Synthesis and characterisation of the novel GIS-type $AlPO_4$: $[NH_2Me_2][Al_2P_2O_8F]$

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A novel fluorinated aluminophosphate with a framework topology closely related to zeolite gismondine is crystallized in the presence of dimethylformamide from a predominantly alcoholic system and its structure is determined from XRD powder data.

One aim of many research groups working on microporous materials is the preparation of new structures usable as catalysts for new applications or as inorganic–organic composites for *e.g.* optical second harmonic generation.[1] The synthesis of molecular sieves in alcoholic systems increases the possibilities to reach this goal.[2] We present here a new molecular sieve $[NH_2Me_2][Al_2P_2O_8F]$ possessing a three-dimensional aluminophosphate framework with the gismondine topology[3] obtained in a polyol medium.

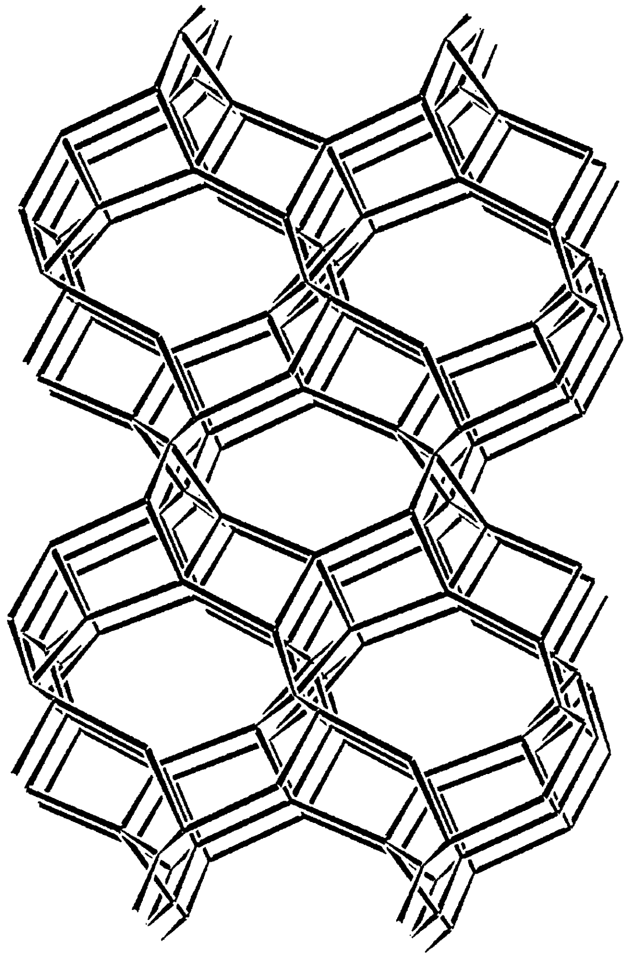

Fig. 1 Framework structure of $AlPO_4$-GIS. View along [100]. The Al and P atoms are located at the vertices, oxygen and fluorine atoms are omitted for clarity.

The starting materials for the synthesis were aluminium triisopropoxide (Aldrich, 98%), phosphoric acid (Fluka, 85 mass% H_3PO_4 in water), triethyleneglycol (TEG, Prolabo, 99%), *N,N*-dimethylformamide (DMF, Fluka, 99%), hydrofluoric acid (HF, Prolabo, 40 mass% in water). A mixture with the molar composition 1 Al_2O_3 : 1.8 P_2O_5 : 18 DMF : 1 HF : 18 TEG : 5 H_2O was stirred until homogeneous. The gel was then heated at 170 °C for 2 d under autogenous pressure in a Teflon-lined stainless-steel autoclave. The resulting microcrystalline product was filtered and washed with distilled water. The pure $AlPO_4$-GIS material was then dried at room temperature.

The presence of HF was found to be critical for the successful synthesis of $AlPO_4$-GIS. When HF is not added to the synthetic medium and depending on the temperature, two different crystalline products were obtained. At 190 °C $AlPO_4$-21[4] is produced, while at 170 °C needles are formed whose XRD powder pattern can be unambiguously indexed in the monoclinic system with a = 18.745(3), b = 20.221(3), c = 18.446(3) Å, β = 110.83(2)°.[5]†

The chemical analysis of $AlPO_4$-GIS in combination with the structure analysis and ^1H, ^{13}C solid- and solution-NMR spectroscopy established that the organic material present in the structure is not DMF but dimethylamine.‡ This phenomenon is not surprising because DMF is catalytically decomposed in acidic media above its boiling point.[6] Attempts to prepare the title compound with dimethylamine in a similar medium were unsuccessful, suggesting a dependence between the decomposition of DMF and the crystallisation of the molecular sieve. Thermogravimetric analysis gave a mass loss of *ca.* 20% occurring in one step at 340 °C. The mass decrease is consistent with the loss of the enclosed dimethylamine and HF. The mass loss was accompanied by a transformation of the structure into the dense phase $AlPO_4$-tridymite.

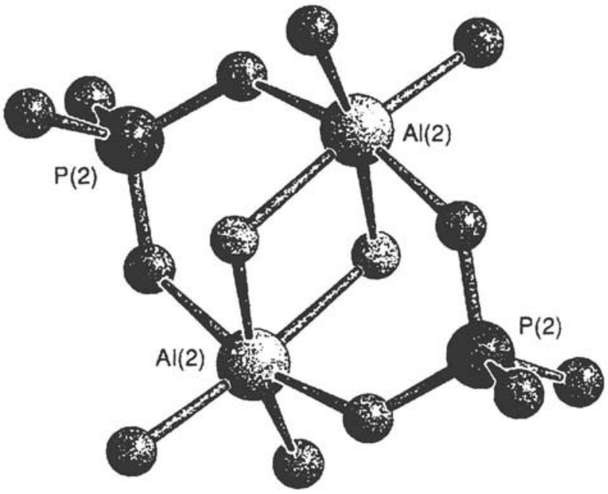

Fig. 2 Arrangement of the interconnected $[AlO_4F_2]$ octahedra

The framework structure[§] of $AlPO_4$-GIS is closely related to the structure of zeolite gismondine. Like gismondine $AlPO_4$-GIS has two types of eight-membered ring channels which intersect and thereby generate a two-dimensional pore system (Fig. 1). However, in contrast to the gismondine framework that consists of only tetrahedrally coordinated aluminium and silicon atoms, two different coordinations are observed for the aluminium atoms of $AlPO_4$-GIS. Four of the eight aluminium atoms present in the unit cell are tetrahedrally coordinated by four oxygens, while the remaining four Al atoms are connected to four oxygen and two fluorine atoms forming a distorted $[AlO_4F_2]$ octahedron. Two octahedra share a common F–F edge (Fig. 2). This leads to a distance of only 2.97 Å between neighbouring Al atoms compared to an Al–Al distance of *ca.* 4.2 Å observed for the corresponding atoms in the structure of gismondine.[3] The presence of two fluorine atoms bridging two Al atoms (Fig. 2) was previously observed for triclinic $AlPO_4$-CHA.[7] The bridging gives rise to a considerable decrease of the free pore diameter in the [1 1 − 1] direction by fluorine atoms protruding from the channel walls (Fig. 3).

To our knowledge, among $AlPO_4$-based materials so far only magnesium- and silicon-containing MAPSO-43,[8] magnesium MAPO-43[9] and cobalt-containing CoAPO[10] having the gismondine topology have been prepared. In the latter case cobalt has a sixfold coordination sphere made up by five oxygen atoms and additionally one nitrogen atom from the ethylenediamine molecule which is located in the pore volume.

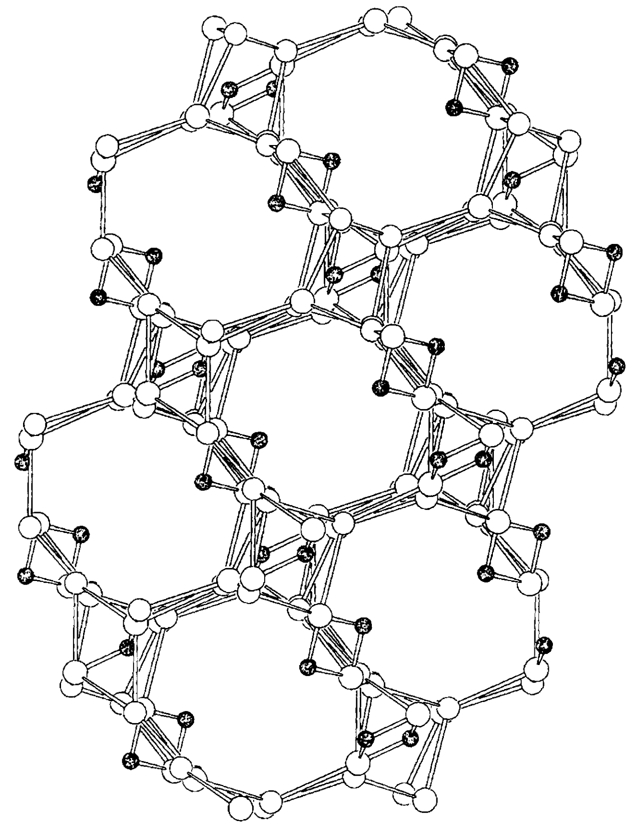

Fig. 3 Framework structure of $AlPO_4$-GIS. View along [1 1 − 1]; (○) Al, P, (●) F

Footnotes

[†] Both chemical analysis and ^1H, ^{13}C (solid and solution) NMR spectroscopy led to the chemical formula $H[NH_2Me_2]_2\ Al_3P_4O_{16}\cdot 6H_2O$.

[‡] The elemental analysis (mass%) of the as-synthesized $AlPO_4$-GIS produced the composition: C, 8.02; N, 4.53; H, 2.90; F, 6.16; Al, 16.8; P, 20.54 which is comparable with the ideal composition: C, 7.80; N, 4.55; H, 2.60; F, 6.17; Al, 17.52; P, 20.11 for $[NH_2Me_2][Al_2P_2O_8F]$. Also, EDX and micro-probe analysis confirmed the Al : P ratio of 1 : 1. The solid-state ^1H MAS NMR and proton-decoupled solid-state ^{13}C MAS NMR spectra of the as-synthesized $AlPO_4$-GIS displayed only one signal at δ 2.8 and a broad signal at δ 39.75 respectively. The high-resolution, ^1H NMR spectrum of the dissolved product in HF and D_2O exhibited a single peak at δ 2.667 and in the corresponding ^{13}C NMR spectrum, a single peak at δ 35.37 (all chemical shifts relative to $SiMe_4$).

[§] The XRD powder data were collected on a Siemens D5000 diffractometer with a linear 6° PSD in Debye–Scherrer geometry (Ge monochromator, λ = 1.5406 Å). The integral intensities were extracted using the XRS-82[11] system. These intensities allowed the solution of the structure by direct methods (SHELXTL).[12] A subsequent Rietveld refinement (XRS-82) (2θ range = 9–99°, number of observations = 10828, number of reflections = 949, number of structural parameters = 55) converged to $R_F = 0.049$ and $R_{WP} = 0.081$, while the statistically expected R_{EXP} is 0.055. The structure is monoclinic with space group $P2_1/c$ and $a = 9.412(3)$, $b = 12.770(4)$, $c = 8.594(3)$, $\beta = 112.84(6)°$. A detailed description of the structure analysis including the atomic coordinates, displacement parameters, bond lengths and bond angles of $AlPO_4$-GIS will be published elsewhere.

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Received, 4th March 1996; Com. 6/01534D