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Cubic Octanuclear Aluminum Fluoride Phosphonate[†]

Jan Kratochvil,[‡] Marek Necas,[‡] Vaclav Petricek,[§] and Jiri Pinkas*,[‡]

Department of Inorganic Chemistry, Masaryk University, Kotlarska 2, CZ-61137 Brno,
Czech Republic, and Institute of Physics, Academy of Sciences of the Czech Republic,
Na Slovance 2, CZ-18221 Praha, Czech Republic

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A crystalline complex $[Al_8F_{12}\{(CH_3)_2C(NH_3)PO_3\}_{12}]$ (**1**) was isolated from the supernatant of the hydrothermal reaction of gibbsite $Al(OH)_3$ with 1-amino-1-methyl-ethylphosphonic acid (AIPA) and the HF mineralizer. The single-crystal X-ray diffraction analysis revealed a highly symmetrical cubic Al_8F_{12} core with aluminum atoms at the corners, bridging fluorides spanning all edges, and 12 bidentate bridging phosphonate ligands completing the octahedral coordination sphere of aluminum centers. The stability of the complex in solution was established by electrospray mass spectrometry and the high molecular symmetry (T_h) was reflected in the appearance of single resonances in the ^1H, ^{19}F, and ^{31}P NMR spectra.

Aluminophosphates and -phosphonates form a structurally rich and diverse class of molecular, chain, layer, and framework compounds.[1,2] They are generally prepared by hydrothermal synthetic procedures that are frequently amended by the use of HF as a mineralizer. The fluoride ions improve the solubility of starting materials, catalyze the bond formation, act as structure-directing agents, and promote the formation of larger crystals.[3] Aluminum-bound fluoride ions are in some instances retained in the resulting structures as terminal or bridging groups, or they may be encapsulated in the cubic D4R building units.[4−8]

In this paper, we report the structural, NMR spectroscopic, and mass spectrometric characterization of a cubic aluminum fluoride phosphonate $[Al_8F_{12}\{(CH_3)_2C(NH_3)PO_3\}_{12}]$ (**1**) obtained as a result of our attempts to synthesize aluminophosphonates from gibbsite and AIPA (1-amino-1-methylethylphosphonic acid) by the hydrothermal route with an HF mineralizer. AIPA is a zwitterionic analogue of *tert*-butylphosphonic acid, which was frequently utilized in the synthesis of both molecular organoaluminophosphonates[9,10] and layer and framework metallophosphonates. Compound **1** is a hybrid species bridging the gap between the aluminophosphonate and fluoroaluminate families.[11]

The zwitterionic nature makes AIPA organics-insoluble, and therefore, we explored the hydrothermal synthetic route and carried out the reactions of the acid with aluminum sources, such as aluminum nitrate, aluminum isopropoxide, and gibbsite, in an autoclave. The two former starting materials provided water-insoluble powder materials that were characterized by XRD, TGA, IR, and NMR spectroscopy as layered aluminophosphonates.[12] The reaction with gibbsite was conducted in a water/2-propanol 1:1 mixture with a 2.0:3.1:2.5 molar ratio of $Al(OH)_3$/AIPA/HF.[13] The reaction mixture was first stirred and heated to 60 °C for 24 h, and then it was kept at 150 °C for 2 weeks without stirring. At a higher reaction temperature above 200 °C, we evidenced a partial AIPA ligand decomposition by observing additional

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[†] Dedicated to Professor H. W. Roesky on the occasion of his 71st birthday.

* To whom correspondence should be addressed. E-mail: jpinkas@chemi.muni.cz.

[‡] Masaryk University.

[§] Academy of Sciences of the Czech Republic.

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(13) A suspension of $Al(OH)_3$ (0.18 g, 2.3 mmol) in H_2O (30 mL) and AIPA (0.50 g, 3.6 mmol) in 2-propanol (30 mL) was mixed in a Teflon autoclave liner, HF was added (40% solution, 0.058 g, 2.9 mmol).

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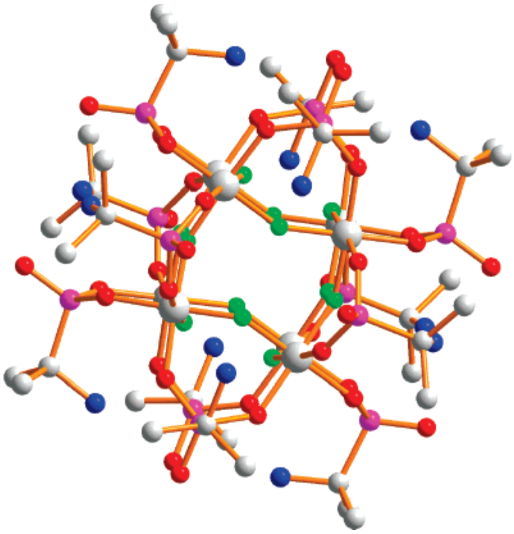


Figure 1. Molecular structure[25] of **1**, with all bridging ligands included. Selected average distances (Å): Al−F 1.84, Al−O 1.90, P−O_b 1.55, P=O_t 1.51. Selected average bond angles (deg): F−Al−F 89.4, Al−F−Al 144.0, O−Al−O 93.6, Al−O−P 135.5, O_b−P−O_b 112.1. When used for uniqueness, the labels O_b and O_t mean bridging and terminal oxygen, respectively.

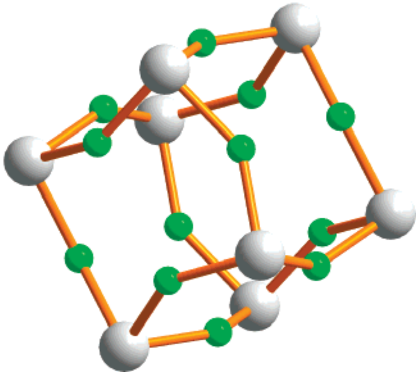
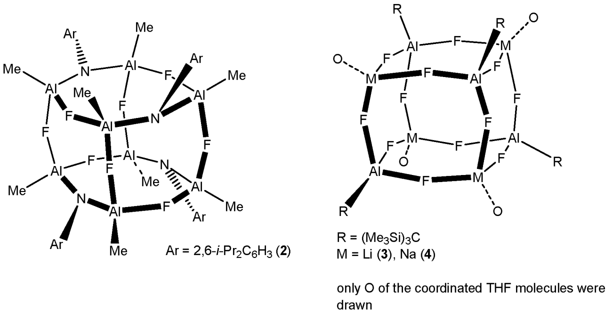


Figure 2. Cubic Al_8F_{12} core of **1**; all phosphonate bridges are omitted for the sake of clarity.[25]

signals in ^{31}P NMR spectra of the liquid phase. After cooling, the solid product was isolated by filtration and identified as a layered aluminophosphonate. No traces of unreacted Al$(OH)_3$ or AIPA were detected in the XRD experiment. A slow evaporation of the mother liquor provided a crop of clear colorless crystals that were suitable for the single-crystal X-ray diffraction analysis.[14] After being removed from the mother liquor, the crystals turned opaque probably because of crystal water loss (see Crystallography). The isolated yield of the reaction was small (5%) but reproducible.

The molecular structure of resulting aluminum fluoride phosphonate is shown in Figure 1. The most conspicuous feature is its cubic Al_8F_{12} core (Figure 2) with octahedral aluminum atoms positioned at the cube vertexes and bridging fluorides at the edges. Each edge is additionally spanned by a bidentate phosphonate group. The ideal point group symmetry of the Al_8F_{12} core is a relatively rare T_h. The related molecules with a cubic shape are organoaluminum fluoride amide **2**[15] and lithium and sodium organo fluoroaluminates **3** and **4** (Chart 1).[16,17] In these cubic clusters, however, the aluminum coordination is only tetrahedral. The molecular Al_8F_{12} core can also be thought of as a cutoff of the α-AlF_3 framework, which consists of AlF_6 octahedra sharing all corners.[18,19] One face of **1** also relates to the anion $[Al_4F_{20}]^{8-}$ composed of four corner-sharing AlF_6 octahedra; that relation includes similarity in geometrical parameters.[20]

Chart 1. Cubic Organoaluminum Fluoride Molecules.



The high symmetry of **1** is reflected in its solution NMR spectra.[21] AIPA possesses geminal $(CH_3)_2C$ groups that are excellent reporters of the presence of symmetry elements. A single CH_3 doublet in the ^{1}H NMR spectra is consistent with the mirror planes in **1** bisecting the $(CH_3)_2C$ angle. Similarly, only single resonances were observed in the ^{19}F and ^{31}P NMR spectra.

Aluminum phosphonates and fluorides are in general insoluble in water. The presence of the protonated amino groups at the periphery of **1** improves its solubility. ESI mass spectra of **1** in water/acetonitrile (50:50) were recorded to assess the solution stability of the cluster structure. In the spectra run in a negative mode, a solitary signal at *m*/*z* 2099 was observed that corresponds to the $[\mathbf{1} - H]^-$ parent ion. This attests to the intact nature of the octanuclear molecule **1** in solution and excludes the possibility of phosphonate or fluoride dissociation or the cluster destruction. AIPA gives under the same conditions a series of oligomer signals. The parent ion was mass selected and fragmented in the MS^2 experiment. The major fragmentation pathway leads by the loss of an AIPA fragment to an *m*/*z* 1958 ion and the subsequent detachment of HF to an *m*/*z* 1938 ion. This ion provided a fragment *m*/*z* 1918 in the MS^3 experiment by the second loss of HF. Furthermore, multiple losses of AIPA and HF resulted in less-abundant fragments 1819 and 1800. Replacing water by D_2O in the solvent mixture caused a

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(14) Crystal data: **1**: $C_{36}H_{178}O_{71}Al_8F_{12}N_{12}P_{12}$, fw = 2724.30, tetragonal, *P*4/*m*, $a = 17.3885(3)$ Å, $c = 19.6855(3)$ Å, $V = 5952.11(17)$ Å^3, $Z = 2$, $d_{calcd} = 1.5196$ Mg/m^3, R1[$I > 3\sigma(F)$] = 0.0810, wR2[$I > 3\sigma(F)$] = 0.0871, $w = 1/(\sigma^2(F) + 0.0001F^2)$.

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(21) NMR data for **1** (*J* in Hz, D_2O). ^{1}H: δ 1.65 (d, $^3J_{PH}$ 13.5, CH_3). ^{31}P: δ 13.8 (sept, $^3J_{PH}$ 13.0). ^{19}F: δ −141.4 (s).

change of the ESI mass spectrum which revealed a cluster of signals from 2099 to 2138. This evidenced the H/D exchange in all 12 NH_3^+ groups on the molecule exterior. The presence of hydrogen-bonded NH_3^+ groups was indicated by broad bands of valence vibrations from 3406 to 2106 cm^{-1} and by symmetric and asymmetric NH_3^+ deformation vibrations in the IR spectrum recorded in a KBr pellet.[22]

Crystallography. As a consequence of being grown from the water/2-propanol-based reaction mixtures, the crystals comprise a large portion of water (about 35 H_2O per one molecule of **1**). The water of crystallization is the source of three main problems: during the crystal selection, data collection, and refinement (mentioned below). First, when removed from the mother liquor, the crystals lose water rapidly until they break apart completely. Second, many attempts to lower the temperature of the successfully mounted samples were accompanied by the rapidly deteriorating quality of the diffraction profiles, most probably as a result of their internal disintegration due to the water freezing. Finally, we found a crystal that could be used for a data collection at 120(2) K. The quality of the data was much lower than for standard crystals but satisfactory to perform the structure analysis.

Diffraction data were collected on a KUMA KM-4 κ-axis diffractometer equipped with a CCD detector, with Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for Lorentz and polarization effects; the structure was solved by direct methods in the $P4/m$ space group, and initial refinement was performed by the ShelXTL program package.[23] After the first few cycles of the refinement, we concluded that there are two cubes in two different orientations sharing the same site in a 1:1 ratio. There are two such symmetrically independent positions in the asymmetric unit, one located at the mirror plane—the special position *4k* and one at a general position. The different orientations of the AlF_3O_3 octahedrons are reflected in the extensive superimposition of atoms in the AIPA ligands. As already mentioned, the intermolecular space is filled with water molecules, which are distributed rather variably throughout the crystal. This contributes to the considerable smearing of the electron density and causes subsequent problems in positioning the lighter atoms of the bridging AIPA ligands (mainly the $H_3N(CH_3)_2C-$ groups).

Therefore, we took advantage of the JANA2000 crystallographic computing system, allowing different parts of the molecule to be treated as rigid bodies during the refinement.[24] We introduced two types of rigid-body AIPA ligands: one having all the atoms independent and one restricted by the local mirror plane. In the subsequent refinement, their positions, described by means of rigid-body rotations and translations, together with the average shapes were used in the refinement. This considerably reduced the number of refined parameters and stabilized the refinement. In the subsequent difference Fourier map, many isolated maxima were found. Some were included in final stages of the refinement and treated as water oxygens with variable occupancies and harmonic atomic displacement parameters. The refinement converged to reasonable R values (R1 = 0.0810, wR2 = 0.0871 for observed data $I > 3\sigma(I)$). For bond lengths given in angstroms, their esd's are in the order of hundredths; among the few exceptions are the bonds originating in aluminum atoms, with su's of their lengths in the order of thousandths.

The above-described disorder could also be a result of twinning in the crystal. Indeed, a description in the space group $P2/m$, a subgroup of the tetragonal $P4/m$, would make it possible to handle the structure without any disorder and the observed tetragonal symmetry of the diffraction pattern can be the result of a 1:1 overlap of two independently diffracting domains related by the 4-fold axis. Two possible twinning models were tested, but none of them gave significantly better results. Thus, we made the conclusion that the structure is affected by a coherent disorder adequately described in the tetragonal space group.

Conclusions. The cubic octanuclear aluminum fluoride phosphonate **1** represents a new structural motif on the borderline of aluminophosphonates and fluoroaluminates. It is the largest molecular cluster in the aluminum/fluoride systems. The chemical stability of this molecule and the presence of reactive amino groups make it a potential precursor to inorganic–organic hybrid materials.

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Supporting Information Available: Crystallographic data of **1** and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] IR (KBr, cm^{-1}): 3406mb, 3062sb, 3023sb, 2948s, 2882m, 2792m, 2711w, 2686w, 2598m, 2106w, 1636s (δ_{as} NH_3^+), 1534s (δ_s NH_3^+), 1473w, 1393w, 1374w, 1280w, 1196vs (ν P=O), 1069vs (ν P–O), 1006vs (ν P–O), 933vw, 842w, 681s, 669s, 591s, 576s, 537m, 510s, 464m, 427w.

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