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Diethylenetriaminium hexafluoroaluminate dihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.063
wR factor = 0.207
Data-to-parameter ratio = 21.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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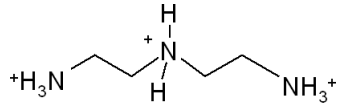
The title compound, $(C_4H_{16}N_3)[AlF_6]\cdot 2H_2O$, was obtained under solvothermal conditions at 463 K for 48 h, involving *in situ* generation of diethylenetriamine from tris(2-aminoethyl)amine. The structure has been determined by single-crystal X-ray diffraction. The $[AlF_6]^{3-}$ anions and triprotonated amine cations build infinite layers, which are hydrogen-bonded to water molecules.

Comment

The title new compound, $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]\cdot[AlF_6]\cdot 2H_2O$ or $[H_3dien]\cdot[AlF_6]\cdot 2H_2O$ (dien is diethylenetriamine), (I), has been synthesized from the chemical system Al_2O_3–(tren)–HF–ethanol [tren is tris(2-aminoethyl)amine]. The dien templating agent was generated by the thermal decomposition of tren. A similar reaction was recently observed during the synthesis of a gallophosphate by the thermal decomposition of cyclohexylformamide into cyclohexylamine (Lakiss *et al.*, 2005).



(I)

The structure of (I) (Fig. 1) is built up from isolated $[AlF_6]^{3-}$ octahedra and charge balance is ensured by triprotonated $[H_3dien]^{3+}$ cations. The AlF_6 octahedra are slightly distorted.

The anionic $[AlF_6]^{3-}$ monomers, water molecules and $[H_3dien]^{3+}$ cations are hydrogen bonded and lie in (001) layers (Fig. 2). These layers are connected by strong O*W*2—H2*W*2···F4 hydrogen bonds [O*W*2···F4 2.694 (3) Å].

The $[H_3dien]^{3+}$ cations exhibit a linear 'spider' shape, with two short [3.160 (3) and 3.102 (3) Å] $N_p\cdots N_s$ distances between the primary and secondary amine groups (Fig. 3). These distances are similar to those found in fluoroaluminates templated by $[H_3tren]^{3+}$ cations having a non-planar spider shape (Adil *et al.*, 2005). Other compounds templated with dien are found either diprotonated (Kongshaug *et al.*, 2001) or triprotonated (Zhao *et al.*, 2001). Compound (I) constitutes the first example of a hybrid fluoroaluminate templated with dien.

Experimental

Compound (I) was prepared from a starting mixture of Al_2O_3, tris(2-aminoethyl)amine (96%, Aldrich), aqueous HF (40%, Prolabo) and

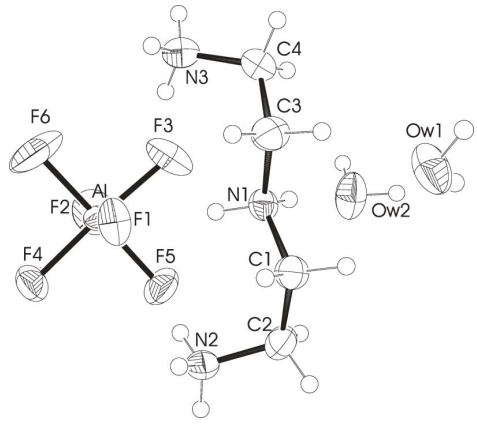


Figure 1
A view of the components of (I), showing the water molecules, $[H_3dien]^+$ cation and $[AlF_6]^{3-}$ anion. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

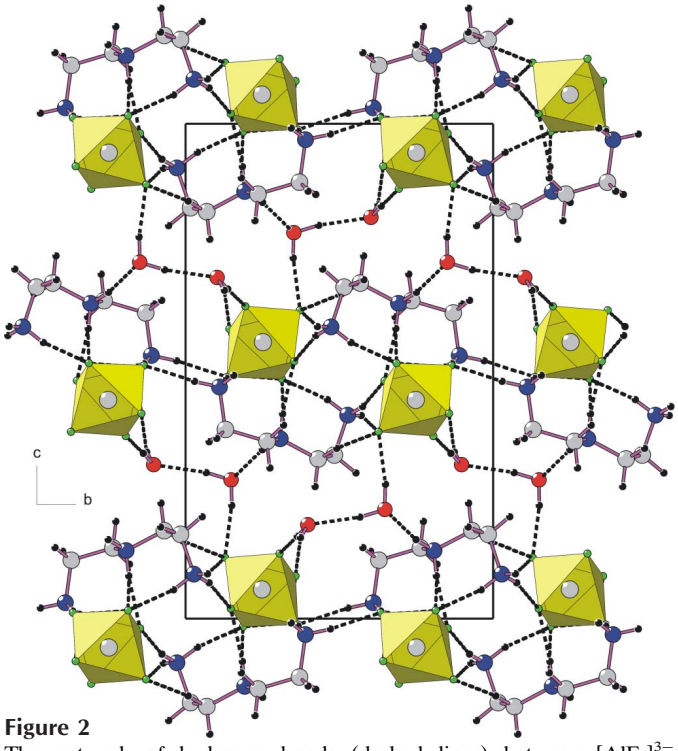


Figure 2
The network of hydrogen bonds (dashed lines) between $[AlF_6]^{3-}$ octahedra, water molecules and $[H_3dien]^{3+}$ cations in (I).

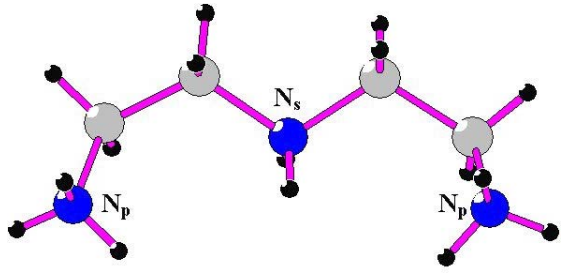


Figure 3
The $[H_3dien]^{3+}$ cation of (I), showing the 'spider' configuration.

ethanol, in the molar ratio 1:6:40:50, under solvothermal conditions (463 K, 2 d, autogenous pressure) in a Teflon-lined autoclave. The resulting crystalline products were washed with ethanol and dried in air. Compound (I) was found as a minor phase together with $(NH_4)_3{\cdot}[AlF_6]$. Crystals of (I) suitable for single-crystal X-ray diffraction were selected using an optical microscope.

Crystal data

$(C_4H_{16}N_3)[AlF_6]{\cdot}2H_2O$
M_r = 283.20
Monoclinic, $P2_1/c$
a = 6.4667 (2) Å
b = 10.5817 (5) Å
c = 17.1328 (8) Å
β = 96.411 (2)°
V = 1165.04 (9) Å^3
Z = 4
D_x = 1.615 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6018 reflections
θ = 2.3–33.4°
μ = 0.25 mm^{-1}
T = 293 (2) K
Parallelepiped, colourless
0.34 × 0.10 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
T_{min} = 0.921, T_{max} = 0.990
16 145 measured reflections
3375 independent reflections
2698 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 30.0°
$h = -7 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.207
S = 1.12
3375 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1271P)^2 + 0.4385P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.044
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Table 1
Selected bond lengths (Å).

Al—F6	1.7532 (18)	N1—C1	1.491 (3)
Al—F4	1.7852 (15)	N1—C3	1.503 (3)
Al—F2	1.7973 (16)	C1—C2	1.504 (3)
Al—F5	1.8113 (15)	C2—N2	1.477 (3)
Al—F3	1.8127 (16)	C3—C4	1.499 (3)
Al—F1	1.8300 (14)	C4—N3	1.475 (3)

Amine H atoms were positioned geometrically, with N—H = 0.89–0.90 Å, and treated as riding. Water H atoms were found in difference Fourier maps and the O—H distances were restrained to 0.90 (1) Å. Carbon-bound H atoms were treated as riding, with C—H distances of 0.97 Å. All H atoms were refined with a common isotropic displacement parameter of 0.062 (2) Å^2.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001) and *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *enCIFer* (CCDC, 2003).

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