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Synthesis and structure of Mu-33, a new layered aluminophosphate $|((CH_3)_3CNH_3^+)_{16}(H_2O)_4|[Al_{16}P_{24}O_{88}(OH)_8]$

Claire Marichal [a,*], Jean Michel Chézeau [a], Mélanie Roux [a], Joël Patarin [a],
José Luis Jordá [b,1], Lynne B. McCusker [b,*], Christian Baerlocher [b], Philip Pattison [c,d]

[a] *Laboratoire de Matériaux à Porosité Contrôlée, ENSCMu, Université de Haute Alsace, CNRS-UMR 7016, 3 rue Alfred Werner,*
F-68093 Mulhouse Cedex, France
[b] *Laboratorium für Kristallographie, ETH Hönggerberg, CH-8093 Zürich, Switzerland*
[c] *Swiss-Norwegian Beamline, ESRF, BP220, F-38043 Grenoble Cedex, France*
[d] *Laboratoire de Cristallographie, EPFL, CH-1015 Lausanne, Switzerland*

Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

Mu-33, a new layered aluminophosphate with an Al/P ratio of 0.66, was obtained from a quasi non-aqueous synthesis in which *tert*-butylformamide (*t*BF) was the main solvent and only limited amounts of water were present. During the synthesis, *t*BF decomposed and the resulting protonated *tert*-butylamine is occluded in the as-synthesized material. The approximate structure was determined from data collected on a microcrystal ($200 \times 25 \times 5\ \mu m^3$) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, but the quality of these data did not allow satisfactory refinement. Therefore the structure was refined using high-resolution powder diffraction data, also collected at the ESRF. The structure ($P2_1/c$, $a = 9.8922(6)$ Å, $b = 26.180(2)$ Å, $c = 16.729(1)$ Å and $\beta = 90.4(1)°$) consists of anionic aluminophosphate layers that can be described as a six-ring honeycomb of alternating corner-sharing AlO_4 and PO_4 tetrahedra with additional P-atoms above and below the honeycomb layer bridging between Al-atoms. The *tert*-butylammonium ions and water molecules located in the interlayer spacing interact via hydrogen-bonds with the terminal oxygens of the P-atoms. The characterization of this new aluminophosphate by ^{13}C, ^{31}P, ^1H–^{31}P heteronuclear correlation (HETCOR) and ^{27}Al 3QMAS solid state NMR spectroscopy is also reported.
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1. Introduction

Since the seminal paper by Wilson et al. on the synthesis of aluminophosphate molecular sieves in 1982 [1], a large variety of these materials have been prepared. They are usually characterized by an Al/P ratio of one and a neutral three-dimensional aluminophosphate framework of alternating, corner-sharing AlO_4 and PO_4 tetrahedra. Some members of this $AlPO_4$-family of microporous materials have structures analogous to

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* Corresponding authors. Tel.: +33 3 89 33 67 31; fax: +33 3 89 33 68 85 (C. Marichal), fax: +41 1 632 1133 (L.B. McCusker).
E-mail addresses: c.marichal@univ-mulhouse.fr (C. Marichal), lynne.mccusker@mat.ethz.ch (L.B. McCusker).
[1] Present address: Instituto de Tecnología Química, Universidad Politécnica de Valencia, E-46022 Valencia, Spain.

those of zeolites. For example, AlPO$_4$-**GIS** and AlPO$_4$-20 are isostructural with gismondine (Framework type: **GIS**) and sodalite (Framework type: **SOD**), respectively. However, other compounds, such as AlPO$_4$-11 (Framework type: **AEL**) and VPI-5 (Framework type: **VFI**) do not have zeolite counterparts.

The synthesis of these solids is usually performed in aqueous medium, but a number of new phosphate-based materials have been prepared from non-aqueous or quasi non-aqueous media. As a result of such syntheses, using an organic solvent and only restricted amounts of water, numerous layered aluminophosphates have been obtained [2–9]. Under these conditions, hydrolysis and condensation reaction kinetics are slower than those of comparable hydrothermal systems. Several compositions of layered structures have been reported (e.g. $[Al_3P_4O_{16}]^{3-}$, $[Al_2P_3O_{12}H_x]^{(3-x)-}$ ($1 \leqslant x \leqslant 2$) [10], $[AlP_2O_8]^{3-}$ [11,12], $[Al(HPO_4)_2(H_2O)_2]^{-}$ [13] or $[Al_4P_5O_{20}H]^{2-}$ [9]), and most are characterized by an Al/P ratio of less than one. These compounds contain layers consisting of 4.6^2, 4.6.8 and 4.6.12 nets.

The alkylformamide family of solvents was used in a series of quasi non-aqueous syntheses to produce a monoclinic variant of |AlPO$_4$|-**SOD** [14], the two layered aluminophosphates, Mu-4 [9] and Mu-7 [15], and, more recently, the two new gallophosphates Mu-30 [16] and Ea-TREN-GaPO [17]. In all cases, with the exception of |AlPO$_4$|-**SOD**, the organic solvent partly decomposed into the corresponding amine, which was occluded in the final structure.

The title compound Mu-33 (Mu for Mulhouse) was prepared in a quasi non-aqueous synthesis procedure using *tert*-butylformamide (*t*BF) as the main solvent. Details of its synthesis, of its characterization by ^{13}C, [27]Al, ^{31}P, [1]H–[31]P heteronuclear correlation (HETCOR) and ^{27}Al 3QMAS solid state NMR spectroscopy, and of its structure analysis are given in the following sections.

2. Experimental section

2.1. Sample preparation

Mu-33 was first prepared from a gel containing mainly *tert*-butylformamide (*t*BF) as the solvent [18]. In order to obtain a pure material, several experiments were performed and the amounts of the reactants were optimized. Typically, 1.23 g of pseudo-boemite (Condéa hydrated alumina, water loss at 600 °C: 22.2 wt%) was slowly added to 3.30 g of 85% orthophosphoric acid (Fluka). The resulting gel was stirred until it was homogeneous. Finally, 8.0 g of an aqueous *tert*-butylformamide solution (BDH, analytical grade) was added to the mixture. The gel, with the composition 0.66 Al$_2$O$_3$: 1.0 P$_2$O$_5$: 3.0 H$_2$O: 5.9 *t*BF, was heated in a Teflon-lined stainless-steel autoclave at 170 °C under autogeneous

pressure for seven days. The solid recovered by filtration was washed with distilled water and dried at 60 °C overnight.

2.2. Characterization

The as-synthesized product was characterized initially by X-ray powder diffraction using a STOE STADI-P diffractometer equipped with a curved germanium 111 primary monochromator and a linear position-sensitive detector (CuKα_1 radiation, $\lambda = 1.5406$ Å).

The morphology and average size of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL30 microscope.

Thermogravimetric (TGA) and differential thermal (DTA) analyses to determine the amount of organic species and water occluded in the as-made solid were performed on a Setaram Labsys thermoanalyser by heating the as-synthesized material under air at a rate of 5 °C min^{-1} up to 750 °C.

C and N analyses were performed by coulometric and catharometric measurements, respectively. The Al and P content were determined by inductively coupled plasma emission spectroscopy.

^{31}P, ^{27}Al, ^{13}C and ^{1}H NMR measurements were carried out at room temperature using a Bruker DSX 400 spectrometer ($B_0 = 9.4$T), at frequencies of 161.9, 104.2, 100.2 and 400.1 MHz, respectively. [31]P Magic Angle Spinning (MAS) NMR experiments were performed using standard double bearing probes with either 4 or 2.5 mm diameter ZrO$_2$ rotors, and data were acquired using spinning frequencies between 3.5 and 25 kHz, a $\pi/2$ pulse duration of 3.5 µs and a recycle delay of 200 s. [1]H–[31]P Cross-Polarization Magic Angle Spinning (CPMAS) spectra were recorded using conventional Hartmann–Hahn matching with a spinning frequency of 4 and 25 kHz, a [1]H $\pi/2$ pulse duration of 4 µs, contact times ranging from 500 µs to 2 ms, and a recycle delay of 4 s. [1]H–[31]P heteronuclear correlation (HETCOR) experiments were performed at a spinning frequency of 25 kHz, with a contact time of 500 µs. ^{27}Al MAS NMR spectra were recorded using a 2.5 mm Bruker MAS probe, a spinning frequency of 15 kHz and a recycle delay of 1 s. The experimental conditions for the [27]Al 3QMAS experiment are described elsewhere [19]. ^{13}C MAS NMR experiments were realized with high power ^{1}H decoupling, a $\pi/2$ pulse duration of 4.5 µs, and a recycle delay of 60 s. Chemical shifts were referenced to an external standard: 85% H$_3$PO$_4$ (^{31}P), an aqueous solution of Al(NO$_3$)$_3$([27]Al) and TMS (^{1}H and ^{13}C).

Although the crystals in the sample appeared to be quite large in two dimensions (see Fig. 1), they proved to be too thin for single-crystal data collection on a laboratory instrument. However, it was possible to collect data on one of these microcrystals using the Oxford Dif-