Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diammonium sodium hexafluoroaluminate, $(NH_4)_2NaAlF_6$

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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.

Received 5 July 2006
Accepted 28 July 2006

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.

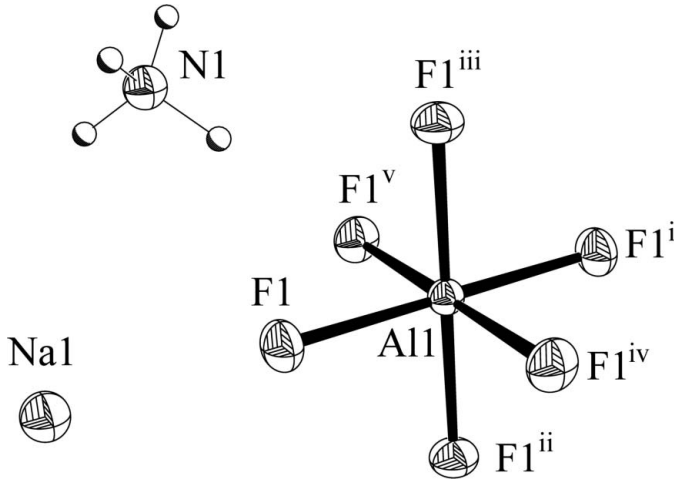

Figure 1
One $[AlF_6]^{3-}$ octahedron, one Na^+ cation and one NH_4 cation in $(NH_4)_2NaAlF_6$, with displacement ellipsoids shown at the 50% probability level. H atoms are shown as spheres of arbitrary radius. [Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{1}{2}+z, x, -\frac{1}{2}+y$; (iii) $\frac{1}{2}-z,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

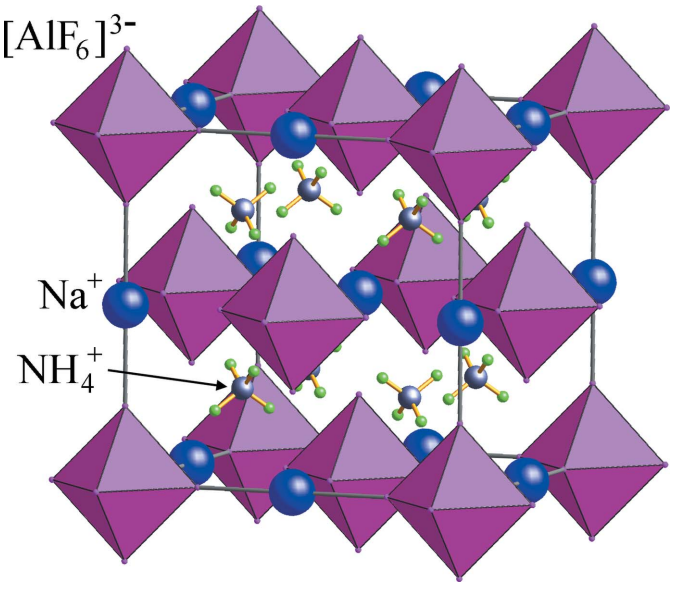

Figure 2
View of $(NH_4)_2NaAlF_6$, showing $[AlF_6]^{3-}$ octahedra (pink) arranged in an fcc manner, with Na^+ cations (blue) lying in all octahedral interstices, and NH_4^+ cations lying in all tetrahedral interstices.

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 trisoctahedron 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, $Fm\bar{3}m$
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}

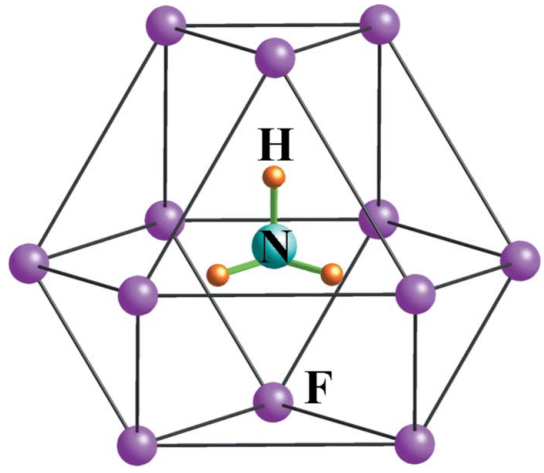

Figure 3
The coordination environment of one NH_4 cation.

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*.

This project was supported by funds from the National Natural Science Foundation of China (No.40472027), the Natural Science Foundation of Fujian Province (No. E0410003) and the project sponsored by SRF for ROCS, SEM in China.

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