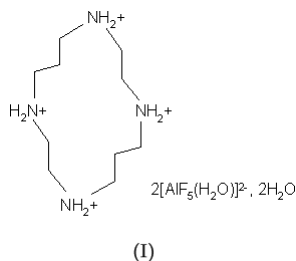


**1,4,8,11-Tetraazacyclodecane-1,4,8,11-tetraium bis(aquapentafluoroaluminate) dihydrate****E. Goreschnik, M. Leblanc and V. Maisonneuve\***Laboratoire des Fluorures—UMR 6010 CNRS,  
Faculté des Sciences, Université du Maine,  
Avenue Olivier Messiaen, 72085 Le Mans  
Cedex 9, FranceCorrespondence e-mail:  
vincent.maisonneuve@univ-lemans.fr**Key indicators**Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.063  
 $wR$  factor = 0.151  
Data-to-parameter ratio = 20.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

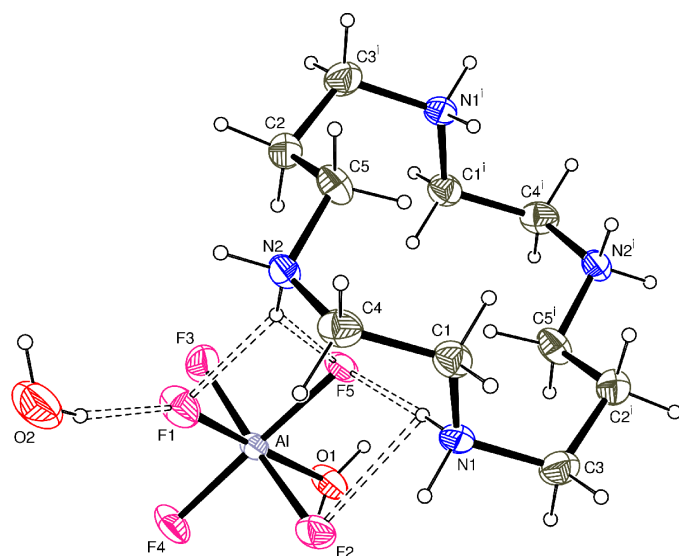
The title compound,  $(\text{C}_{10}\text{H}_{28}\text{N}_4)[\text{AlF}_5(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ , obtained solvothermally at 473 K and isostructural with the iron analogue, consists of isolated  $[\text{AlF}_5(\text{H}_2\text{O})]$  octahedral anions and centrosymmetric tetraprotonated 1,4,8,11-tetraazacyclodecane ( $\text{cyclamH}_4^{4+}$ ) moieties connected by a network of  $\text{N}-\text{H} \cdots \text{X}$  ( $\text{X} = \text{O}, \text{F}$ ) hydrogen bonds. One water molecule participates in the aluminium coordination, whereas the second water molecule connects two neighbouring  $[\text{AlF}_5(\text{H}_2\text{O})]$  octahedra *via*  $\text{F1} \cdots \text{H2WB}-\text{O2}-\text{H2WA} \cdots \text{F3}$  bridges.

Received 3 October 2003  
Accepted 17 October 2003  
Online 23 October 2003**Comment**

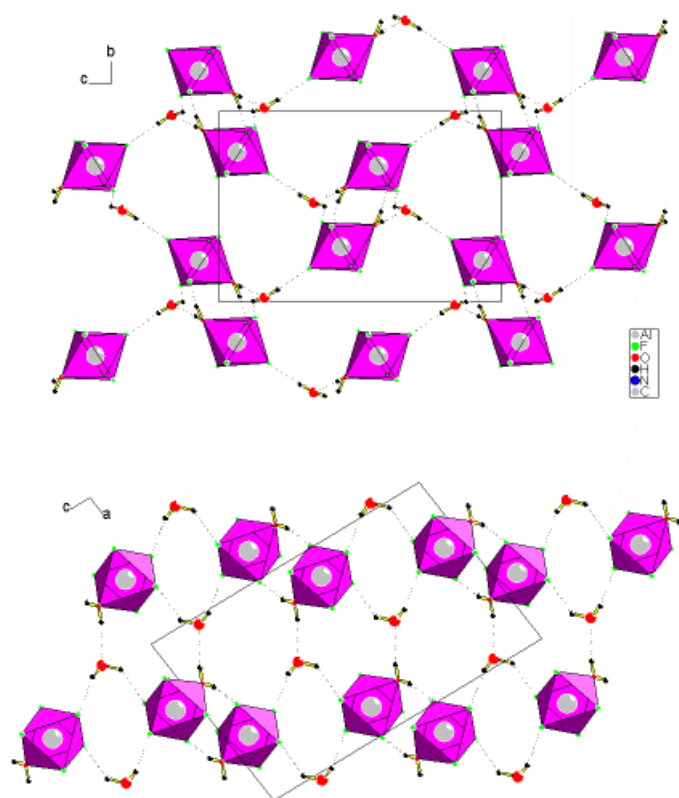
In our search for new hybrid fluorides with a high dimensionality of the inorganic component, we have applied solvothermal synthesis, under subcritical conditions ( $T < 473$  K and  $P < 20$  bars), in mixing an oxide, an HF solution and an organic amine (Goreschnik, Maisonneuve *et al.*, 2002; Goreschnik, Leblanc *et al.*, 2002). 1,4,8,11-Tetraazacyclodecane (cyclam) was chosen as an example having four secondary amines and a cyclic shape. In ethanol, a new fluoroaluminate was synthesized,  $(\text{C}_{10}\text{H}_{28}\text{N}_4)[\text{AlF}_5(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ , (I), isostructural with  $(\text{C}_{10}\text{H}_{28}\text{N}_4)[\text{FeF}_5(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$  (Rother *et al.*, 1997; Rother, 1998). It contains isolated  $[\text{AlF}_5(\text{H}_2\text{O})]^{2-}$  octahedra and centrosymmetric tetraprotonated 1,4,8,11-tetraazacyclodecane ( $\text{cyclamH}_4^{4+}$ ) moieties connected by a network of  $\text{N}-\text{H} \cdots \text{X}$  ( $\text{X} = \text{O}, \text{F}$ ) hydrogen bonds (Fig. 1). One water molecule participates in the aluminium coordination, whereas the second water molecule connects two neighbouring  $[\text{AlF}_5(\text{H}_2\text{O})]$  octahedra *via*  $\text{F1} \cdots \text{H2WB}-\text{O2}-\text{H2WA} \cdots \text{F3}$  bridges. This structure can also be described in terms of a negatively charged three-dimensional network formed by  $[\text{AlF}_5(\text{H}_2\text{O})]$  octahedra linked through the isolated water molecule by hydrogen bonds (Table 2). The anionic inorganic component exhibits channels along the  $a$  and  $b$  axes (Fig. 2), in which the  $\text{cyclamH}_4^{4+}$  cations are found.

**Experimental**

The title compound was prepared from a starting mixture of aluminium oxide ( $\text{Al}_2\text{O}_3$ ), HF solution (40%), 1,4,8,11-tetraazacyclodecane



**Figure 1**  
ORTEP-3 view (Farrugia, 1997) of the cyclamH<sub>4</sub><sup>4+</sup> cation, the [AlF<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> anion and the free water molecule, together with the atom-labelling scheme. Displacement ellipsoids are shown at the 40% probability level. [Symmetry code: (i) 1 - x, -y, 1 - z.]



**Figure 2**  
Projections of (I) along the *a* (top) and *b* axes (bottom), showing the channels in which cyclamH<sub>4</sub><sup>4+</sup> cations are located; these cations are not shown.

(cyclam) and ethanol in the molar ratio 1:10:4:320 under solvothermal conditions (473 K, 96 h, autogenous pressure) in a Teflon-lined autoclave. The resulting product was washed in ethanol and dried in air. Suitable single crystals were isolated by optical microscopy.

### Crystal data

(C<sub>10</sub>H<sub>28</sub>N<sub>4</sub>)[AlF<sub>5</sub>(H<sub>2</sub>O)]<sub>2</sub>·2H<sub>2</sub>O  
*M<sub>r</sub>* = 520.37  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 8.4930 (8) Å  
*b* = 8.9320 (10) Å  
*c* = 13.434 (2) Å  
 β = 97.141 (8)°  
*V* = 1011.2 (2) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.709 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 32 reflections  
 θ = 2.5–10°  
 μ = 0.26 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Parallelepiped, colourless  
 0.08 × 0.06 × 0.04 mm

### Data collection

Siemens AED-2 diffractometer  
 2θ/ω scans  
 Absorption correction: none  
 2955 measured reflections  
 2955 independent reflections  
 1591 reflections with *I* > 2σ(*I*)  
 θ<sub>max</sub> = 30.0°

*h* = -11 → 11  
*k* = 0 → 12  
*l* = 0 → 18  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 15%

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.063  
*wR* (*F*<sup>2</sup>) = 0.151  
*S* = 1.09  
 2955 reflections  
 148 parameters  
 H atoms treated by a mixture of independent and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0473*P*)<sup>2</sup> + 0.517*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.45 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.47 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Al—F4	1.713 (2)	N1—C3	1.497 (4)
Al—F5	1.741 (2)	N2—C5	1.407 (4)
Al—F2	1.762 (2)	N2—C4	1.491 (5)
Al—F3	1.781 (2)	C1—C4	1.506 (5)
Al—F1	1.804 (2)	C2—C3 <sup>i</sup>	1.454 (5)
Al—O1	1.933 (3)	C2—C5	1.503 (5)
N1—C1	1.478 (4)		

Symmetry code: (i) 1 - x, -y, 1 - z.

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1WA...F4 <sup>ii</sup>	0.83 (2)	1.676 (18)	2.501 (3)	172 (4)
O1—H1WB...O2 <sup>iii</sup>	0.82 (2)	1.84 (2)	2.626 (4)	161 (4)
O2—H2WA...F3 <sup>iv</sup>	0.82 (4)	1.92 (4)	2.610 (4)	141 (5)
O2—H2WB...F1 <sup>v</sup>	0.81 (2)	1.92 (2)	2.718 (4)	166 (4)
N1—H1A...F5 <sup>vi</sup>	0.90	1.89	2.787 (4)	173
N1—H1A...F2 <sup>vi</sup>	0.90	2.34	2.789 (4)	111
N1—H1B...F2 <sup>v</sup>	0.90	1.61	2.478 (3)	161
N2—H2A...F1 <sup>vi</sup>	0.90	1.97	2.732 (4)	141
N2—H2A...F5 <sup>vi</sup>	0.90	2.07	2.842 (4)	144
N2—H2B...F3	0.90	1.76	2.655 (4)	173

Symmetry codes: (ii) 1 - x, -y, -z; (iii) x, y, z - 1; (iv) -x, -y, 1 - z; (v) x - ½, ½ - y, ½ + z; (vi) ½ - x, y - ½, ½ - z.

H atoms bonded to C and N were positioned geometrically and refined with a riding model, with N—H = 0.90 and C—H = 0.97 Å. In the water molecules, O—H distances were restrained to 0.82 Å. For all H atoms, *U*<sub>iso</sub> was set to 1.2 times *U*<sub>eq</sub> of the carrier atom.

Data collection: *STADIA* (Stoe & Cie, 1998); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular

graphics: *DIAMOND* (Brandenburg, 2001), *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3* Farrugia, 1997); software used to prepare material for publication: *enCIFer* (CCDC, 2002).

## References

- Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- CCDC (2002). *enCIFer*. Version 1.0. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Goreshnik, E., Leblanc, M., Gaudin, E., Taulelle, F. & Maisonneuve, V. (2002). *Solid State Sci.* **4**, 1213–1219.
- Goreshnik, E., Maisonneuve, V. & Leblanc, M. (2002). *Z. Anorg. Allg. Chem.* **628**, 162–166.
- Rother, G. (1998). PhD thesis, Humboldt University, Berlin, Germany.
- Rother, G., Worzala, H. & Bentrup, U. (1997). *Z. Krist. New Cryst. Struct.* **212**, 395–396.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger and R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1998). *STAD14* (Version 1.07) and *X-RED* (Version 1.10). Stoe & Cie GmbH, Darmstadt, Germany.