



# The missing hydrate $\text{AlF}_3 \cdot 6\text{H}_2\text{O} = [\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$ : Ionothermal synthesis, crystal structure and characterization of aluminum fluoride hexahydrate



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## ABSTRACT

$\text{AlF}_3$  is a strong Lewis acid and several hydrates of it are known, namely the monohydrate, the trihydrate (of which two polymorphs have been described) and the nonhydrate, which forms in the abundance of water, as well as a more complex fluoride of composition  $\text{Al}_{0.82}\square_{0.18}\text{F}_{2.46}(\text{H}_2\text{O})_{0.54}$  whose structure has been related to the  $\text{ReO}_3$  type. The monohydrate features edge connected  $[\text{AlF}_6]$  octahedra, in the tri- and nonhydrate mixed F/O coordination of aluminum is observed. Here we report on a new aluminium fluoride hydrate,  $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$ , which could be obtained via ionothermal synthesis in the ionic liquid *n*-hexyl-pyridinium tetrafluoroborate. The ionic liquid serves in the synthesis of  $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$  as the reaction partner (fluoride source) and solvent. Overmore it controls the water activity allowing access to the missing  $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$ . Single-crystal X-ray diffraction analysis of  $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$  shows that it crystallizes in the anti- $\text{Li}_3\text{Bi}$ -type of structure according to  $\text{F}_3[\text{Al}(\text{H}_2\text{O})_6]$  (*Fm-3m*,  $a = 893.1(2)$  pm,  $Z = 4$ ) featuring hexaqua aluminium(III) cations and isolated fluoride anions. The compound was further characterized by powder X-ray diffraction, TG/DTA, IR analyses.

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## 1. Introduction

Aluminum halides are important inorganic compounds which have found wide applications. The most prominent is maybe their use in Lewis acid catalysed reactions [1]. The structures of aluminium(III) halides have been known for a long time [2–6]. However, recent structural investigations in the multinary Al–F phase space led to the identification of new phases [7–12]. As a strong Lewis acid,  $\text{AlF}_3$  forms with Lewis bases such as alkali metal fluorides ternary compounds such as  $\text{MAlF}_4$  ( $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) [13–18] or  $\text{M}_3\text{AlF}_6$  ( $M = \text{Li}, \text{Na}, \text{K}$ ) [19–22] which all feature octahedral hexafluoroaluminate(III) units,  $[\text{AlF}_6]^{3-}$ . Water is also a comparatively strong Lewis base and several  $\text{AlF}_3$  hydrates have been characterized so far. The most well characterized hydrate of aluminum fluoride perhaps is that with the highest water content, the nonhydrate  $\text{AlF}_3 \cdot 9\text{H}_2\text{O}$  [23,24]. On the other side, the monohydrate

$\text{AlF}_3 \cdot \text{H}_2\text{O}$  is also known to exist [25]. Recently, the structures of two polymorphs of the trihydrate,  $\alpha$ - and  $\beta$ - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ , have been restudied based on X-ray/neutron diffraction and nuclear magnetic resonance (NMR) spectroscopy [23]. In 2009, a new aluminum fluoride hydrate with  $\text{ReO}_3$ -type structure was synthesized by a microwave hydrothermal process [26]. It has been ascribed the empirical formula of  $\text{Al}_{0.82}\square_{0.18}\text{F}_{2.46}(\text{H}_2\text{O})_{0.54}$  according to chemical analysis. All  $\text{AlF}_3$  hydrate structures feature Al(III) in an octahedral coordination environment. Whilst the monohydrate features edge connected  $[\text{AlF}_6]$  octahedra, in the nonhydrate and the trihydrate a mixed F/O coordination environment is observed, which crystallographically could only be resolved for  $\beta$ - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ . A hexahydrate,  $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$ , has not been reported yet.

Recently, our group successfully utilized ionic liquids (ILs) in the synthesis of metal fluoride and metal oxide materials [27]. It was observed that when tetrafluoroborate or hexafluorophosphate ionic liquids are used in the synthesis, they can serve not only as the solvent and reaction medium, but also as a mild source of fluoride. Using this approach  $\beta$ - $\text{NH}_4\text{AlF}_4$  was synthesized from aluminum isopropoxide in the presence of phosphoric acid using 1-ethyl-3-methylimidazolium hexafluorophosphate as the solvent and fluoride source provider [28].

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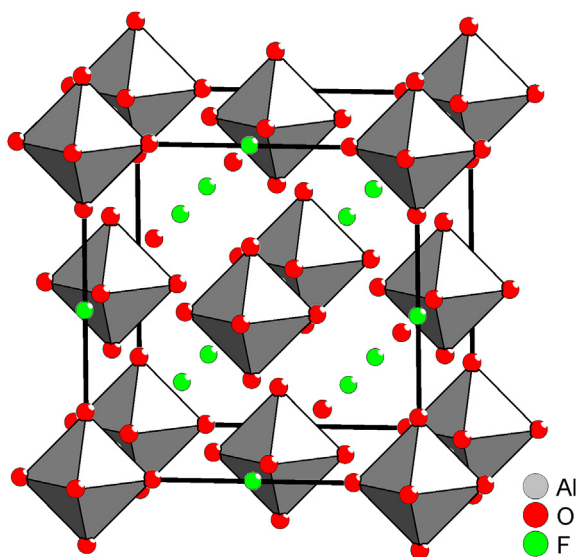


Fig. 1. Structure of  $[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$ .

Here, we report the ionothermal synthesis and characterization of a new aluminum fluoride hydrate,  $\text{AlF}_3 \cdot 6\text{H}_2\text{O} = [\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$ , using the ionic liquid *n*-hexyl-pyridinium tetrafluoroborate,  $[\text{C}_6\text{py}][\text{BF}_4]$ . The ionic liquid acts not only as the solvent and fluoride source but most importantly permits to control the water activity allowing access to an aluminum fluoride hydrate with intermediate water content. The new structure features topologies unprecedented in the family of aluminum fluoride hydrates.

## 2. Experimental section

$[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$  was prepared under ionothermal conditions from a mixture of aluminium(III) isopropoxide, phosphoric acid, 1,3-diaminopropane in the ionic liquid *N*-hexyl-pyridinium tetrafluoroborate,  $[\text{C}_6\text{py}][\text{BF}_4]$ , with a molar ratio of 1:6:7.7:36.9. In a typical synthesis of  $[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$ , 0.025 g aluminium(III) isopropoxide (Fluka, 89%) was dissolved in 1 ml *N*-hexyl-pyridinium tetrafluoroborate (IOLITEC). Then 0.05 ml  $\text{H}_3\text{PO}_4$  (J. T. Baker, 85 wt% in  $\text{H}_2\text{O}$ ), 0.08 ml 1,3-diaminopropane (Aldrich) were added under continuous stirring. A homogeneous gel formed after stirring for another hour. The gel was transferred to a Teflon-lined stainless steel autoclave (2 ml) and heated at 180 °C for 10 days under the static conditions. The resulting colorless single crystals were

isolated by filtration, washed several times with deionized water and acetone, and finally dried in air. The phase purity of  $[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$  was confirmed by its X-ray powder diffraction pattern.

A suitable single crystal of  $[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$  was selected for single-crystal X-ray diffraction (XRD) analysis. The data were collected at ambient temperature using graphite-monochromated Mo- $K\alpha$  radiation on an Image Plate Diffraction System, IPDS I, (Stoe, Darmstadt, Germany). The data were corrected for Lorentz and polarization effects. Data correction was carried out with the program X-RED [29]. A face-indexed numerical absorption correction (X-SHAPE) was applied [30]. The structure was solved by direct methods (SIR 92) [31] and refined by full-matrix least-squares techniques with the SHELXTL crystallographic software package [32,33]. The Al, F, and O atoms could be unambiguously located. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein - Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting the respective database number 431916.

Crystal data for  $[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$  (192.08 g mol<sup>-1</sup>); diffractometer: IPDS-I, Stoe, Darmstadt; Mo- $K\alpha$  (graphite monochromator,  $\lambda = 71.073$  pm);  $T = 293(2)$  K;  $\theta_{\text{max}} = 28.09^\circ$ ; 100 images,  $0^\circ \leq \varphi \leq 200^\circ$ ;  $\Delta\varphi = 2^\circ$ ; indices:  $-11 \leq h \leq 8$ ,  $-11 \leq k \leq 11$ ,  $-11 \leq l \leq 8$ ; transmission (min, max) = 0.9398, 0.9659;  $\rho_{\text{calc}} = 1.791$  g cm<sup>-3</sup>; 837 reflection intensities measured of which 69 were symmetrically independent,  $R_{\text{int}} = 0.0272$ ,  $F(000) = 400$ ,  $\mu = 0.329$  mm<sup>-1</sup>, F face-centered Bravais lattice,  $Fm\bar{3}m$ ,  $a = 893.1(2)$  pm,  $V = 712.3(3) \cdot 10^6$  pm<sup>3</sup>,  $Z = 4$ . R values:  $R_1/wR_2$  for final indices with  $[I_0 > 2\sigma(I_0)]$ : 0.0968/0.2498 and for all data: 0.1061/0.2700;  $S_{\text{all}} = 1.406$ .

Powder XRD data were collected on an image plate G670 Guinier camera (Huber, Rimsting, Germany) with Mo- $K\alpha$  radiation  $\lambda = 71.073$  pm TGA studies were carried out on a TG-50 thermogravimetric analyzer (Shimadzu Corp., Tyoto, Japan) in air with a heating rate of 1 K min<sup>-1</sup>. IR spectra were obtained with a Bruker  $\alpha$  (Bruker, Bremen, Germany) in the ATR (diamond crystal) mode.

## 3. Results and discussion

$[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$  is obtained from a mixture of aluminium(III) isopropoxide, phosphoric acid and 1,3-diaminopropane in the ionic liquid *N*-hexyl-pyridinium tetrafluoroborate under ionothermal conditions, hence heating in an ionic liquid where it acts in the synthesis both as the solvent and structure directing agent. The original objective of our experiments was to produce complex aluminophosphates. Surprisingly, we got phase-pure a new

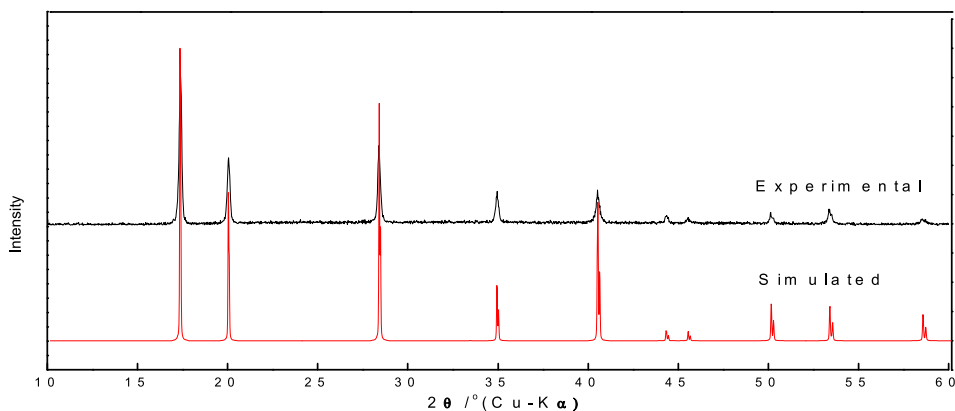


Fig. 2. Measured (top, black) and from single crystal structure data simulated PXRD pattern of  $[\text{Al}(\text{H}_2\text{O})_6]\text{F}_3$ .

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