The First Aluminophosphonate Cluster Analogue of the 4=1 SBU of Zeolites: Structure and Multinuclear Solid-State NMR Study, Including ^{1}H NMR

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The first Al–O–P analogue of the so-called 4=1 Secondary Building Unit (SBU) of zeolites is presented and characterized by single-crystal X ray diffraction (compound **1**). The 4=1 building unit structure is very rarely encountered in zeolites and microporous materials. Compound **1** was carefully studied by ^{31}P and ^{27}Al solid-state MAS NMR, resulting in the precise spectroscopic description of the phosphorus and aluminium sites. Unusual ^{27}Al quadrupolar parameters were measured. Moreover, we also present a high-resolution solid-state ^{1}H NMR study of **1** at 600 MHz and 33 kHz MAS; a remarkable improvement in resolution is observed, allowing definite assignments. The new opportunities offered by very high speed ^{1}H NMR at high field were further demonstrated with the study of a cubane-shaped Al–O–P cluster (compound **2**) and of phenylphosphonic acid.

Introduction

Description of zeolites and porous aluminophosphate derivatives in terms of Secondary Building Units (SBUs) is now well established.[1] The geometrical features of each structural type are adequately described by connecting these small portions of solids. The synthesis of clusters mimicking SBUs[2] remains a great chemical challenge for the following reasons: (i) the SBUs may be considered as intermediates in the synthesis of microporous materials, and so it follows that reactions between these well-defined entities could give rise to new framework structures, and (ii) these clusters are suitable for fine spectroscopic studies, including solid-state NMR. Interactions such as the chemical shift anisotropy (CSA) or the quadrupolar interaction (for nuclei with $I > 1/2$) can be related to structural features around nuclei. These parameters are therefore of prime importance for NMR studies of more complex derivatives, such as microporous compounds.

Among the 18 SBUs described in the literature,[1] six types have synthetic analogues. If we restrict the list to Al−O−P-containing entities, only five types of clusters mimicking the following SBUs have been reported: the S4R (or 4) ring,[3] the S6R (or 6) ring,[4] the cubane-shaped D4R (or 4−4),[3c,3h,5] the prismatic D6R (6−6),[3h,5c] and the 6≡1 SBU.[6] Here we present the first cluster involving Al−O−P bonds to mimic the so-called 4=1 SBU: [(μ$_2$-hydroxo)bis{μ$_3$-phenylphosphonato(2−)-*o*,*o*′,*o*"}-decaethanoltrialuminium](4+) chloride·water(1:1): $[Al_3(\mu_2\text{-}OH)(\mu_3\text{-}C_6H_5PO_3)_2(C_2H_5OH)_{10}]Cl_4\cdot H_2O$ (compound **1**). The 4=1 SBU is encountered only very rarely; only three zeolites can be considered as derivatives of 4=1 units: natrolite ($Na_2Al_2Si_3O_{10}\cdot 2H_2O$), thomsonite ($NaCa_2Al_5Si_5O_{20}\cdot 6H_2O$), and edingtonite ($Ba_{2.02}Al_{4.03}Si_{5.07}O_{20}\cdot 7.8H_2O$).[1,7−9] These compounds exclusively involve Al−O−Si bonds. No aluminophosphate (-onate, -inate) derivative containing the 4=1 SBU has ever been described. We conjecture that it might be possible to synthesize such a derivative, as compound **1** definitely shows that the 4=1 Al−O−P architecture is realistic. Only two clusters involving Ga−O−P bonds and resembling the 4=1 SBU have previously been reported in the literature.[10] Finally, we stress the fact that compound **1** is an analogue of the 4=1 SBU but differs in terms of Al coordination: Al atoms are sixfold coordinated in compound **1**, whereas the Al atoms in zeolites are fourfold coordinated.

Cluster analogues of SBUs have generally been characterized by IR and solution NMR (^{1}H, ^{13}C, ^{27}Al, ^{31}P) techniques, after dissolution. Surprisingly, these compounds have never been studied by solid-state NMR, whereas this technique has been extensively applied to the structural characterization of microporous aluminophosphates (such as $AlPO_4$-*n*). Very recently, we have fully characterized

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S4R[11] and D4R[12] Al−O−P analogues by high-resolution ^{27}Al and ^{31}P MAS NMR spectroscopy. In this paper we present the structure of compound **1**, which was obtained as single crystals, and a multinuclear solid-state study, ^{31}P and ^{27}Al NMR for the inorganic core, and ^{13}C and ^{1}H NMR for the organic part. We have extracted precise data related to CSA (^{31}P) and quadrupolar interaction (^{27}Al) for compound **1** and analyze them in terms of the crystallographic structure. We also introduce (for the first time in the field of the study of inorganic clusters) ^{1}H MAS experiments at high field (600 MHz, 14 T) and at very high rotation frequency (up to 33 kHz). Spectacular improvements have been observed in terms of resolution, and these allow clear interpretation of spectra. These new opportunities in solid-state ^{1}H NMR are further illustrated by results obtained for the cubane-shaped Al−O−P cluster $[Al_4(HPO_4)_4(C_2H_5OH)_{12}]Cl_4{\cdot}4C_2H_5OH$ (compound **2**)[12] and phenylphosphonic acid [$C_6H_5PO(OH)_2$, precursor of **1**]. One original insight of this paper concerns the solid-state ^{1}H MAS experiments.

Results and Discussion

The structure of compound **1** is presented in Figure 1, a). It presents a very unusual geometry. Two Al atoms (Al2, Al3) and two P atoms (P1, P2), linked through oxo bonds, form a ring. On one side, this ring is capped with a third Al atom (O2Al1O3) between P atoms, and there is a hydroxo bridge (O5) on the other side between Al atoms [Figure 1, b)]. All Al atoms are sixfold coordinated, involving three (Al2, Al3) or four (Al1) ethanol ligands. Selected bond lengths are reported in Table 1. Average bond lengths involving oxo bridges are 1.84 Å around Al2 and Al3 atoms and 1.80 Å around Al1. Distances between O of ethanol ligands and Al atoms are much longer: 1.94 Å (Al2, Al3) and 1.93 Å (Al1). The mean bond length for the μ-OH bridge is about 1.85 Å. Distortions of polyhedra are discussed quantitatively below. P atoms are fourfold coordinated; in addition to three O atoms, each P atom is bonded to one phenyl ring (C11→C16 and C21→C26). The average P−O bond length is 1.52 Å, whereas the mean P−C bond length is about 1.79 Å. Cl^- counter-ions (Cl1→Cl4) are present in the structure. H···Cl hydrogen bonds are strongly suggested by O···Cl distances shorter than 3.35 Å.[13] All Cl atoms are involved in several hydrogen bonds, two for Cl1 (with O11 and O12) and for Cl4 (with O15 and O17), three for Cl2 (with O8, O14, and O16), and four for Cl3 (with O5, O9, O10, and O13). The inorganic core of **1** strongly mimics the geometry of the 4=1 SBU [Figure 1, c)]. In the case of compound **1**, however, a μ-OH bridge is observed between Al2 and Al3, although there is no such bridge in the 4=1 SBU. We note that the Ga−O cluster,[10] which also looks like the 4=1 SBU, has a marked difference with the SBU; a phosphonate group links two Al atoms, as does the μ-OH bridge in compound **1**.

Compound **1** was fully characterized by solid-state ^{31}P, ^{27}Al, and ^{13}C MAS NMR spectroscopy (Figure 2). The ^{31}P CP (cross polarization from ^{1}H) MAS spectrum of **1** exhibits two sharp lines located at δ = 1.7 and 2.8 ppm, in agreement with the crystallographic data. At 3 kHz, numerous spinning sidebands are observed, allowing the principal values of the chemical shift tensors δ_{ii} to be determined. All data are reported in Table 2. In terms of NMR parameters (δ_{iso}, η_{CSA}, and $\Delta\delta$), the two sites are clearly distinguished, whereas crystallographic data show that the chemical environments of the P atoms are very similar. The next challenge is therefore to correlate NMR spectroscopic data with slight distortions of polyhedra around P atoms by ab initio CSA calculations. In other words, the next step of our research is to assign P1 and P2 definitely to the two observed ^{31}P lines.

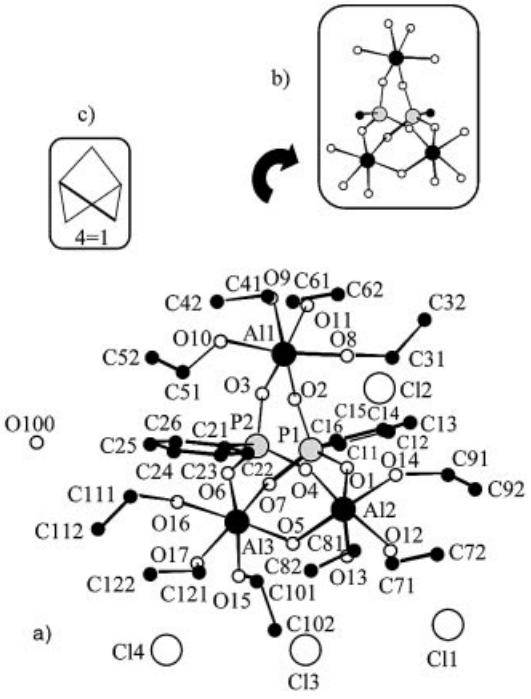

Figure 1. a) Representation of compound **1**: H atoms are omitted for clarity; b) the inorganic core of compound **1**, mimicking the 4=1 SBU of zeolites [c)]

Table 1. Selected bond lengths [Å] for $[Al_3(\mu_2\text{-}OH)(\mu_3\text{-}C_6H_5PO_3)_2(C_2H_5OH)_{10}]Cl_4{\cdot}H_2O$ (**1**)

	Distances [Å]		Distances [Å]
Al1−O2	1.805(4)	Al1−O9	1.932(4)
Al1−O3	1.804(3)	Al1−O10	1.935(4)
Al1−O8	1.925(4)	Al1−O11	1.932(4)
Al2−O1	1.842(4)	Al2−O12	1.937(4)
Al2−O4	1.833(4)	Al2−O13	1.953(4)
Al2−O5	1.845(4)	Al2−O14	1.944(4)
Al3−O6	1.835(4)	Al3−O15	1.969(4)
Al3−O7	1.840(3)	Al3−O16	1.928(4)
Al3−O5	1.852(4)	Al3−O17	1.932(4)
P1−O1	1.528(4)	P1−O7	1.512(3)
P1−O2	1.519(4)	P1−C11	1.787(5)
P2−O3	1.515(3)	P2−O6	1.519(3)
P2−O4	1.516(4)	P2−C21	1.784(5)

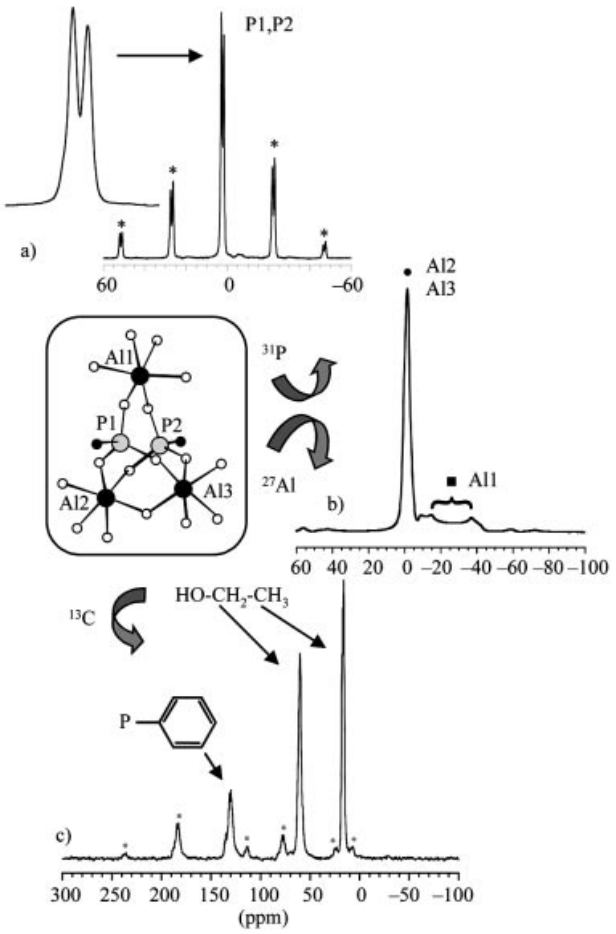

Figure 2. a) ^{31}P CP MAS NMR spectrum of compound **1**; b) ^{27}Al MAS NMR spectrum; c) ^{13}C CP MAS spectrum (see Exp. Sect.)

Table 2. ^{31}P and ^{27}Al NMR spectroscopic data for compound **1**; for CSA: $\delta_{iso} = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$ with $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$; $\eta_{CSA} = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$; $\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2$; $\delta_{iso}(^{31}P)$: ± 0.1; $\eta_{CSA}(^{31}P)$: ±0.05; for the quadrupolar interaction: $C_Q = (e^2qQ)/h$ (±0.05 MHz); $\eta_Q = (V_{22} - V_{11})/V_{33}$ (±0.02)

^{31}P			^{27}Al		
δ_{iso} [ppm]	η_{CSA}	$\Delta\delta$ [ppm]	δ_{iso} [ppm]	C_Q [MHz]	η_Q
1.7	0.60	70.1	−2.2 (Al1)	4.92 (Al1)	0.2 (Al1)
2.8	0.75	73.1	1.5 (Al2,3)	<< 1[a]	–

[a] The quadrupolar interaction for (Al2, Al3) is very small(see text).

The ^{27}Al MAS spectrum of **1** [Figure 2, b)] exhibits two major lines. The first one is centered at $\delta \approx 1.5$ ppm and is narrow. The second is strongly broadened and exhibits the characteristic features of a second-order quadrupolar broadened line (i.e. "horns" at $\delta \approx -15$ and -35 ppm). Quantitative experiments[14] show that the two lines are in the ratio 2:1. Therefore, the line centered at $\delta \approx 1.5$ ppm is assigned to Al2 and Al3, the other to Al1. At low rotation frequency (4.5 kHz), the sub-spectrum corresponding to Al1 is a complex superposition of the central transition, spinning sidebands of the central transition (full square), and spinning sidebands of satellite transitions (open square) [Figure 3, a)]. However, the full spectrum can be satisfactorily simulated by the SIMPSON program, available on the web (see the Exp. Sect.).[15] The quadrupolar parameters are very precisely determined (see Table 2), as all the discontinuities of the spectrum are sensitive to (C_Q, η_Q). For instance, the calculated shift of one particular discontinuity (boxed **1**) versus η_Q is plotted in Figure 3, b). The experimental shift unambiguously gives $\eta_Q = 0.2 \pm 0.02$. The final set of quadrupolar parameters for Al1, including second-order corrections for the chemical shift,[16] is: Al1 ($\delta_{iso} = -2.2$ ppm; $C_Q = 4.92$ MHz; $\eta_Q = 0.2$). Chemical shifts for Al2 and Al3 are located at $\delta_{iso} = 1.5$ ppm. The C_Q values for (Al2, Al3) are very small, as shown in Figure 3 (a). Indeed, only two spinning sidebands corresponding to (Al2, Al3) are observed at a rotation frequency of 4.5 kHz (open circle). At this stage, the C_Q parameters can be analyzed in terms of the correlation established by Ghose et al:[17] C_Q of octahedrally coordinated aluminium atoms increases with the longitudinal strain $|\alpha|$ with

$$|\alpha| = \sum_{i=1}^{6} |\ln(l_i / l_0)|$$

where l_i are the individual Al−O bond lengths and l_0 is the ideal bond length for a perfect octahedron with the same volume as the distorted polyhedron.

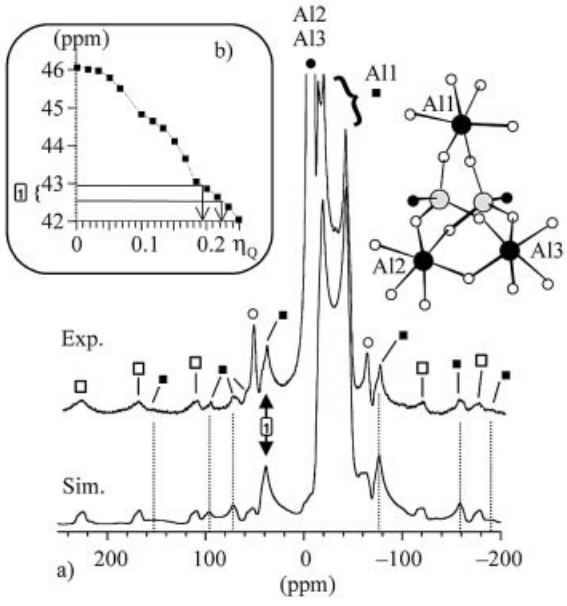

Figure 3. a) ^{27}Al MAS {^{1}H dec} spectrum of compound **1** at moderate spinning frequency (4.5 kHz); full circle: central transition of (Al2,Al3); open circle: spinning sidebands related to the satellite transitions; full square: central transition of Al1 and corresponding sidebands; open square: spinning sidebands related to the satellite transitions; simulation obtained by use of the SIMPSON program with: $\delta_{iso} = -2.2$ ppm, $C_Q = 4.92$ MHz, and $\eta_Q = 0.2$; b) calculated shift of the discontinuity (boxed **1**) versus η_Q; the experimental shift (with uncertainty) is shown by boxed **1** {; arrows indicate the derived values of η_Q

From the crystallographic data of compound **1**, the following calculated longitudinal strains are obtained: $|\alpha|$ = 0.155 and 0.165 for Al1 and Al2, respectively; $|\alpha|$ = 0.182 for Al3. These values are high and should be connected to $C_Q > 8$ MHz, as stated by Ghose et al. for aluminium oxide derivatives.[12,17] Obviously, the extracted experimental data are not in agreement with the previously reported results: (i) the C_Q values for Al1, Al2, and Al3 are much lower than 8 MHz, and (ii) C_Q(Al1,Al2) << C_Q(Al3) although $|\alpha|$ is almost identical for Al1, Al2, and Al3. This study proves unambiguously that a simple approach of the electric field gradient, taking into account only the first oxygen neighbors of Al atoms, is not suitable for the fine description of clusters such as **1**.

The ^{13}C CP MAS spectrum of **1** [Figure 2, c)] shows three main groups of resonances centered at δ = 17.3, 60.2, and 132.5 ppm and corresponding to $^{13}CH_3$, $^{13}CH_2$, and aromatic groups, respectively. The resolution is not high enough to count C atoms in the asymmetric unit (ten $^{13}CH_3$, ten $^{13}CH_2$, and twelve aromatic C). Experiments at higher field (up to 17.5 T) should allow a much improved resolution of spectra, and therefore direct counting of C atoms.

The ^{1}H MAS NMR spectra of phenylphosphonic acid [$C_6H_5PO(OH)_2$] and of compound **1** are presented in Figure 4. At $\nu_0(^1H)$ = 300 MHz and high rotation frequency (up to 14 kHz), the spectra are broad and almost featureless [Figure 4, a) and c)]. This is mainly due to the homogeneous character of the strong ^{1}H-^{1}H homonuclear dipolar interaction.[18] In the case of inhomogeneous interactions, such as CSA or first-order quadrupolar interaction, MAS is efficient even at low spinning frequency: sharp isotropic lines and sharp spinning sidebands are obtained [see, for instance, the ^{31}P CP MAS spectrum of compound **1** in Figure 2, a)]. It follows that high resolution is obtained. In contrast, slow MAS is inefficient to remove the broadening due to strong homonuclear coupling, unless the MAS frequency equals or exceeds the magnitude of the interaction. The problem was partially circumvented by the use of the so-called Combined Rotation And Multi Pulse Spectroscopy (CRAMPS), combining MAS and multi-pulse irradiation during the acquisition of the ^{1}H signal.[19] CRAMPS is a very demanding technique and is rarely implemented in laboratories. In this paper we present a second approach, involving a high field [14 T, $\nu_0(^1H)$ = 600 MHz] − to increase resolution − and a very high rotation frequency (33 kHz) − to average the homonuclear interaction efficiently. The observed increase of resolution is indeed dramatic [Figure 4, b) and d)]. In the case of the phenylphosphonic acid, two main lines located at δ = 8 ppm and 12 ppm [experimental intensity ratio: 5.6:2; calculated ratio for $C_6H_5PO(OH)_2$: 5:2] are observed and can safely be assigned to phenyl and P−OH groups, respectively. In the case of compound **1**, three main groups of resonances located at δ = 1.5, 4.5, and ca. 8 ppm are observed. The first two lines are attributable to CH_3 and CH_2 groups of ethanol molecules, respectively. The line at δ ≈ 8 ppm is complex, and involves several resonances. These are related to phenyl groups, OH (ethanol and μ-OH), and H_2O. Deconvolution of groups of resonances at δ = 1.5, 4.5, and ca. 8 ppm by Gaussian lines gives the following experimental integration: 30 (CH_3):16 (CH_2):16 (OH, H_2O, phenyl); the integrals of signals include the contributions of the first spinning sidebands, which represent ca. 10% of the total signal. The calculated integral for compound **1** gives: 30 (CH_3):20 (CH_2):23 (OH, H_2O, phenyl). The experimental results therefore indicate good general trends. The noted discrepancies between calculated and experimental data may be attributed to the strong overlapping of lines in the δ = 7−12 ppm region.

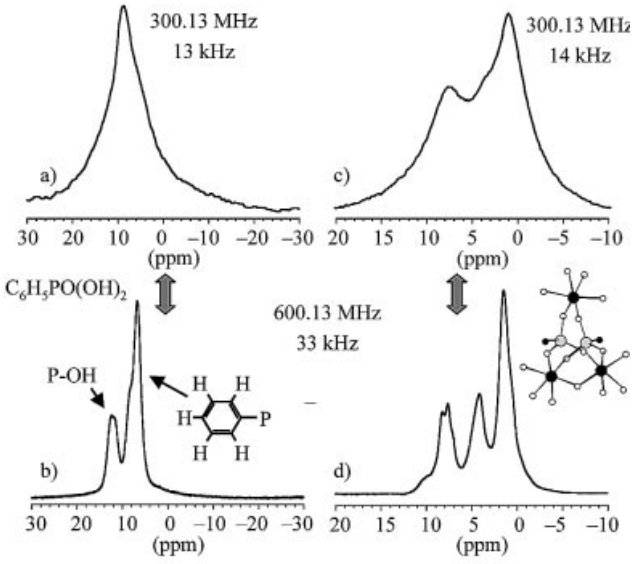

Figure 4. ^{1}H MAS NMR spectra (single pulse experiment) of phenylphosphonic acid: at $\nu_0(^1H)$ = 300.13 MHz and ν_{rot} = 13 kHz [a)]; at $\nu_0(^1H)$ = 600.13 MHz and ν_{rot} = 33 kHz [b)]; compound **1**: at $\nu_0(^1H)$ = 300.13 MHz and ν_{rot} = 14 kHz [c)]; at $\nu_0(^1H)$ = 600.13 MHz and ν_{rot} = 33 kHz [d)]

In order to highlight the new possibilities offered by ^{1}H very fast MAS NMR, we present experimental data (Figure 5) related to the cubane-shaped Al−O−P cluster $[Al_4(HPO_4)_4(C_2H_5OH)_{12}]Cl_4{\cdot}4C_2H_5OH$ (compound **2**).[12] For compound **2**, four types of protons may be distinguished, namely CH_3 and CH_2 groups from ethanol ligands and solvates, OH groups from ethanol, and OH groups from P−OH entities. Once again, at $\nu_0(^1H)$ = 600 MHz and 33 kHz, a spectacular gain in resolution is demonstrated. Assignments can be safely proposed (Figure 5). Experimental integration of lines at δ = 1.2 (CH_3), 3.9 (CH_2), 7.4 (OH), and 8.7 ppm (P-OH) gives 48:32.3:13.7:2. The calculated values for compound **2** are 48:32:16:4. An excellent agreement is noted between experimental and calculated data.

The examples presented above clearly show that solid-state ^{1}H NMR is now available as an analytical tool for the study of Al−O−P clusters, or more generally, for inorganic cores linked to organic groups. Very high MAS frequencies (up to 33 kHz) result (in these particular cases), in sufficient

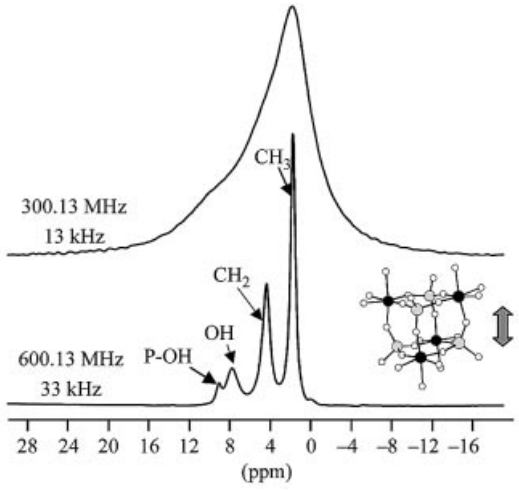

Figure 5. ^{1}H MAS NMR spectra (single pulse experiment) of compound **2** at [$\nu_0(^1H)$ = 300.13 MHz, ν_{rot} = 13 kHz] and [$\nu_0(^1H)$ = 600.13 MHz and ν_{rot} = 33 kHz]; each Al atom is coordinated to three ethanol ligands; four ethanol solvate molecules (per each cube) are present; each P atom is bonded to an OH group; see ref.[12]

averaging of the strong ^{1}H-^{1}H homonuclear interaction. Caution must be taken to ensure that no degradation due to high rotation frequency (heating[20] and gigantic pressure inside the rotor) occurs in samples. Spectra were first recorded at low rotation speeds, and the frequency of rotation was then increased. After high rotation speed experiments, checking of the integrity of the products was performed by recording spectra at low speed, and comparing them to the initial spectra.

Solid-state NMR therefore offers a two-level approach for the study of Al−O−P clusters. Firstly, the inorganic core can be studied by standard ^{31}P and ^{27}Al MAS NMR. The latest developments in ab initio calculation of chemical shifts and quadrupolar interaction[21] show that it is now possible to calculate these parameters safely for structures involving a reasonable number of atoms per cell. SBUs could act as good candidates for precise comparison between calculated and experimental data. Secondly, the organic part of the cluster, which acts as a link between inorganic cores, may now be investigated by high-resolution ^{1}H MAS NMR.

Finally, we believe that compound **1** could serve as a valuable precursor for the direct synthesis of complex aluminophosphonate frameworks. Our experience is that such a compound is slightly soluble in ethanol (see Exp. Sect.) and that the structure is preserved in solution (as checked by solution-state ^{31}P NMR). The compound may appear much more soluble in other solvents such as DMF, CH_3CN, etc., but the structure is usually not preserved in solution (several resonances with various intensities are observed in the corresponding ^{31}P spectra; see also refs.[11,12]). However, we note that treatment of **1** under solvothermal conditions (with ethanol) resulted in highly crystalline compounds with interesting solid-state NMR features. These compounds are under investigation in the laboratory.

Experimental Section

Synthesis of $[Al_3(\mu_2\text{-}OH)(\mu_3\text{-}C_6H_5PO_3)_2(C_2H_5OH)_{10}]Cl_4\cdot H_2O$ (1): Anhydrous $AlCl_3$ (4.33 g, 32.5 mmol) was slowly added to cooled ethanol (25 mL, 0 °C, exothermic reaction). $C_6H_5PO(OH)_2$ (5.14 g, 32.5 mmol) was then added to the solution. After 48 h at 5 °C, colorless crystals were obtained. Yield: 65%. Elemental analysis (Vernaison, France): $C_{32}H_{73}Al_3Cl_4P_2O_{18}$ (1030.6): calcd. C 37.29, H 7.14, Al 7.85, Cl 13.76, P 6.01; found C 35.87, H 6.63, Al 7.60, Cl 14.48, P 6.35. Chemical analyses were hardly reliable due to the extreme instability of compound **1** to air and moisture (several attempts were made).

Simultaneous Differential Thermal and Thermogravimetric Analyses: TA Instrument SDT 2960; air flow, 5 °C·min^{-1}, 25 °C up to 1250 °C; 25 to 1250 °C, TGA, 71.3 wt% loss (calcd. 71.4%); 25 to 160 °C: 50.3 wt% loss, endothermic event: ethanol loss; 500 to 650 °C: 11.3 wt% loss, complex exothermic event: phenyl decomposition/combustion; 1035 °C: weak exothermic event: poor crystallization into cristobalite and tridymite ($AlPO_4$) (powder XRD); 1180 to 1240 °C, 3.0 wt% loss, exothermic event: residual carbon combustion. End of DTA-TGA: gray powder containing traces of carbon, poorly crystallized (cristobalite and tridymite); no crystalline alumina detected.

Crystal Data for 1: $[Al_3(\mu_2\text{-}OH)(\mu_3\text{-}C_6H_5PO_3)_2(C_2H_5OH)_{10}]Cl_4\cdot H_2O$, (0.1 × 0.1 × 0.1 mm, rapidly brought out of the mother liquor, put in a capillary with oil), Enraf−Nonius MACH-3, monoclinic, $P2_1/a$, a = 20.083(5), b = 12.011(4), c = 24.36(1) Å, β = 114.00(3)°, V = 5368(3) Å^3, $\rho_{calcd.}$ = 1.28 ·cm^{-3}, Mo-K_α (λ = 0.71069 Å), ω/2θ, θ = 1−26°, T = 200 K, measured reflections: 11383, independent reflections: 10524, reflections included in the refinement: 6484 with $(F_o)^2 > 3\sigma(F_o)^2$, data corrected for Lorentz and polarization effects, no absorption correction, 534 parameters, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0812$; $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.0985$, $w = w'\,[1 - (||F_o| - |F_c||/6\sigma(F_o)^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with 3 coefficients 12.1, 5.48, and 8.53 for the Chebyshev series for which X is $F_C/F_{C(max)}$, Δρ(min.) = −0.81, Δρ(max.) = 1.85 e·Å^{-3}. Scattering factors corrections for anomalous absorption were taken from ref.[22] Structures were solved by direct methods (SHELXS)[23] and refined by full-matrix, least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions as fixed contributors in the last refinement. CCDC-182720 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Solid-State NMR: All ZrO_2 rotors were filled under argon in a dried glove-box, as compounds **1** and **2** were very sensitive to air moisture. ^{31}P CP MAS: Ξ^{31}P: 121.44 MHz; δ = 0 ppm: H_3PO_4 (85%); diameter of rotor (φ): 4 mm; MAS: ν_{rot} = 3−5 kHz. ^{1}H 90° pulse duration: 4 μs; for each ν_{rot}, the Hartmann−Hahn (H-H) condition was matched with compound **2**; contact time: 3 ms; relaxation delay (RD): 15 s, number of scans (NS): 40. ^{31}P (in ethanol-OD): Ξ^{31}P: 161.92 MHz, δ = 2.3 ppm (relative to H_3PO_4). ^{13}C CP MAS: Ξ^{13}C: 75.43 MHz; spectra referenced to TMS via solid adamantane; φ: 4 mm; MAS: 4 kHz. ^{1}H 90° pulse duration: 5 μs; H-H condition was matched with adamantane; contact time: 3 ms; RD = 15 s; NS = 2000. ^{27}Al MAS: Ξ^{27}Al: 78.17 MHz; δ = 0 ppm: $Al(NO_3)_3$, HNO_3 (1 M); φ: 4 mm; flip angles ≤ π/12; MAS-{^{1}H} high power decoupling: 4.5−15 kHz; RD = 1 s; NS = 7200.

^{1}H MAS: Ξ^1H: 600.13 MHz; spectra referenced to TMS via solid adamantane; φ: 2.5 mm; very high speed Bruker probe; MAS: 33 kHz; RD = 15 s; NS = 8.

Simulation of Spectra: See the SIMPSON package, available on the web.[15] Simulations of second-order ^{27}Al spectra (Figure 3) include the following parameters: ^{27}Al frequency, MAS frequency, quadrupolar Hamiltonian up to second-order, central transition and all satellite transitions, isotropic chemical shift δ_{iso} (no CSA), quadrupolar parameters (C_Q, η_Q), powder averaging type.

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[1] C. Baerlocher, W. M. Meier, D. H. Olson in *Atlas of Zeolite Framework Types*, 5th ed., Elsevier, Amsterdam, **2001**.
[2] M. G. Walawalkar, H. W. Roesky, R. Murugavel, *Acc. Chem. Res.* **1999**, *32*, 117.
[3] [3a] S. A. Sangokoya, W. T. Pennington, G. H. Robinson, D. C. Hrncir, *J. Organomet. Chem.* **1990**, *385*, 23. [3b] J. M. Corker, D. J. Browning, M. Webster, *Acta Crystallogr., Sect. C* **1996**, *52*, 583. [3c] M. R. Mason, R. M. Matthews, M. S. Mashuta, J. F. Richardson, *Inorg. Chem.* **1996**, *35*, 5756. [3d] J. Pinkas, D. Chakraborty, Y. Yang, R. Murugavel, M. Noltemeyer, H. W. Roesky, *Organometallics* **1999**, *18*, 523. [3e] C. G. Lugmair, T. D. Tilley, A. L. Rheingold, *Chem. Mater.* **1999**, *11*, 1615. [3f] D. Chakraborty, S. Horchler, H. W. Roesky, M. Noltemeyer, H-G. Schmidt, *Inorg. Chem.* **2000**, *39*, 3995. [3g] K. L. Fujdala, T. Don Tilley, *J. Am. Chem. Soc.* **2001**, *123*, 10133. [3h] M. R. Mason, A. M. Perkins, V. V. Ponomarova, A. Vij, *Organometallics* **2001**, *20*, 4833. [3i] for a review: M. R. Mason, *J. Cluster Sci.* **1998**, *9*, 1.
[4] Y. Yang, J. Pinkas, M. Noltemeyer, H. W. Roesky, *Inorg. Chem.* **1998**, *37*, 6404.
[5] [5a] J. E. Cassidy, J. A. J. Jarvis, R. N. Rothon, *J. Chem. Soc., Dalton Trans.* **1975**, 1497. [5b] Y. Yang, H.-G. Schmidt, M. Noltemeyer, J. Pinkas, H. W. Roesky, *J. Chem. Soc., Dalton Trans.* **1996**, 3609. [5c] Y. Yang, M. G. Walawalkar, J. Pinkas, H. W. Roesky, *Angew. Chem.* **1998**, *37*, 96. [5d] J. Pinkas, H. Wessel, Y. Yang, M. L. Montero, M. Noltemeyer, M. Froba, H. W. Roesky, *Inorg. Chem.* **1998**, *37*, 2450.
[6] Y. Yang, J. Pinkas, M. Schafer, H. W. Roesky, *Angew. Chem.* **1998**, *37*, 2650.
[7] W. M. Meier, *Z. Kristallog.* **1960**, *113*, 430.
[8] E. Galli, *Acta Crystallogr., Sect. B* **1976**, *32*, 1623.
[9] A. Alberti, G. Vezzalini, V. Tazzoli, *Zeolites* **1981**, *1*, 91.
[10] [10a] M. R. Mason, A. M. Perkins, R. M. Matthews, J. D. Fisher, M. S. Mashuta, A. Vij, *Inorg. Chem.* **1998**, *37*, 3734. [10b] C. C. Landry, W. M. Cleaver, I. A. Guzci, A. L. Rheingold, *Organometallics* **1998**, *17*, 5209.
[11] T. Azaïs, L. Bonhomme-Coury, J. Vaissermann, P. Bertani, J. Hirschinger, J. Maquet, C. Bonhomme, *Inorg. Chem.* **2002**, *41*, 981.
[12] T. Azaïs, C. Bonhomme, L. Bonhomme-Coury, J. Vaissermann, Y. Millot, P. P. Man, P. Bertani, J. Hirschinger, J. Livage, *J. Chem. Soc., Dalton Trans.* **2002**, 609.
[13] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
[14] D. Massiot, C. Bessada, J-P. Coutures, F. Taulelle, *J. Magn. Reson.* **1990**, *90*, 251.
[15] [15a] SIMPSON, http://NMR.imsb.au.dk [15b] M. Bak, J. T. Rasmussen, N. C. Nielsen, *J. Magn. Reson.* **2000**, *147*, 296.
[16] P. P. Man in *Encyclopedia of Nuclear Magnetic Resonance*, Wiley, Chichester, **1996**, p. 3838.
[17] S. Ghose, T. Tsang, *Am. Mineral.* **1973**, *58*, 748.
[18] K. Schmidt-Rohr, H. W. Spiess in *Multidimensional Solid-State NMR and Polymers*, Academic Press, London, **1996**, p. 115.
[19] B. C. Gerstein, R. G. Pembleton, P. C. Wilson, L. M. Ryan, *J. Chem. Phys.* **1977**, *66*, 361.
[20] J. Brus, *Solid State Nucl. Magn. Reson.* **2000**, *16*, 151.
[21] C. J. Pickard, F. Mauri, *Phys. Rev. B* **2001**, *63*, 245101-1-13.
[22] D. T. Cromer in *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, **1974**, vol. IV.
[23] G. M. Sheldrick, *SHELXS-86, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen,Germany, **1986**.

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