Ammonium scandium tetrafluoride

Nicholas F. Stephens and Philip Lightfoot*

School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: pl@st-and.ac.uk

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.
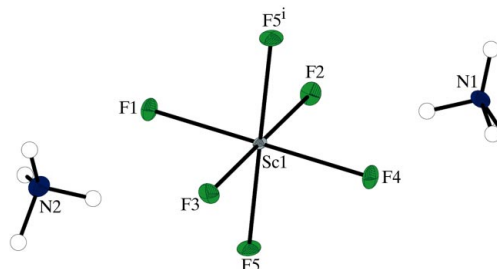

Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$].
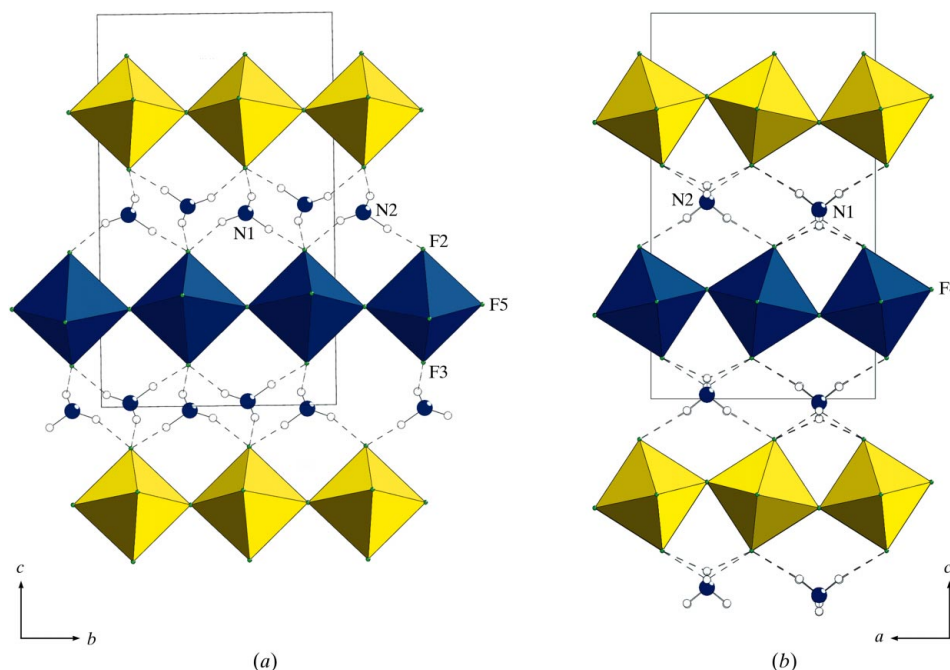

Figure 2
(a) A projection along [100], showing staggered octahedra. (b) A projection along [010], showing eclipsed octahedra.
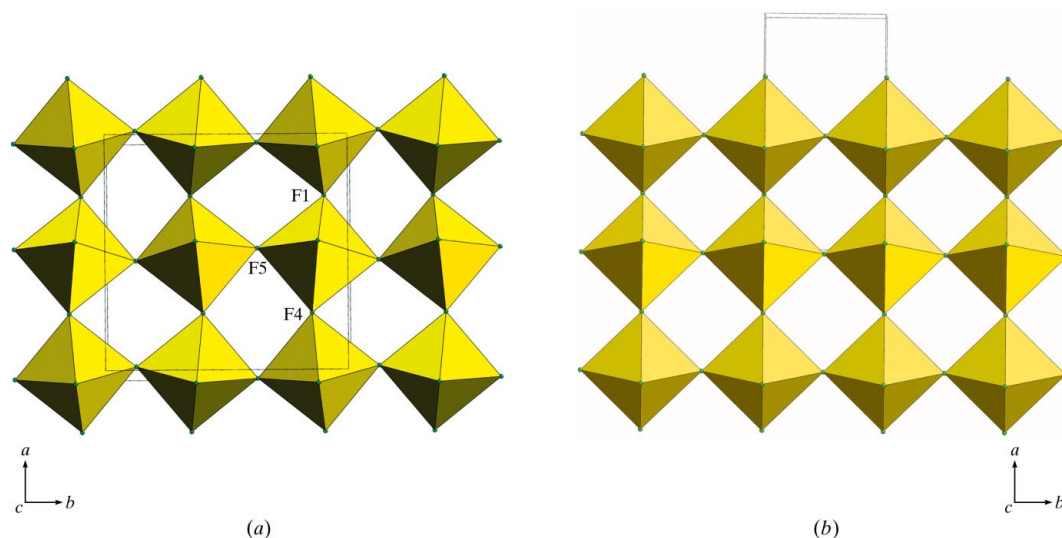
inorganic compounds

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 KFeF₄ (Lapasset *et al.*, 1986), which undergoes a structural phase transition from KFeF₄(III) to KFeF₄(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 *AM*F₄ compounds, (I) is isotypic with KGaF₄ (Courbion *et al.*, 1989). Interestingly, however, more precisely similar compositions have different structure types; for example, NH₄FeF₄ (Leblanc *et al.*, 1985) has the same type of layer as (I), but the [ScF₄]⁻ sheets are eclipsed along both *a* and *b*, whereas KScF₄, 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 ScF₃. Compound (I) was heated to 1073 K at a rate of 5 K min⁻¹ under N₂ 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 ScF₃.

Crystal data

NH₄ScF₄	$Z = 8$
$M_r = 139.00$	$D_x = 2.151$ Mg m⁻³
Orthorhombic, *Pmcn*	Mo *Kα* radiation
$a = 7.862$ (2) Å	$\mu = 1.67$ mm⁻¹
$b = 8.088$ (2) Å	$T = 93$ (2) K
$c = 13.503$ (4) Å	Prism, colourless
$V = 858.6$ (4) Å³	$0.10 \times 0.03 \times 0.02$ mm

Data collection

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

Refinement

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

Table 1
Selected geometric parameters (Å, °).

Sc—F2	1.9904 (12)	Sc—F4	2.0273 (7)
Sc—F3	1.9919 (12)	Sc—F5ⁱ	2.0320 (19)
Sc—F1	2.0272 (7)	Sc—F5	2.0325 (19)
F2—Sc—F3	179.61 (9)	Scⁱⁱ—F1—Sc	151.46 (10)
F1—Sc—F4	179.82 (7)	Scⁱⁱⁱ—F4—Sc	151.82 (10)
F5ⁱ—Sc—F5	179.713 (18)	Scⁱᵛ—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, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H1···F2	0.91 (3)	1.97 (3)	2.836 (2)	159 (2)
N1—H2···F3[v]	0.97 (4)	2.11 (3)	2.858 (3)	132.0 (9)
N1—H3···F2[vi]	0.86 (4)	2.21 (3)	2.853 (3)	131.3 (14)
N2—H4···F3[vii]	0.84 (4)	2.24 (3)	2.867 (3)	132.1 (14)
N2—H5···F3	0.93 (3)	1.95 (3)	2.837 (2)	158 (2)
N2—H6···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 $U_{\text{iso}}(\text{H})$ 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*.

References

Brandenburg, K. (2001). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Bruker (1999). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Champarnaud-Mesjard, J. C. & Frit, B. (1992). *Eur. J. Solid State Inorg. Chem.* **29**, 161–170.
Courbion, G., Randrianohavy, J. V. & Rousseau, J. J. (1989). *J. Solid State Chem.* **81**, 285–292.
Dion, M., Ganne, M. & Tournoux, M. (1981). *Mater. Res. Bull.* **16**, 1429–1435.
Lapasset, J., Sciau, P., Moret, J. & Gros, N. (1986). *Acta Cryst.* B**42**, 258–262.
Leblanc, M., Ferey, G., De Pape, R. & Teillet, J. (1985). *Acta Cryst.* C**41**, 657–660.
Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Release 97-2. University of Göttingen, Germany.
Stephens, N. F. & Lightfoot, P. (2006). *Solid State Sci.* **8**, 197–202.
Stephens, N. F., Slawin, A. M. Z. & Lightfoot, P. (2004). *Chem. Commun.* pp. 614–615.