabutylammonium bromide, and H_2O in a molar ratio of 1:5:7:0.5:555 in a Teflon-lined acid digestion bomb at 160 °C for 5 d produced colorless crystals of NCUGa-1 in 81% yield based on Ga. The X-ray powder pattern of the bulk product is in good agreement with that simulated from the atomic coordinates derived from single-crystal X-ray diffraction. Energy-dispersive X-ray fluorescence spectroscopy confirms the presence of Ga and P in the crystals. Results of elemental analysis are consistent with the stoichiometry. (Anal. Found: C, 13.05; H, 2.12; N, 5.81. Calcd: C, 12.82; H, 2.37; N, 5.98.)

Single-Crystal X-ray Diffraction. Intensity data were collected on a colorless columnar crystal of NCUGa-1 with dimensions 0.41 × 0.21 × 0.2 mm on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed-tube X-ray source. The orientation matrix and unit cell dimensions were determined by a least-squares fit of 1008 reflections. Octants collected and $2\theta_{max}$: $-13 \leq h \leq +24$, $-24 \leq k \leq +23$, $-9 \leq l \leq +9$, 56.52°. Number of measured reflections, unique reflections, and observed unique reflections [$I > 2\sigma(I)$]: 7522, 2841, and 2765. Empirical absorption corrections were performed by using the SADABS program for the Siemens area detector ($T_{min,max} = 0.673, 0.942$). On the basis of statistics for intensity distribution and successful solution and refinement of the structure, the space group was determined to be *Aba*2 (no. 41). The structure was solved by direct methods. The Ga and P atoms were first located, and the C, N, and O atoms were found in difference Fourier maps. O(9) and O(10) are water oxygen atoms. All the hydrogen atoms of the water molecules were found in difference Fourier maps. The hydrogen atoms, which are bonded to carbon atoms, were positioned geometrically and refined using a riding model with fixed isotropic thermal parameters. To balance charge, the organic template should be a monoprotonated amine cation. Because aniline has a larger value of pK_b than that for pyridine, protonation on the pyridine nitrogen in aminopyridine is more favorable, which is confirmed by ^1H NMR study (vide infra). However, the hydrogen atom, which is bonded to nitrogen atom, was not found in difference Fourier maps. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms and a fixed isotropic thermal parameter for all water hydrogen atoms. The reliability factors converged at R1 = 0.025 and wR2 = 0.062, and $S = 1.11$. The Flack x parameter was 0.03(1), indicative of a correct absolute structure. The final difference Fourier maps were flat ($\Delta\rho_{max,min} = 0.54, -0.48$ e/Å^3). Neutral-atom scattering factors for all atoms were used. Anomalous dispersion and secondary extinction corrections were applied. All calculations were performed using the SHELXTL Version 5.1 software package.[21]

Solid-State NMR Measurements. All NMR spectra were acquired on a Bruker AVANCE-400 spectrometer, operating at 400.1, 161.9, and 122.0 MHz for ^1H, ^{31}P, and ^{71}Ga nuclei, respectively. A Bruker probe equipped with 2.5 mm rotors for MAS allowed spinning speeds of up to 35 kHz to be achieved. Typically, ^{31}P MAS NMR spectra with high-power proton decoupling were acquired with $\pi/2$ pulses of 5.2 μs and recycle delays of 10 s. The Hartmann−Hahn conditions for $^1H \rightarrow {}^{31}P$ cross polarization (CP) experiments were set on $(NH_4)_2HPO_4$. $^1H \rightarrow {}^{31}P$ CP/MAS NMR spectra were recorded as a function of contact time ranging from 0.1 to 25 ms. Single-pulse experiments with small flip angles of less than 15°, recycle delays of 1 s, and a spinning speed of 30 kHz were employed to record ^{71}Ga MAS NMR spectra. This experimental condition enables a quantitative estimate of the ^{71}Ga central transition intensity. ^1H MAS NMR spectra were obtained at a spinning speed up to 35 kHz to achieve good spectral resolution. Simulations of ^{71}Ga MAS NMR spectra were performed with the WINFIT program of the Bruker WINNMR software package. Chemical shifts of ^1H, ^{31}P, and ^{71}Ga were externally referenced to tetramethylsilane (TMS), 85% H_3PO_4, and $Ga(H_2O)_6^{3+}$ in 1 M $Ga(NO_3)_{3(aq)}$, respectively.

Results and Discussion

Description of the Structure. The crystallographic data, atomic coordinates, equivalent isotropic thermal parameters, and selected bond lengths are given in Tables 1−3, respectively. The asymmetric unit consists of 22 distinct non-hydrogen atoms. O(11) is at the 4a special position with a local symmetry of C_2, and all other atoms are at general positions. There is one monoprotonated 4-aminopyridinium cation per asymmetric unit. The structure is shown in Figure 1. It consists of discrete $Ga_4(PO_4)_4(H_2O)_4$ D4R units hosting O^{2-} anions. The D4R unit has C_2 symmetry. The organic cations balance the negative charge of the occluded oxide anions. Each D4R unit is linked to adjacent units by hydrogen bonds, as indicated by the short O⋯O distances between water and phosphate oxygen atoms (O(9)⋯O(1), 2.640, 2.638 Å; O(10)⋯O(5), 2.606, 2.642 Å). There is also hydrogen bonding between $P(1)O_4$ and the pyridinium group of the cation, as is inferred from the short

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(20) Wragg, D. S.; Morris, R. E. *J. Am. Chem. Soc.* **2000**, *122*, 11246.

(21) Sheldrick, G. M. SHELXTL Programs, Version 5.1, Bruker AXS, 1998.

Table 2. Atomic Coordinates for (4-HAP)[$Ga_4O(PO_4)_4(H_2O)_4$] (AP = aminopyridine)

atom	x	y	z	U_{eq}[a]
Ga(1)	0.50930(2)	0.09116(2)	0.54305(5)	0.0139(1)
Ga(2)	0.59319(2)	−0.00960(2)	0.86475(6)	0.0150(1)
P(1)	0.48695(5)	−0.12838(5)	0.9386(1)	0.0153(2)
P(2)	0.62783(5)	−0.01379(5)	0.4672(1)	0.0150(2)
O(1)	0.4797(1)	−0.1940(1)	0.0566(4)	0.0211(5)
O(2)	0.5567(2)	−0.0898(2)	0.9760(5)	0.0378(8)
O(3)	0.4240(2)	−0.0776(2)	0.9725(4)	0.0354(8)
O(4)	0.4852(2)	−0.1519(2)	0.7405(4)	0.0316(7)
O(5)	0.6919(1)	−0.0212(2)	0.3498(4)	0.0227(5)
O(6)	0.5766(2)	−0.0771(2)	0.4342(4)	0.0355(8)
O(7)	0.5894(2)	0.0578(2)	0.4303(4)	0.0348(8)
O(8)	0.6502(2)	−0.0149(2)	0.6654(4)	0.0388(8)
O(9)	0.5226(2)	0.1838(2)	0.4088(4)	0.0233(6)
O(10)	0.6818(2)	−0.0212(2)	0.0017(4)	0.0305(7)
O(11)	0.5	0	0.7010(6)	0.0145(7)
N(1)	0.3635(3)	−0.2899(4)	0.716(1)	0.095(2)
N(2)	0.1688(4)	−0.2022(6)	0.673(1)	0.112(3)
C(1)	0.3011(3)	−0.2613(3)	0.7042(7)	0.047(1)
C(2)	0.2399(4)	−0.3053(4)	0.7171(9)	0.066(2)
C(3)	0.2916(4)	−0.1890(3)	0.675(1)	0.063(2)
C(4)	0.1783(4)	−0.2706(6)	0.698(1)	0.094(3)
C(5)	0.2251(5)	−0.1594(5)	0.663(1)	0.092(3)
H(2A)	0.2425	−0.3549	0.7375	0.079
H(3A)	0.3310	−0.1592	0.6642	0.076
H(4A)	0.1376	−0.2990	0.7028	0.113
H(5A)	0.2196	−0.1098	0.6469	0.111
H(9A)	0.5186	0.1884	0.2807	0.05
H(9B)	0.4902	0.2120	0.4520	0.05
H(10A)	0.6877	−0.0051	0.1240	0.05
H(10B)	0.7213	−0.0213	0.9450	0.05

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Lengths (Å) for (4-HAP)[$Ga_4O(PO_4)_4(H_2O)_4$] (AP = aminopyridine)

Ga(1)−O(4)	1.856(3)	Ga(1)−O(6)	1.833(3)
Ga(1)−O(7)	1.837(3)	Ga(1)−O(9)	2.000(3)
Ga(1)−O(11)	2.064(2)	Ga(2)−O(2)	1.834(3)
Ga(2)−O(3)	1.830(3)	Ga(2)−O(8)	1.840(3)
Ga(2)−O(10)	1.973(3)	Ga(2)−O(11)	2.150(2)
P(1)−O(1)	1.506(3)	P(1)−O(2)	1.523(3)
P(1)−O(3)	1.536(3)	P(1)−O(4)	1.542(3)
P(2)−O(5)	1.500(3)	P(2)−O(6)	1.538(3)
P(2)−O(7)	1.533(3)	P(2)−O(8)	1.539(3)
N(1)−C(1)	1.295(7)	N(2)−C(4)	1.29(1)
N(2)−C(5)	1.33(1)	C(1)−C(2)	1.415(8)
C(1)−C(3)	1.365(8)	C(2)−C(4)	1.34(1)
C(3)−C(5)	1.37(1)	O(9)−H(9A)	0.963
O(9)−H(9B)	0.866	O(10)−H(10A)	0.967
O(10)−H(10B)	0.857	O(1)···H(9A)	1.678
O(1)···H(9B)	1.915	O(5)···H(10A)	1.714
O(5)···H(10B)	1.787		

O(1)···N(2) distance of 2.942 Å. The arylamine does not form any hydrogen bonds with phosphate oxygen atoms. The detailed hydrogen-bonding scheme is shown in Figure 2. The D4R unit is observed from a comparison of the thermal parameters of its constituent atoms with those of the organic cation to be more tightly bound by hydrogen bonds in the structure.

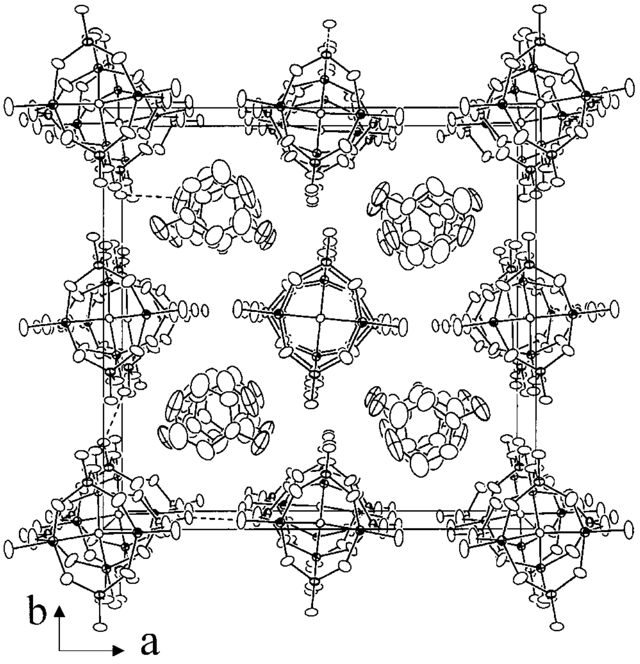

Figure 1. Structure of (4-HAP)[$Ga_4O(PO_4)_4(H_2O)_4$] viewed along the *c* axis. Key: ellipsoid with shaded segments, Ga; ellipsoid boundary ellipse and principal ellipses, P and N; ellipsoid boundary ellipse, O and C. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are not shown for clarity. Dotted lines represent hydrogen bonds.

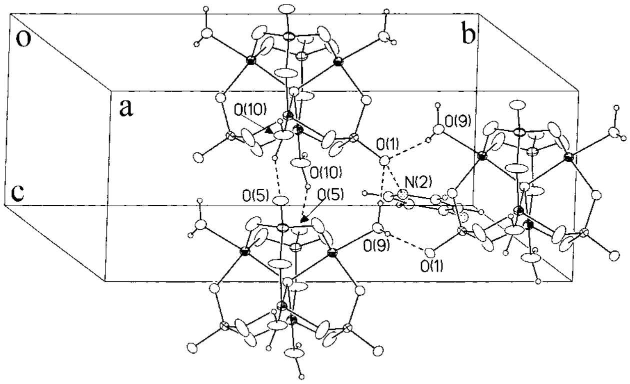

Figure 2. Hydrogen-bonding scheme in (4-HAP)[$Ga_4O(PO_4)_4(H_2O)_4$]. Key: large open circle, C; large open circle with dot pattern, N; small open circle, H. Dashed lines represent hydrogen bonds.

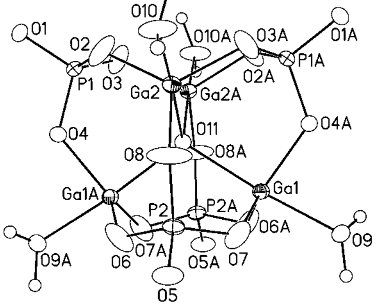

Figure 3. D4R unit in (4-HAP)[$Ga_4O(PO_4)_4(H_2O)_4$].

The D4R unit has a μ_4-oxygen atom, O(11), at the center of the Ga_4 tetrahedron; each Ga has a trigonal bipyramidal configuration with an apical oxygen as the common vertex with apical Ga−O distances of 1.97−2.15 Å and equatorial Ga−O distances of 1.83−1.86 Å (Figure 3). The apical atoms trans to the μ_4-oxygen are water oxygens. The Ga(1)O_5 trigonal bipyramid is observed from a comparison of Ga−O bond lengths to be more regular than Ga(2)O_5. Each PO_4 tetrahedron shares three corners with three Ga atoms within a unit, with the fourth corner being hydrogen-bonded to a water molecule of an adjacent unit or the pyridinium group of a cation. Alternately, the unit has a cubane-type structure with a Ga_4P_4 cube surrounding a central μ_4-

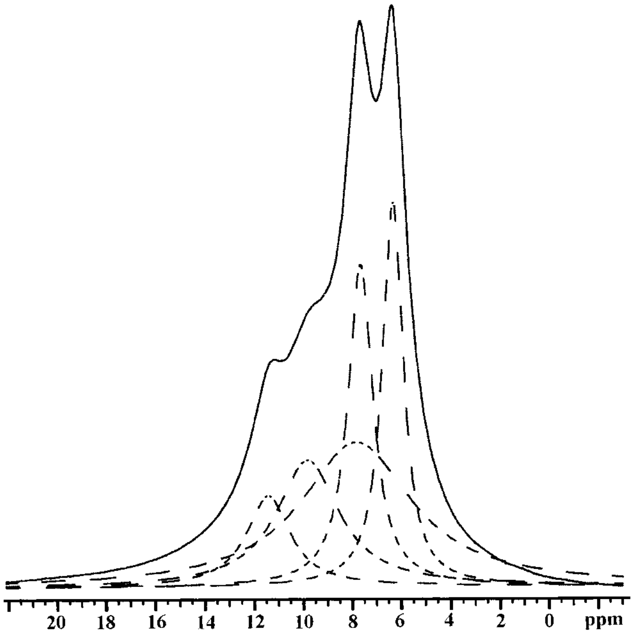

Figure 4. ^1H MAS NMR spectrum of $(4\text{-HAP})[Ga_4O(PO_4)_4(H_2O)_4]$ acquired at a spinning speed of 35 kHz. The spectrum was deconvoluted using five peaks in an intensity ratio close to 1:2:2:2:4 for four different types of protons in monoprotonated 4-aminopyridine and one type of proton in H_2O molecules, respectively, as shown as dashed lines. The broadest component represents the water signal.

oxygen with the bridging oxygen approximately on each edge of the cube.

^{1}H MAS NMR. To address the issue of protonation of aminopyridine, ^1H MAS NMR experiments were performed at a high spinning rate (35 kHz) to largely reduce strong $^1H-^1H$ dipolar coupling, and thus to achieve high spectral resolution. Figure 4 shows the ^1H MAS NMR spectrum of NCUGa-1. Four major resonances are observed at 6.4, 7.7, 9.8, and 11.5 ppm. Compared with the ^1H solution NMR spectrum of 4-aminopyridine, the peaks at 7.7 and 9.8 ppm are assigned to the protons in the aromatic ring, and the peak at 6.4 ppm is ascribed to the arylamine group. The peak at 11.5 ppm can be assigned to the proton bonded to the pyridine nitrogen atom, because its downfield characteristic excludes the existence of a NH_3^+ group that normally resonates at about 7−9 ppm. The above ^1H NMR evidence shows that protonation is on the pyridine nitrogen in aminopyridine, as is also inferred from the pK_b values for pyridine and aniline. It is noted that there are no distinct peaks attributed to water molecules. The signals from water molecules are believed to be underneath the envelope of the spectrum. The ^1H spectrum was therefore deconvoluted in accordance with the stoichiometry of NCUGa-1 using five peaks in an intensity ratio close to 1:2:2:2:4 for four different types of protons in monoprotonated 4-aminopyridine and one type of proton in H_2O molecules, respectively, as shown as dashed lines in Figure 4.

^{31}P MAS NMR. The proton-decoupled ^{31}P MAS NMR spectrum of NCUGa-1 exhibits three resonances at 3.8, 3.4, and 0.9 ppm (Figure 5a). The intensity ratio of the resonances at 3.8 and 3.4 ppm is close to 1:1, which corresponds to two distinct phosphorus sites as determined by X-ray diffraction. The weak peak at 0.9 ppm, which is not observed in the CP spectrum (Figure 5b), is probably due to a small amount of phosphorus-containing impurity that is not in proximity to any hydrogen atoms.

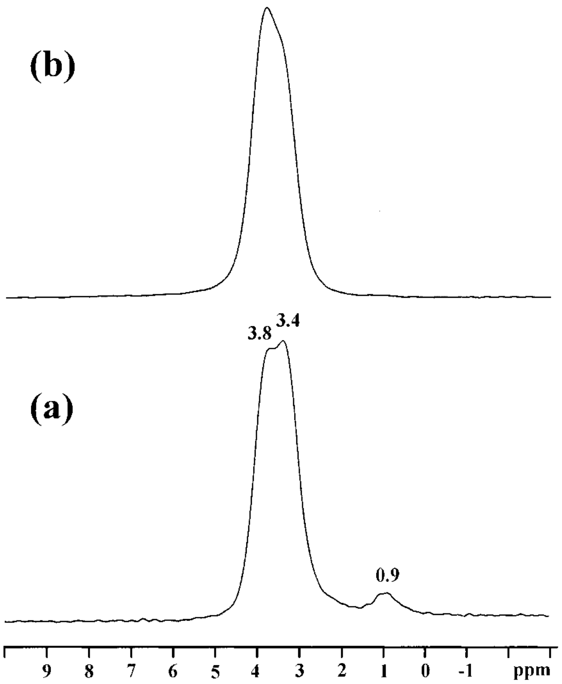

Figure 5. (a) Proton-decoupled ^{31}P MAS NMR spectrum of $(4\text{-HAP})[Ga_4O(PO_4)_4(H_2O)_4]$, recorded at a spinning speed of 12 kHz. (b) $^1H \rightarrow ^{31}P$ CP/MAS NMR spectrum obtained with a contact time of 2.5 ms.

$^1H \rightarrow ^{31}P$ CP/MAS NMR experiments with various contact times were performed to study the $^1H-^{31}P$ dipolar interaction between the hydrogen atoms and the ^{31}P spins. The resonance at 3.8 ppm has a faster magnetization transfer from proton spins than that at 3.4 ppm at short contact times. The T_{HP} values, i.e., the CP time constant, for the resonances at 3.8 and 3.4 ppm, obtained from the analysis of ^{31}P CP signal intensities as a function of contact time, are 270 μs and 4.3 ms, respectively. The resonance at 3.8 ppm consequently experiences a stronger $^1H-^{31}P$ dipolar coupling, indicating that the phosphorus atom is in closer proximity to hydrogen atoms. The resonances at 3.8 and 3.4 ppm are assigned to P(1) and P(2), respectively, because $P(1)O_4$ forms hydrogen bonds with both $H_2O(9)$ and the pyridinium group of the cation whereas $P(2)O_4$ is H-bonded to $H_2O(10)$ only.

^{71}Ga MAS NMR. ^{71}Ga NMR spectra are often affected by the quadrupolar broadening, which arises from the interaction of the nuclear quadrupolar momentum with the electric field gradient (EFG) tensor at the nucleus position. The quadrupolar interaction can easily become so large that the satellite transitions become unobservable while only the central transition $\langle -1/2 \leftrightarrow +1/2 \rangle$ is visible but suffers from the strong second-order quadrupolar interaction.

Figure 6 shows the ^{71}Ga MAS NMR spectrum of NCUGa-1, obtained at a spinning speed of 30 kHz, together with the simulated line shapes. The spectrum exhibits two well-resolved line shapes that are only influenced by the second-order quadrupolar broadening as chemical shift anisotropy (CSA) is averaged by fast sample spinning, spreading in the range from −500 to

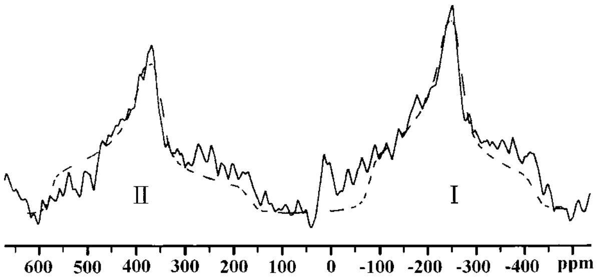

Figure 6. Experimental ^{71}Ga MAS NMR spectrum (solid line) of (4-HAP)[$Ga_4O(PO_4)_4(H_2O)_4$] collected at a spinning speed of 30 kHz. The dashed line represents the simulated spectrum.

+600 ppm. The ^{71}Ga spectrum has been fitted to retrieve isotropic chemical shifts and EFG tensors. A simulated spectrum (Figure 5, dashed lines), neglecting CSA, yields NMR parameters for ^{71}Ga sites, i.e., site I, $\delta_{CS} = -32 \pm 10$ ppm, η (asymmetry parameter) $= 0.90 \pm 0.02$, and C_Q (quadrupolar coupling constant) $= 9.5 \pm 0.3$ MHz, and site II, $\delta_{CS} = 576 \pm 10$ ppm, $\eta = 0.90 \pm 0.02$, and $C_Q = 9.3 \pm 0.3$ MHz. These two signals have an area ratio equal to 0.53:0.47, which agrees well with the crystallographic study. Bradly et al. reported that there is a linear correlation between ^{27}Al and ^{71}Ga NMR chemical shifts in isostructural Al and Ga compounds having only oxygen in the first coordination sphere.[22] The estimated ^{71}Ga NMR chemical shift ranges were 80−125 ppm for four-coordinate, 40−70 ppm for five-coordinate, and −65 to −20 ppm for six-coordinate gallium. For example, two ^{71}Ga resonances were observed of the as-synthesized cloverite (ambient humidity) at 92 and −24 ppm.[23] The first of these is assigned to five-coordinate and the second to six-coordinate gallium. The presence of a fluoride ion rather than an oxide in the D4R unit in cloverite would exert a deshielding influence, thus causing a downfield shift. It is unclear to us why the chemical shift values observed here are considerably different from the values in the literature. Kallus et al. reported the gallofluorophosphate [Cp_2Co][$Ga_4FP_4O_{12}(OH)_8$] (Mu-1), whose structure also consists of discrete D4R units.[19] The structure was not fully determined because of disordering of the Cp_2Co^+ cation. It was concluded that the D4R unit consisted of four P−OH and four Ga−OH groups. Two ^{31}P signals at 3.9 and −3.0 ppm with an intensity ratio close to 1:7 were observed. Nevertheless, no satisfactory explanation of the presence of the weak peak at 3.9 ppm was given. The ^{71}Ga NMR spectrum was not reported.

In the course of this work a new discrete gallium phosphate D4R unit containing occluded oxygen was reported by Wragg and Morris.[20] The compound ($C_5H_5NH)_2[H_8Ga_4P_4O_{21}$] was prepared by a solvothermal synthesis using a mixture of pyridine and water as the solvent. The structure was described in a tetragonal space group using a smaller unit cell. Several oxygen atoms showed large thermal parameters, which is indicative of possible disorder/twinning. The ^{31}P NMR chemical shift (4.0 ppm) is consistent with that of NCUGa-1. The ^{71}Ga NMR was not reported. The authors have also postulated that the D4R unit has a OH^- or OH_2 occluded at its center. In contrast our study indicates unambiguously that the charge balance of the monoprotonated amines is fulfilled by a dianionic oxygen, O^{2-}, placed at the center of the D4R units.

NCUGa-1 was obtained in the presence of 4-aminopyridine as an organic template. This new gallophosphate is one of the few examples containing discrete D4R units. Férey showed that all the structures of AlPOs and GaPOs are built up from a small number of SBUs.[2] The introduction of a given amine in the reaction medium determines the evolution in size and charge of the SBUs until the latter reach a charge density and electronegativity equal to that of the condensed amine. This could explain why amines or metal complexes with low charge density such as quinuclidine, pyridine, 4-aminopyridine, and bis(cyclopentadienyl)cobalt can lead to discrete D4R units.

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Supporting Information Available: Tables of complete crystal data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Bradley, S. M.; Howe, R. F.; Kydd, R. A. *Magn. Reson. Chem.* **1993**, *31*, 883.

(23) Bradley, S. M.; Howe, R. F.; Hanna, J. V. *Solid State Nucl. Magn. Reson.* **1993**, *2*, 37.