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Hydrothermal scandium fluoride chemistry: syntheses and crystal structures of $[C_2N_2H_{10}][ScF_5]$, $[NH_4]_2[Sc_3F_{11}]$ and $[H_3O][C_6N_2H_{16}][ScF_6]\cdot H_2O$

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Abstract

The hydrothermal syntheses and crystal structures of three new scandium fluorides are reported. $[enH_2][ScF_5]$ **1** exhibits continuous chains of vertex linked ScF_6 octahedra, which adopt two differing conformations (eclipsed and staggered). $[NH_4]_2[Sc_3F_{11}]$ **2**, displays a three-dimensional framework structure composed of edge and corner-shared ScF_7 pentagonal bipyramids interlinked via octahedral scandium centres. This structure encloses 'butterfly'-shaped channels, and may be regarded as an 'expanded' version of the KSc_2F_7 structure, derived by insertion of the additional octahedral unit between neighbouring pentagonal bipyramidal chains. $[H_3O][C_6N_2H_{16}][ScF_6]\cdot H_2O$ **3** is composed of isolated ScF_6 octahedra hydrogen-bonded to *trans*-1,4-diaminocyclohexane cations and water molecules/hydronium cations. Crystal data for **1**: tetragonal, space group P4/ncc, $a = 13.035(2)$ Å, $c = 8.142(2)$ Å; for **2**: orthorhombic, space group Cmmm, $a = 18.501(12)$ Å, $b = 6.613(5)$ Å, $c = 4.025(3)$ Å; for **3**: monoclinic, space group $P2_1/n$, $a = 9.543(2)$ Å, $b = 6.704(1)$ Å, $c = 9.873(2)$ Å, $\beta = 90.349(5)°$.

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1. Introduction

The structural chemistry of metal fluorides synthesised under 'traditional' solid state conditions is well understood [1,2]. In contrast, solvothermal metal fluoride chemistry has been much less well explored. The use of HF as a mineralising agent and structure-directing agent in hydrothermal syntheses is, however, fairly well-developed, with many phosphates in particular being discovered using this methodology [3]. Fluoride is often incorporated into the products of such reactions along with phosphate or other oxyanions. However, there has been surprisingly little work in hydrothermal systems where fluoride represents the only anionic ligand, especially when considering the use of organic structure-directing agents. The great range of N-containing organic species typically used in such chemistry will inevitably lead to a much larger range of metal fluoride crystal architectures than is currently known, as has been observed in the chemistry of metal phosphates during the past 20 years or so.

Earlier work on fluorometalates containing organic cations has been reviewed by Bentrup et al. [4]. Remarkably, most of the structures reviewed in this work were characterised by isolated $MF_x(H_2O)_y$ polyhedral groups connected only via hydrogen bonding. Some polynuclear units were reported, together with a few chain structures, containing infinite –M–F–M– arrays. No two- or three-dimensional covalently bonded metal fluoride arrays were observed! More recently, several groups have begun to explore organically templated metal fluoride chemistry, and several examples of one-, two- and three-dimensional structures have been reported in aluminium [5,6], uranium [7], zirconium [8–10] and beryllium [11,12] fluoride systems. The hydrothermal chemistry of scandium is also in its infancy. Recently, examples of sulphate-phosphates [13] and phosphates [14,15] have been isolated. As scandium is known to be a strongly fluorophilic element [16] our own work has so far focussed on scandium fluoride systems, and we have previously reported the first organically-templated scandium fluoride, $[enH_2]_{0.5}[ScF_4]$ **4**, which has a 2-D layer structure reminiscent of the tungsten bronze family [17]. Here we report three further novel phases isolated from similar systems, $[enH_2][ScF_5]$ **1**, $[NH_4]_2[Sc_3F_{11}]$ **2** and $[H_3O][C_6N_2H_{16}]$-$[ScF_6]\cdot H_2O$ **3**, which exhibit 1-D, 3-D and 0-D architectures, respectively.

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2. Experimental

2.1. Synthesis

$[C_2N_2H_{10}][ScF_5]$ **1** was synthesised hydrothermally. Sc_2O_3 (0.138 g, 1 mmol) was placed into a polypropylene bottle with 0.5 ml 40% HF and 5 ml H_2O. This was heated at 100 °C for one hour, then the contents of the bottle were transferred into a Teflon-lined stainless steel autoclave, with addition of 5 ml ethylene glycol. Ethylenediamine, 99% (0.2 ml) was added to the mixture to give a pH of 3. The autoclave was heated at 190 °C for five days. The product was filtered, washed with water and dried at room temperature to give colourless, needle-like crystals. Elemental analysis, obs. (calc.): C 11.84 (11.89), H 4.73 (4.99), N 13.48 (13.86) %. The observed X-ray powder diffraction pattern is consistent with that simulated on the basis of the crystal structure.

In a previous paper [17] we have reported the isolation of another ethylenediamine-templated scandium fluoride, $[enH_2]_{0.5}$-$[ScF_4]$ **4**. In order to pinpoint the differences in reaction conditions leading to the two different products we carried out a series of reactions of varying HF/en composition as shown in Table 1.

$[NH_4]_2[Sc_3F_{11}]$ **2** was prepared by a similar method. Sc_2O_3 (0.138 g) was placed into a polypropylene bottle with 0.5 ml HF and 5 ml H_2O. This was heated at 100 °C for one hour, then the contents of the bottle were transferred into a Teflon-lined stainless steel autoclave, with addition of 5 ml ethylene glycol and 0.5 ml tris(2-aminoethyl)amine (tren). The autoclave was heated at 180 °C for five days. Initial reaction mixture pH was 9. The product was isolated as hexagonal plate-like crystals. Elemental analysis, obs. (calc.): H 1.93 (2.12), N 7.23 (7.37) %. Sample purity was also demonstrated by agreement of observed and simulated X-ray powder diffraction patterns. For **3**, Sc_2O_3 (0.138 g), 1.5 ml HF and 5 ml H_2O were again subjected to a pre-treatment at 100 °C for one hour, with subsequent addition of 5 ml ethylene glycol and 0.57 g of *trans*-1,4-diaminocyclohexane. The autoclave was heated at 190 °C for five days, with the pH remaining at 3 throughout the reaction. X-ray powder diffraction revealed ScF_3 (PDF no. 44-1096) was present as a significant impurity phase in this product.

Table 1
Reaction conditions leading to crystallisation of **1** and **4**

	Sc_2O_3 (g)	H_2O (ml)	48% HF (ml)	Ethylene glycol (ml)	en (ml)	Initial pH	Product
1	0.138	5	0.5	5	0.065	1	**4**
2	0.138	5	0.5	5	0.1	2	**4**
3	0.138	5	0.5	5	0.2	3	**1**
4	0.138	5	0.5	5	0.4	9	**1**
5	0.138	5	1	5	0.1	1	**4**
6	0.138	5	1	5	0.2	2	**1** and **4**
7	0.138	5	1	5	0.4	3	**1**
8	0.138	5	1	5	0.75	9	**1**
9	0.138	5	0.25	5	0.1	9	ScF_3
10	0.138	5	0.25	5	0.2	10	ScF_3
11	0.138	5	0.25	5	0.4	12	ScF_3

Note: All reactions were carried out for 5 days at 190 °C in 40 ml autoclaves.

Table 2
Crystal data for **1**, **2** and **3**

	1	**2**	**3**
Molecular formula	$C_2H_{10}N_2ScF_5$	$N_2H_8Sc_3F_{11}$	$C_6H_{21}N_2O_2F_6Sc_1$
Crystal system	tetragonal	orthorhombic	monoclinic
Space group	P4/ncc	Cmmm	$P2_1/n$
a/Å	13.035(2)	18.501(12)	9.543(2)
b/Å	$= a$	6.613(5)	6.704(1)
c/Å	8.142(2)	4.025(3)	9.873(2)
β/deg			90.349(5)
V/Å^3	1383.4(5)	492.5(6)	631.6(2)
T/K	125	125	113
Z	8	2	2
Total/unique reflections	6364/639	1595/291	4173/1347
Ind. reflections $> 2\sigma(I)$	455	235	759
$R1\ [I > 2\sigma(I)]$	0.051	0.077	0.058
$wR2\ [I > 2\sigma(I)]$	0.131	0.184	0.144

2.2. Characterisation

Single crystal X-ray diffraction studies were carried out on a Bruker SMART system (for **1** and **2**) or Rigaku Mercury CCD (for **3**) with graphite monochromated MoK_α radiation. Intensity data were collected using 0.3° steps to give at least a full hemisphere of coverage. All data sets were corrected for absorption via multiscan methods. Data analyses used the SHELXS, SHELXL and WINGX packages. Details of the crystal structure determinations are given in Table 2. Powder X-ray diffraction data were collected on a Stoe STADI/P transmission diffractometer using $CuK_{\alpha 1}$ radiation. Thermogravimetric analysis was carried out on a TA Instruments SDT2960 dual TGA/DTA, in the temperature range 25–750 °C, under flowing N_2 at a heating rate of $5\,°C\,min^{-1}$. For **1**, the TGA shows one continuous weight loss of 42.8% between about 250 and 400 °C after which the product is ScF_3 (PDF no. 44-1096; expected weight loss 49.6%). For **2**, one continuous weight loss is also observed (300–410 °C); the product is once again ScF_3 (observed weight loss 19.3%, expected 19.5%).

3. Results and discussion

The crystal structure of **1** is composed of infinite *trans*-vertex sharing $(ScF_5)_\infty$ chains running parallel to the c-axis. The asymmetric unit (Fig. 1) includes two crystallographically distinct Sc sites, both of which are octahedral, with quite regular local geometry (Table 3). Bridging Sc–F bond lengths are somewhat longer than terminal ones as is normally found in such structural moieties. Figs. 2 and 3 show that there are two distinct types of $(ScF_5)_\infty$ chain, with differing chain conformations. Both have 180° Sc–F–Sc angles, but in the Sc(1) chain neighbouring octahedra are eclipsed relative to each other whereas in the Sc(2) chain they are staggered, with a dihedral F–Sc–Sc–F angle of 21.3°. As shown in Table 3, the bond valence sums [18] for the bridging F atoms, F(2) and F(3), are satisfied by bonding to scandium. The net underbonding of the terminal F atoms, F(1) and F(4), is accommodated by these F atoms acting as acceptors for N–H···F hydrogen bonds.

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