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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(I–F) = 0.002 Å
R factor = 0.020
wR factor = 0.052
Data-to-parameter ratio = 8.0

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

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Diammonium sodium hexafluoroaluminate, $(NH_4)_2NaAlF_6$, obtained by hydrothermal synthesis, comprises $[AlF_6]^{3-}$ octahedra forming a face-centred cubic (*fcc*) arrangement, with Na^+ cations filling all octahedral interstices and NH_4^+ cations filling all tetrahedral interstices.

Comment

Metal complex fluorides with the elpasolite structure are of interest to both physical scientists and chemists on account of their rich structural chemistry (Xu *et al.*, 2000) and phase transitions. A considerable number of complex fluoride compounds have been characterized in the past decades, with general formula A_2BCF_6 (A = Na, K, NH_4, Rb, Cs, Tl; B = Li, Na, K, Rb, Cs, Tl; C = Al, Ni, Co, Cr, Ga, V, Fe, Mn, Ti, Sc, In, Yb, Tl, Tm, Er, Y, Ho, Dy, Tb, Gd, Eu, Sm, Ce, Bi). To date, only one ammonium-based compound has been reported, namely $(NH_4)_2NaInF_6$ (Roloff *et al.*, 1995). We describe here the isotypic aluminium analogue, $(NH_4)_2NaAlF_6$ (Fig. 1).

The crystal structure of $(NH_4)_2NaAlF_6$ is characterized by an array of alternate $[NaF_6]$ and $[AlF_6]$ corner-connected octahedra (Fig. 2). The structure can be visualized as $[AlF_6]^{3-}$ octahedra forming a face-centred cubic (fcc) arrangement, with Na^+ cations filling all octahedral interstices and NH_4^+ cations filling all tetrahedral interstices. Each NH_4^+ cation lies between four $[AlF_6]^{3-}$ octahedra, and is coordinated by 12 F atoms (Fig. 3). Each $[AlF_6]^{3-}$ octahedron is surrounded by eight NH_4^+ cations in an octahedral shape.

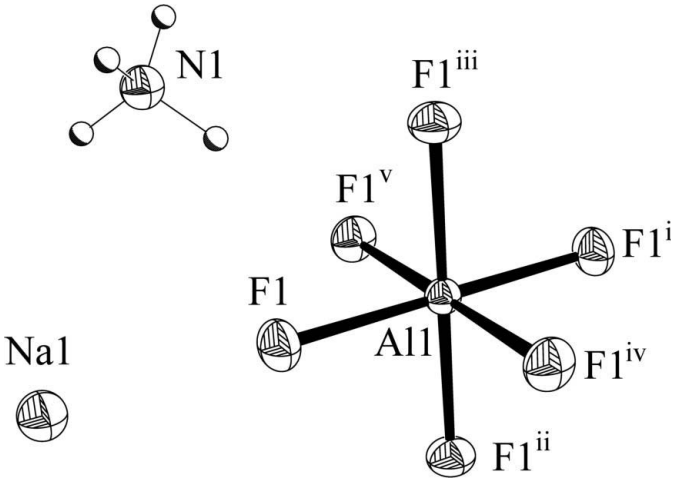

Figure 1
One $[AlF_6]^{3-}$ octahedron, one Na^+ cation and one NH_4 cation in $(NH_4)_2NaAlF_6$, with displacement ellipsoids shown at the 50% probability level. H atoms are shown as spheres of arbitrary radius. [Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{1}{2}+z, x, -\frac{1}{2}+y$; (iii) $\frac{1}{2}-z, 1-x, \frac{1}{2}-y$; (iv) $y, \frac{1}{2}+z, -\frac{1}{2}+x$; (v) $1-y, \frac{1}{2}-z, \frac{1}{2}-x$].

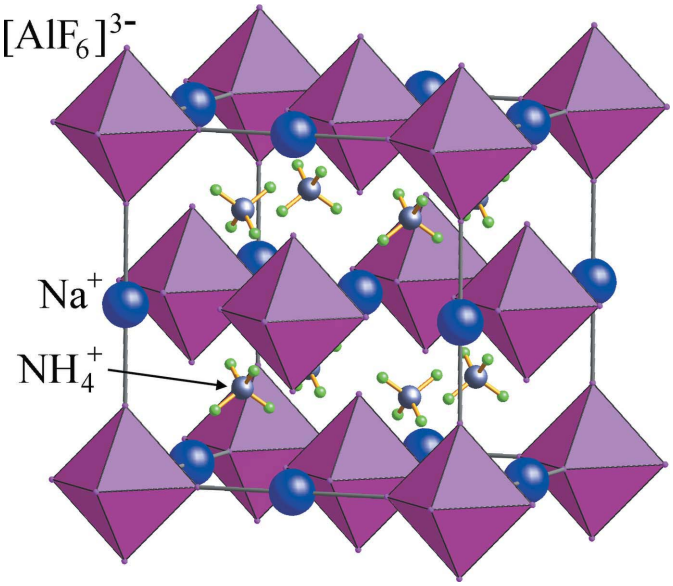

Figure 2
View of $(NH_4)_2NaAlF_6$, showing $[AlF_6]^{3-}$ octahedra (pink) arranged in an fcc manner, with Na^+ cations (blue) lying in all octahedral interstices, and NH_4^+ cations lying in all tetrahedral interstices.

Experimental

The title compound was synthesized hydrothermally from a typical mixture of $(NH_4)H_2PO_4$ (1.024 g), $(NH_4)HF_2$ (0.272 g), $NaHF_2$ (0.051 g), $AlCl_3{\cdot}6H_2O$ (0.100 g), and 0.8 ml 85% aqueous H_3PO_4 in the molar ratio (NH_4):Na:Al:F = 33:2:1:27. The mixture was dissolved in 9 ml distilled water, and heated at 453 K for 7 d under autogenous pressure in a 30 ml Teflon-lined autoclave (*ca* 30% filled). The title compound was obtained in *ca* 15% yield (based on Al), with $(NH_4)_2AlF_5(H_2O)$ (Knop *et al.*, 1985) also present. Colourless transparent crystals of $(NH_4)_2NaAlF_6$, which showed a trigonal tris-octahedron shape, were manually selected under the microscope and used for powder X-ray diffraction. The chemical composition was confirmed by semi-quantitative EDX analysis.

Crystal data

$(NH_4)_2NaAlF_6$
M_r = 400.11
Cubic, $Fm\overline{3}m$
a = 8.3450 (3) Å
V = 581.14 (4) Å^3
Z = 2
D_x = 2.287 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 295 (2) K
Prism, colourless
0.17 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.923, T_{max} = 0.954
1631 measured reflections
56 independent reflections
56 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.052
S = 1.36
56 reflections
7 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.8143P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

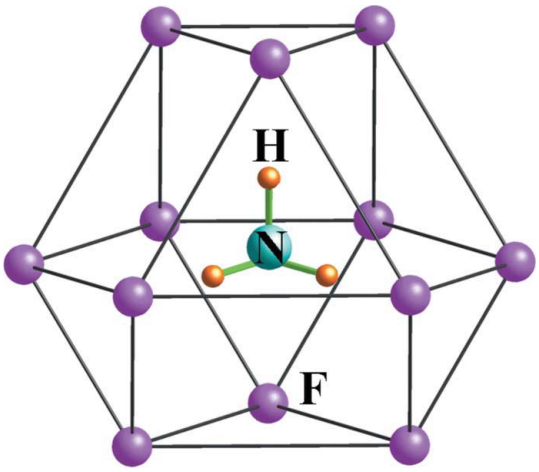

Figure 3
The coordination environment of one NH_4 cation.

Table 1
Selected bond lengths (Å).

Al1—F1^{i}	1.8151 (16)	N1—F1^{ii}	2.9628 (2)
Na1—F1	2.3574 (16)		

Symmetry codes: (i) $-y+1, -z+\frac{1}{2}, -x+\frac{1}{2}$; (ii) $y-\frac{1}{2}, z, x-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···F1^{iii}	0.886	2.240	2.9628 (2)	139

Symmetry code: (iii) z, x, y.

Atom H1 was located in a difference Fourier map, and its positional and isotropic displacement parameters were refined independently in successive cycles of refinement, leading to significant improvement in the R values. After several cycles, stable parameters were obtained for H1, and these were fixed for the final cycles of refinement. The final N—H distance is 0.89 Å, and the final U_{iso} value is 0.176 Å^2. The magnitude of this latter value is likely to reflect considerable motion for the NH_4^+ cation at 295 K.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXL97*.

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