COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A novel scandium fluoride, $[C_2N_2H_{10}]_{0.5}[ScF_4]$, with an unprecedented tungsten bronze-related layer structure.

Nicholas F. Stephens, Alexandra M. Z. Slawin and Philip Lightfoot*
School of Chemistry, University of St Andrews, St Andrews, Fife, UK KY16 9ST. E-mail: pl@st-and.ac.uk

Received (in Cambridge, UK) 16th December 2003, Accepted 15th January 2004
First published as an Advance Article on the web 9th February 2004

$[C_2N_2H_{10}]_{0.5}[ScF_4]$ exhibits isolated anionic layers of corner-linked ScF_6 octahedra enclosing 3-, 4-, 5- and 6-membered rings, with features reminiscent of both hexagonal and tetragonal tungsten bronze-type structures.

The use of HF as a mineralising agent in hydrothermal syntheses is now well developed, with many phosphates in particular being discovered using this methodology.[1] Besides a mineralising effect, fluoride has also been shown to have a structure-directing effect, most notably in templating the synthesis of small structural units such as the cube-like 'double-four ring' in zeolite chemistry.[2] Many solvothermal syntheses of phosphates have also resulted in the incorporation of F^- as a ligand, competitive with OH^-.[3] In more recent work, the specific targeting of metal fluorides, as opposed to oxyfluorides, has been attempted in solvothermal systems. This field is still largely unexplored, but has so far produced novel phases, and unusual structural features, in beryllium fluoride[4] and uranium fluoride[5] chemistry. The former series display tetrahedrally connected nets, whereas the latter display uranium typically in eight- or nine-coordination to fluorine, with varying dimensionality. In the present work, we report a structure exhibiting layers of corner-linked ScF_6 octahedra; the structure may be compared to the well-known 'layered' perovskite families, *e.g.* K_2NiF_4, as well as 'layered' versions of the hexagonal (HTB) and tetragonal (TTB) tungsten bronze structure.

The title compound was first observed in solvothermal reactions consisting of Sc_2O_3, GeO_2, HF, ethylenediamine, water and ethylene glycol. Single crystal X-ray diffraction† and chemical analysis‡ revealed that neither Ge nor ethylene glycol were incorporated into the structure. Therefore, simpler reactions were pursued. Phase-pure $[C_2N_2H_{10}]_{0.5}[ScF_4]$ can be prepared as described below‡. It appears that ethylene glycol is necessary for the synthesis, under these conditions.

The structure of $[C_2N_2H_{10}]_{0.5}[ScF_4]$ consists of single anionic $[ScF_4]^-$ layers of corner-linked octahedra separated by H-bonded organocations. Within each layer, the octahedral units display a surprisingly complex, and unique, connectivity (Fig. 1). The structure contains five crystallographically distinct Sc atoms, which may be considered as the 'bow-tie'-shaped building unit highlighted in Fig. 1. This building unit is also observed in the HTB structure type, but the mode of connection of these units in the present case is more complex. Indeed, this new connectivity leads to an overall topology which includes a regular array of four distinct ring sizes, *viz.* 3-, 4-, 5- and 6-membered rings. In the HTB structure, there are only 3- and 6-membered rings, whereas in the related TTB structure type, only 3-, 4- and 5-membered rings are observed.[6] Moreover, to the best of our knowledge, neither of these structure types has ever been observed in a purely 'layered' format. Both HTB and TTB structure types generally refer to three-dimensionally connected phases of general formula 'MX_3' or 'A_xMX_3'; however, there are examples of 'layered' HTB materials, though these all have 'capping' oxo-anions on either one or both sides of the $[MO_4]$ layer. Examples include $(NH_4)_2(MoO_3)_3SeO_3$ and $Cs_2(MoO_3)_3SeO_3$.[7]

The interlayer regions in $[C_2N_2H_{10}]_{0.5}[ScF_4]$ consist of well-ordered ethylenediammonium cations that act as H-bonded bridges between the layers (Fig. 2). The overall structure is, therefore, reminiscent of a 'layered' perovskite. There are several families of inorganic 'layered' perovskites, the most relevant here being the Ruddlesden–Popper and Dion–Jacobson phases, typified in fluoride chemistry by K_2NiF_4 and $KAlF_4$, respectively. These consist of single $[MF_4]^-$ sheets of corner-linked octahedra enclosing 4-rings only. A vast range of hybrid organic–inorganic analogues of these materials has been prepared by Mitzi using metal iodides and organoamine cations.[8] The majority of these phases accommodate the basic perovskite-like layer topology, although some display unusual layer types such as metal-deficient layers[9] or mixed corner/edge-sharing octahedral layers.[10] However, none reported so far form a HTB- or TTB-like layer.

Scandium is known to be a relatively fluorophilic metal, and it is clear from our original reactions that the fluoride is formed in preference to the anticipated germanate. Expansion of this chemistry may therefore reasonably be expected to produce further novel scandium fluorides. There are no previously known organ-

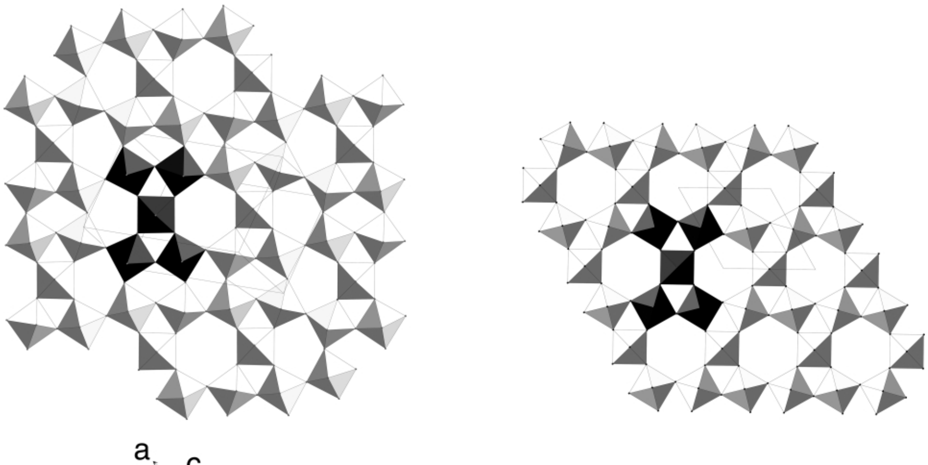

Fig. 1 (a) Plan view of the $[ScF_4]^-$ layer in the title compound, showing the pentameric 'bow-tie' building unit. (b) A single layer of the HTB structure of WO_3, showing a similar building unit.

DOI: 10.1039/b316312a

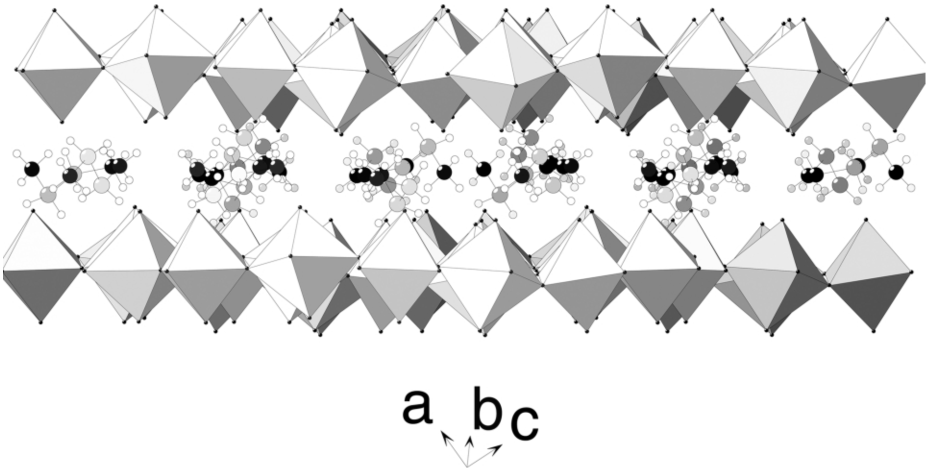

Fig. 2 View perpendicular to the $[ScF_4]^-$ layers, showing the separating enH_2^{2+} cations.

ically templated scandium fluorides. One unusual, closely related structure type, apparently unique to scandium, is that of $KScF_4$,[11] which also has a perovskite-related $[ScF_4]^-$ layer, but in this case containing corrugated layers caused by partial *cis*- rather than *trans*-sharing of octahedral vertices.

It is quite probable that the organic moieties in the present example have a more pro-active structure-directing role than merely 'layer separators', and may actually influence the detailed topology of the $[ScF_4]^-$ layer. Given the wealth of known variants on the basic 'layered' perovskite structure type, and the additional flexibility inherent in organically templated solvothermal syntheses, it is anticipated that the title compound may represent the first in a rich family of new layered structure types based on these general structural and compositional features.

We thank the University of St Andrews for funding.

Notes and references

† *Crystal data*: $C_{10}H_{50}N_{10}F_{40}Sc_{10}$, M_r = 1520.1, triclinic $P\bar{1}$, a = 8.889(1), b = 10.324(2), c = 14.178(2) Å, α = 83.299(3), β = 88.383(3), γ = 67.516(2)°, V = 1193.8(3) Å^3, Z = 1, D_c = 2.12 g cm^{-3}, 7112 reflections measured, of which 4301 were unique and 3836 observed [$I > 2\sigma(I)$]. Final agreement factors $R1$ = 0.0350, $wR2$ = 0.1048 (observed data). CCDC 227104. See http://www.rsc.org/suppdata/cc/b3/b316312a/ for crystallographic data in CIF or other electronic format.

‡ Phase-pure $[C_2N_2H_{10}]_{0.5}[ScF_4]$ was prepared by heating Sc_2O_3 (0.138 g) in 0.5 ml HF–5 ml H_2O at 100 °C for 1 h, followed by addition of 0.5 ml ethylenediamine and 5 ml ethylene glycol. This mixture was heated in a Teflon-lined autoclave at 190 °C for 5 days. The product was recovered by filtration and washed with water. Powder XRD provided an excellent match to a pattern simulated on the basis of the single crystal structure. Elemental analysis, obs. (calc.): C 7.94 (7.90), H 3.43 (3.32), N 9.22 (9.21)%. EDX indicated negligible Ge content for reactions containing GeO_2.

1 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
2 L. A. Villaescusa, P. Lightfoot and R. E. Morris, *Chem. Commun.*, 2002, 2220.
3 C. Serre, F. Taulelle and G. Férey, *Chem. Commun.*, 2003, 2755.
4 L. A. Gerrard and M. T. Weller, *Chem. Commun.*, 2003, 716.
5 R. J. Francis, P. S. Halasyamani, J. S. Bee and D. O'Hare, *J. Am. Chem. Soc.*, 1999, **121**, 1609.
6 R. J. D. Tilley, *Int. J. Refract. Met. Hard Mater.*, 1995, **13**, 93.
7 W. T. A. Harrison, L. L. Dussack and A. J. Jacobson, *Inorg. Chem.*, 1994, **33**, 6043.
8 D. B. Mitzi, *J. Chem. Soc., Dalton Trans.*, 2001, 1.
9 D. B. Mitzi, *Inorg. Chem.*, 2000, **39**, 6107.
10 Z. Xu and D. B. Mitzi, *Inorg. Chem.*, 2003, **42**, 6589.
11 J. C. Champarnaud-Mesjard and B. Frit, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 161.