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Ammonium scandium tetrafluoride

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The title compound, NH_4ScF_4, is an addition to the AMF_4 family of layered perovskite-like structures. The structure consists of a two-dimensional array of corner-sharing ScF_6 octahedra, which produces anionic sheets of stoichiometry $[ScF_4]^-$ stacked along the *c* axis. The layers are separated by charge-balancing ammonium cations, which hydrogen bond to the apical F atoms of adjacent layers. This structure may be viewed as a 'single-layer' fluoride analogue of the Dion–Jacobson family of oxides.

Comment

The title compound, NH_4ScF_4, (I), was produced during our exploratory studies in the hydrothermal chemistry of organically templated scandium fluorides (Stephens *et al.*, 2004; Stephens & Lightfoot, 2006). This compound arises from an *in situ* breakdown of the organic template (see *Experimental*). It is related to several other layered fluorides of stoichiometry AMF_4 and may also be regarded as an $n = 1$ Dion–Jacobson phase (Dion *et al.*, 1981).

The asymmetric unit (Fig. 1) contains one unique Sc site on a general position, having quite regular octahedral symmetry (Table 1). There are five crystallographically independent F sites and two N sites, both on mirror planes.

Fig. 2 shows that (I) is built from puckered layers of vertex-sharing octahedra, typical of layered perovskites. The layers are eclipsed relative to each other with respect to the *a* axis, but staggered by *b*/4 along *b*. Extensive hydrogen bonding occurs between adjacent layers, mediated by the ammonium cations (Table 2). The only N—H⋯F hydrogen bonds are those between ammonium cations and the 'apical' F atoms that project into the interlayer space. This hydrogen bonding fulfills bond-valence requirements around the apical F atoms F2 and F3, as shown in Table 3.

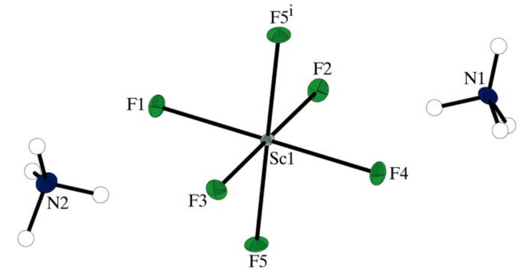

Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$].

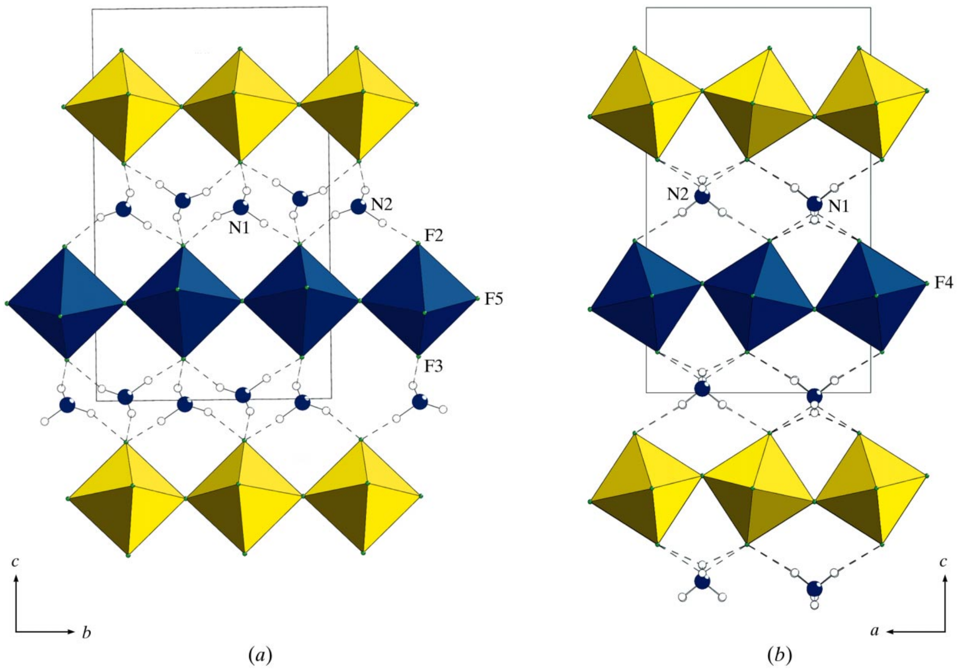

Figure 2
(*a*) A projection along [100], showing staggered octahedra. (*b*) A projection along [010], showing eclipsed octahedra.

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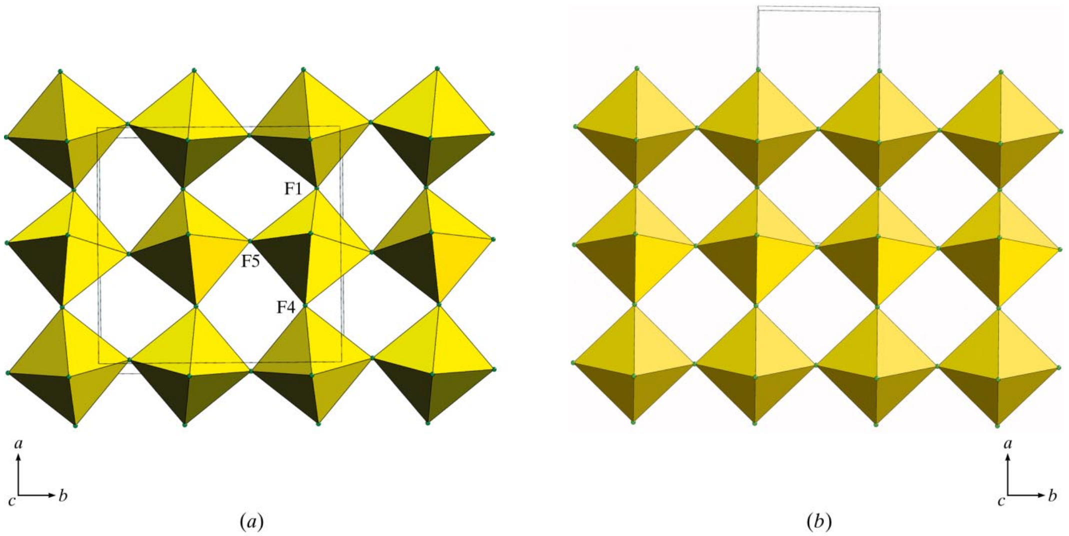

Figure 3
A view of a single layer along [001], showing (*a*) the *Pmcn* model with the additional *c* axis tilt mode and (*b*) the *Amma* model, with $b' = b/2$.

Both the raw diffraction data and the derived model display a significant degree of pseudosymmetry (*e.g.* the bond lengths involving F1/F4 and F2/F3). An alternative model in space group *Amma*, with $b' = b/2$, was also considered. However, our refinements confirm that the chosen model is correct; refinements in the higher-symmetry model lead to anomalously elongated ellipsoids for the 'in-plane' F atoms, transverse to the Sc—F—Sc linkages. In fact, the pseudosymmetry is due to 'octahedral tilting', and the difference between the two models is clarified in Fig. 3. In addition to the tilting relative to the *b* axis, shown in Fig. 2(*b*), there is a second tilt mode around the *c* axis, which is allowed in the correct *Pmcn* model but forbidden in the approximate *Amma* model. The two models are analogous to those in $KFeF_4$ (Lapasset *et al.*, 1986), which undergoes a structural phase transition from $KFeF_4$(III) to $KFeF_4$(II) at 368 K, corresponding to *Pmcn* to *Amma*. We have not explored the possibility of such a phase transition in the present case.

In comparison with other compositionally related AMF_4 compounds, (I) is isotypic with $KGaF_4$ (Courbion *et al.*, 1989). Interestingly, however, more precisely similar compositions have different structure types; for example, NH_4FeF_4 (Leblanc *et al.*, 1985) has the same type of layer as (I), but the $[ScF_4]^-$ sheets are eclipsed along both *a* and *b*, whereas $KScF_4$, has a unique 'corrugated sheet' structure containing both *cis*- and *trans*-vertex-sharing octahedra (Champarnaud-Mesjard & Frit, 1992).

Experimental

Scandium oxide (0.138 g), water (5 ml) and a 40% aqueous solution of HF (0.5 ml) were heated in a Teflon-lined steel autoclave for 1 h at 463 K. To this, ethylene glycol (5 ml) and 1,3-diaminopropane (0.4 ml) were added, and the resulting mixture was heated at the same temperature for four days. The product was filtered off, washed with water and allowed to dry at room temperature overnight. Powder X-ray diffraction revealed predominantly (I) as the product, together with a small amount of ScF_3. Compound (I) was heated to 1073 K at a rate of 5 K min^{-1} under N_2 gas. Thermogravimmetric analysis shows a single-step weight loss of 19.6% from 573 to 698 K (20% calculated). Powder X-ray diffraction of the residue shows that this decomposition product is ScF_3.

Crystal data

NH_4ScF_4
$M_r = 139.00$
Orthorhombic, *Pmcn*
$a = 7.862$ (2) Å
$b = 8.088$ (2) Å
$c = 13.503$ (4) Å
$V = 858.6$ (4) Å^3
$Z = 8$
$D_x = 2.151$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 1.67$ mm^{-1}
$T = 93$ (2) K
Prism, colourless
0.10 × 0.03 × 0.02 mm

Data collection

Rigaku/MSC CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.825$, $T_{max} = 0.970$
5191 measured reflections
847 independent reflections
587 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.102$
$S = 1.11$
847 reflections
75 parameters
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.1485P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sc—F2	1.9904 (12)	Sc—F4	2.0273 (7)
Sc—F3	1.9919 (12)	Sc—F5^i	2.0320 (19)
Sc—F1	2.0272 (7)	Sc—F5	2.0325 (19)
F2—Sc—F3	179.61 (9)	Sc^{ii}—F1—Sc	151.46 (10)
F1—Sc—F4	179.82 (7)	Sc^{iii}—F4—Sc	151.82 (10)
F5^i—Sc—F5	179.713 (18)	Sc^{iv}—F5—Sc	168.48 (8)

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

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{N1-H1\cdots F2}$	0.91 (3)	1.97 (3)	2.836 (2)	159 (2)
$\mathrm{N1-H2\cdots F3^{v}}$	0.97 (4)	2.11 (3)	2.858 (3)	132.0 (9)
$\mathrm{N1-H3\cdots F2^{vi}}$	0.86 (4)	2.21 (3)	2.853 (3)	131.3 (14)
$\mathrm{N2-H4\cdots F3^{vii}}$	0.84 (4)	2.24 (3)	2.867 (3)	132.1 (14)
$\mathrm{N2-H5\cdots F3}$	0.93 (3)	1.95 (3)	2.837 (2)	158 (2)
$\mathrm{N2-H6\cdots F2^{viii}}$	0.99 (4)	2.11 (3)	2.872 (4)	132.1 (9)

Symmetry codes: (v) $-x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+2, -z$; (vii) $x-\frac{1}{2}, -y+2, -z+1$; (viii) $-x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Table 3
Bond valence parameters.

Bond	s_{ij}	$\sum s_{ij}$
Sc F2	0.54	–
Sc F3	0.53	–
Sc F1	0.49	–
Sc F4	0.49	–
Sc F5	0.48	–
Sc F5	0.48	–
	–	3.00
F1 Sc	0.49 × 2	0.97
F2 Sc	0.54	0.54
F3 Sc	0.53	0.53
F4 Sc	0.49 × 2	0.97
F5 Sc	0.48	–
F5 Sc	0.48	0.96

Note: s_{ij} values calculated for $B = 0.37$; Brese & O'Keeffe (1991) extrapolated.

Systematic absences were consistent with space groups *Pmcn* (62) or $P2_1cn$ (33). Successful refinement of the structure in centrosymmetric *Pmcn*, together with the lack of any contradictory physical property measurements, meant that this was preferred over $P2_1cn$. *Pmcn* [a non-standard setting of *Pnma* (62)] was chosen as this defines the perovskite-like layers to lie perpendicular to *c*, which is the convention in perovskite chemistry. H atoms were located from a difference Fourier map and were refined freely; the $U_{\mathrm{iso}}(\mathrm{H})$ values were fixed at 0.018 Å^2.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3020). Services for accessing these data are described at the back of the journal.

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