

# An organically templated yttrium fluoride with a ‘Super-Diamond’ structure

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## Abstract

An organically templated yttrium fluoride has been prepared hydrothermally and characterised by X-ray powder diffraction. The crystal structure of  $[\text{C}_3\text{N}_2\text{H}_{12}]_{0.5}[\text{Y}_3\text{F}_{10}]$  may be regarded as a ‘Super-Diamond’ framework, space group  $Fd\bar{3}m$ ,  $a = 15.4817(1) \text{ \AA}$ , where each carbon atom site of the diamond structure is replaced by a polyhedral  $[\text{Y}_6\text{F}_8\text{F}_{24/2}]^{2-}$  unit. The basic framework type is isostructural with the known phase  $(\text{H}_3\text{O})[\text{Yb}_3\text{F}_{10}] \cdot \text{H}_2\text{O}$ . The novelty in the present case lies in the use of the organic structure-directing agent 1,3-diaminopropane.

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## 1. Introduction

Despite being well-developed in the field of oxide and oxyanion-based solid-state chemistry, the use of hydrothermal methods, and in particular the exploitation of organic moieties as templates or structure-directing agents, in the preparation of metal fluorides is still relatively unexplored. Bentrup et al. [1] have reviewed the solution-based synthesis of transition metal fluorides templated by organic amines. Most of these materials adopt crystal structures containing isolated, polyhedral  $\text{MF}_x$  units, rather than extended framework structures. More recently, several groups have extended this work to various framework-forming metal fluorides, such as those of aluminium [2], zirconium [3], uranium [4] and beryllium [5], and several extended chain or layer-type structures have been discovered.

In terms of functional materials, metal fluorides often have poorer properties than their oxide counterparts, cooperative phenomena such as electronic conductivity or magnetic ordering being hindered by the more ionic nature

of the  $M\text{--F}$  versus  $M\text{--O}$  bond. Optical properties represent one class of physical property which takes advantage of this higher ionicity [6], with higher bandgaps leading to increased transparency window, and low polarisability leading to lower refractive index. Metal fluorides, and in particular lanthanide-based systems, are thus often excellent materials for applications requiring luminescent behaviour, for example up-conversion of IR to visible light [7,8].

All current materials of this type use simple inorganic fluorides such as  $\text{NaYF}_4$  as host structures for luminescent lanthanide cations. The choice of host structure is therefore currently limited by the relatively narrow field of structural and compositional chemistry of these inorganic fluorides. With this in mind, we have recently initiated an exploratory study of Group III element fluoride hydrothermal chemistry, using organic amines as structure-directing agents, in order to open up a new area of structural solid-state chemistry, and ultimately expand the range of potential luminescence hosts for lanthanide-containing fluorides. Our first examples of organically templated scandium [9,10] and yttrium fluorides [11] have recently been described. We now present the second member of the yttrium fluoride family  $[\text{C}_3\text{N}_2\text{H}_{12}]_{0.5}[\text{Y}_3\text{F}_{10}]$ ,

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which is found to adopt a ‘Super-Diamond’ framework structure [12].

## 2. Experimental

### 2.1. Synthesis

[C<sub>3</sub>N<sub>2</sub>H<sub>12</sub>]<sub>0.5</sub>[Y<sub>3</sub>F<sub>10</sub>] was prepared by hydrothermal reaction. About 0.0383 g Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 5 mL H<sub>2</sub>O and 2 mL HF (48% aq.) were heated in a polypropylene bottle at 100 °C for 1 h. The contents were transferred to a Teflon-lined stainless steel autoclave, washing with 5 mL ethylene glycol. 1.5 mL 1,3-diaminopropane was added to give a gel with a pH of 6, which was heated at 180 °C for 5 days. The pH at the end of this period was 6. The white polycrystalline product was washed with water, filtered and dried at room temperature. Subsequent attempts to prepare single crystals suitable for X-ray analysis were unsuccessful. Powder X-ray diffraction (PXRD) data were collected on a Stoe STADI/P transmission diffractometer using CuKα<sub>1</sub> radiation. Elemental analysis confirmed phase purity (C 3.73%, H 1.21%, N 2.97% (calc. for C<sub>3</sub>H<sub>12</sub>F<sub>20</sub>N<sub>2</sub>Y<sub>6</sub>: C 3.64%, H 1.22%, N 2.83%). Thermogravimetric analysis under N<sub>2</sub> revealed a continuous weight loss of around 2% between room temperature and 400 °C (perhaps due to a small amount of surface or intra-crystalline water), followed by an abrupt loss of about 11% between 400 and 475 °C, corresponding to the loss of organic moiety plus HF; the residue was identified as YF<sub>3</sub> (PDF no. 32-1431) by PXRD.

### 2.2. Structure determination

In the absence of single crystals, the crystal structure was determined from the PXRD data. The pattern was indexed on the basis of the first 20 diffraction maxima, using the algorithm of Visser, within the Stöe WinXPOW software [13]. A face-centred cubic unit cell, with a ~15.48 Å was found, with a figure-of-merit,  $F_{20} = 163$ . A clear resemblance to the structure of the lanthanide fluoride structure type typified by (H<sub>3</sub>O)[Yb<sub>3</sub>F<sub>10</sub>]·H<sub>2</sub>O<sup>12</sup> was apparent, and this was subsequently used as a starting model for a Rietveld analysis, using the GSAS suite [14]. A pseudo-Voigt peak shape was used, which has five refined parameters, including a correction for asymmetry at low  $2\theta$  values. Positions of framework Y and F atoms in space group  $Fd\bar{3}m$  were input from Ref. [12], and these were refined, along with the usual lattice, background and profile parameters. A good-quality Rietveld fit was obtained at this stage ( $R_{wp} = 0.161$ ,  $\chi^2 = 41$ ). Subsequent difference Fourier maps clearly revealed (as the highest peak) a plausible position for the nitrogen atom, within a large open cage of the structure, and within sensible hydrogen-bonding distance of framework F atoms. Unfortunately, unambiguous location of the remaining C atoms of the template directly from the PXRD data proved difficult, due to the inherent disorder expected from the cubic host symmetry.

## 3. Results and discussion

### 3.1. Framework structure

The [Y<sub>3</sub>F<sub>10</sub>]<sup>−</sup> framework structure is represented in Fig. 1(a). This framework is isostructural with that of (H<sub>3</sub>O)[Yb<sub>3</sub>F<sub>10</sub>]·H<sub>2</sub>O<sup>12</sup> and may be described, using the concept of ‘Scale Chemistry’ [15,16] as a ‘Super-Diamond’ network; i.e. a direct analogue of the diamond structure with each carbon atom being replaced by a [Y<sub>6</sub>F<sub>32</sub>]<sup>14−</sup> secondary building unit (SBU). Each yttrium atom is surrounded by 8 fluorine atoms forming a distorted square antiprismatic [YF<sub>8</sub>] primary building unit (PBU), with one square face markedly smaller than the other one. Six of these PBUs are linked together *via* edge sharing, whereby all 4 edges of the smaller square face are shared with neighbouring PBUs, forming the octahedral building unit (SBU) (Fig. 2) at the centre of which is a vacancy. The [Y<sub>6</sub>F<sub>32</sub>] SBUs are further linked into the resultant three-dimensional structure via the F1 vertices, such that the resultant framework formula may be represented as Y<sub>6</sub>F(2)<sub>4</sub>F(3)<sub>4</sub>F(1)<sub>24/2</sub>≡[Y<sub>6</sub>F<sub>20</sub>]<sup>2−</sup>, with Z = 8 SBUs per unit cell. The central vacancy within each SBU is at the position of a carbon atom in the diamond structure (position 8a (1/8, 1/8, 1/8)). For ease of comparison, the ‘classic’ view of the diamond structure is given in Figure 1(b), and the position occupied by the [Y<sub>6</sub>F<sub>32</sub>] SBU in Fig. 1(c). The final atomic coordinates obtained from Rietveld refinement of a completed model are given in Table 1, and bond lengths in Table 2. The final Rietveld fit is given in Fig. 3.

### 3.2. Template location

As stated previously, it proved straightforward to locate the nitrogen atom of the 1,3-diaminopropane cation directly from the Fourier maps during Rietveld analysis. However, due to the inherent disorder of the template moiety in such a high symmetry environment, an unambiguous model of the template position could not be determined from the PXRD data. The template is located in a large polyhedral cage defined by 28 fluorine atoms at the vertices (Fig. 4). The centre of this F<sub>28</sub> cage is at a position 8b ( $\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$ ) of  $\bar{4}3m$  point symmetry. The faces of the F<sub>28</sub> polyhedron consist of four ‘capped’ hexagons, four uncapped hexagons and six rectangles. The nitrogen atom, N(1), located by PXRD lies on a 32e position directly above the uncapped hexagonal face of the F<sub>28</sub> cage, and forms hydrogen bonds (Table 2) with these six F(1) atoms. The N(1) position is 50% occupied; in other words, within any cage, two of the four possible uncapped hexagonal faces are interacting with the template in this manner. A plausible template conformation can therefore be proposed simply by assuming that the central C atom, C(2), of the 1,3-diaminopropane cation lies on the high symmetry 8b position at the centre of the cage. This leads naturally to sensible bond lengths within the template moiety by placing the remaining atom, C(1), at a 96g position shown

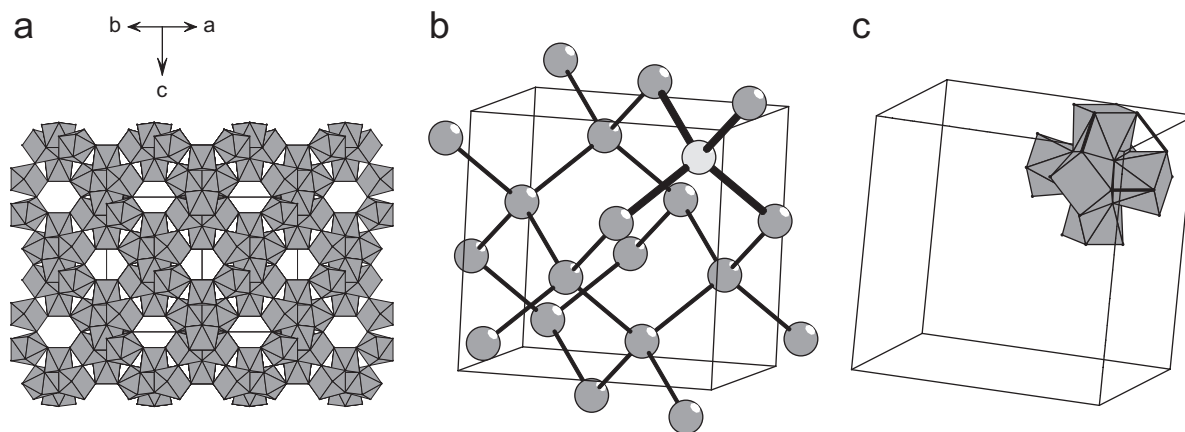


Fig. 1. (a) Polyhedral representation of the  $[Y_3F_{10}]$  framework, which is based on the diamond structure, with the  $[Y_6F_{32}]$  SBU occupying the carbon sites. (b) Corresponding view of the diamond structure, with C atoms represented as spheres. (c) Position occupied by the  $[Y_6F_{32}]$  SBU for ease of comparison with (b). Note that one of the ‘capped’ hexagons is highlighted.

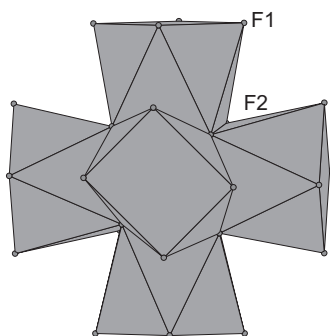


Fig. 2. The  $[Y_6F_{32}]$  SBU.

Table 1  
Refined atomic parameters for  $[C_3N_2H_{12}]_{0.5}[Y_3F_{10}]$ , from Rietveld analysis of the (*syn*, *syn*) model

Atom	Site	Occ.	x	y	z	$U_{iso}$ ( $\times 100$ )
Y(1)	48f	1	0.30245(5)	$\frac{1}{8}$	$\frac{1}{8}$	0.45(2)
F(1)	96h	1	0.3764(2)	0.1264(2)	$\frac{1}{4}$	0.64(7)
F(2)	32e	1	0.2151(2)	0.2151(2)	0.2151(2)	0.64(7)
F(3)	32e	1	0.2031(2)	0.2031(2)	0.0469(2)	0.64(7)
N(1)	32e	$\frac{1}{2}$	0.4519(2)	0.2981(2)	0.2981(2)	2.4(5)
C(1)	96g	$\frac{1}{6}$	0.3632(4)	0.3176(2)	0.3176(2)	2.4(5)
C(2)	32e	$\frac{1}{4}$	0.3402(2)	0.4099(2)	0.3402(2)	2.4(5)

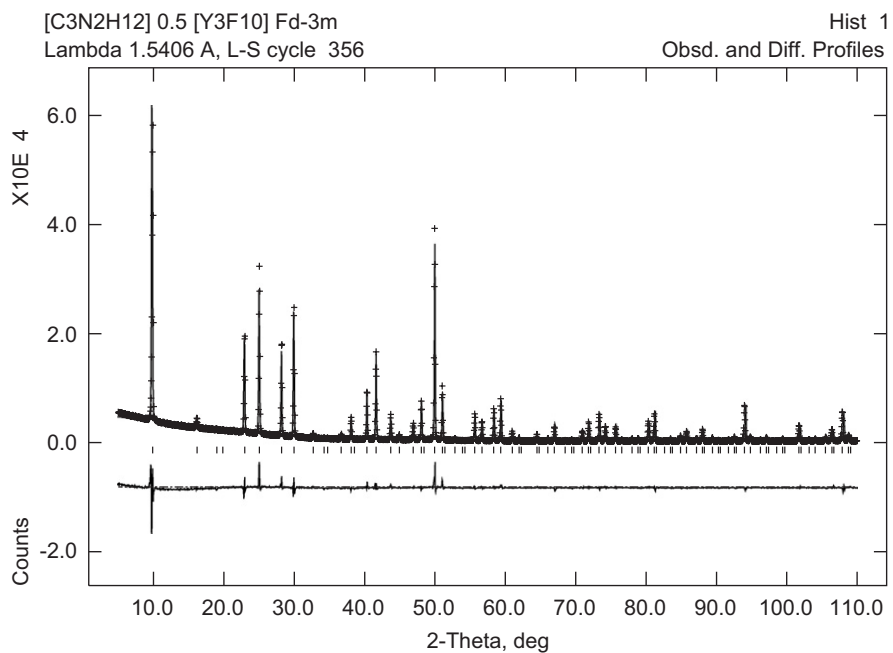
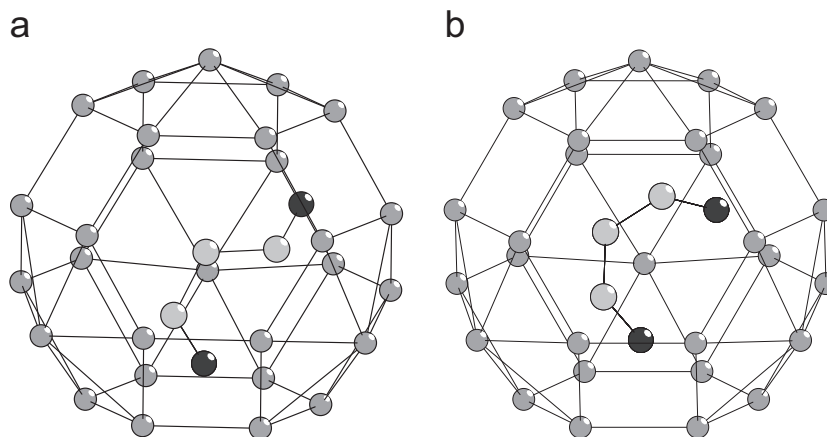
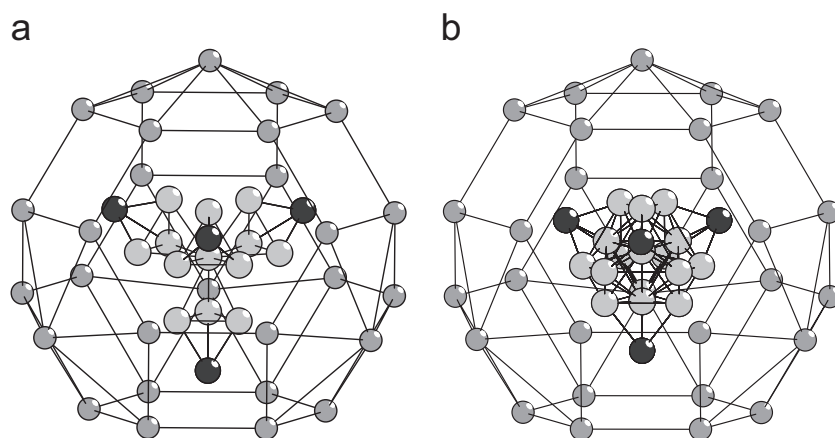
Space group  $Fd\bar{3}m$  (origin choice 2),  $a = 15.4817(1)\text{\AA}$  ( $T = 25^\circ\text{C}$ ),  $R_{wp} = 0.097$ ,  $R(F^2) = 0.064$ ,  $\chi^2 = 14.4$ , for 10,500 data points, 236 contributing reflections, 9 restraints and 31 variables,  $5 < 2\theta < 110^\circ$ .

in Fig. 4a, leading to a (*antiperiplanar*, *synclinal*) conformation (torsion angles approximately  $140^\circ$  and  $30^\circ$ ) for the template. Bond length and angle restraints were applied to this model C–N 1.48 Å, C–C 1.51 Å, C–C–C  $108^\circ$ , N–C–C  $108^\circ$ , and subsequent Rietveld refinement led to a final agreement factors,  $R_{wp} = 0.097$ ,  $\chi^2 = 16.4$ .

Table 2  
Selected bond distances (Å) in  $[C_3N_2H_{12}]_{0.5}[Y_3F_{10}]$

Y(1)–F(1) $\times 4$	2.248(2)	F(1)–F(1) $\times 2$	2.707(4)
Y(1)–F(2) $\times 2$	2.392(2)	F(1)–F(1) $\times 2$	2.766(4)
Y(1)–F(3) $\times 2$	2.300(1)	F(1)–F(2) $\times 2$	2.901(2)
		F(1)–F(3) $\times 2$	3.038(4)
C(1)–N(1)	1.438(4)	F(2)–F(3) $\times 3$	2.618(5)
C(1)–C(2)	1.514(4)		
N(1)–F(1) $\times 6$	2.999(4)		

An alternative position and conformation of the C–C–C backbone of the template can also be proposed, consistent with the positions of the N atoms. This postulated model was therefore also refined against the PXRD data, using the same type of restraints, leading to the resulting position shown in Fig. 4b, and final atomic parameters and agreement factors are given in Table 1. Note that in this case the 1,3-diaminopropane cation adopts a (*synclinal*, *synclinal*) conformation (torsion angles approximately  $80^\circ$  and  $80^\circ$ ). In fact, the main difference between the two template models lies in the position of the central atom C(2), the location of which can only be ‘assumed’ from the PXRD data; the positions of the C(1) and N(1) atoms are within 0.5 Å of each other between the two models. The template locations for the two different models are represented in Fig. 5, in this case showing all possible positions over the disordered sites; the clear similarity of the two, averaged out over the X-ray diffraction length-scale is evident. We conclude that, due to the inherent disorder of the template within the  $F_{28}$  cage, the PXRD data are unable to distinguish definitively between the two models but, intuitively, it might be expected that the (*syn*, *syn*) conformation would be preferred energetically. This is supported by the smaller atomic displacement parameters of the template species, together with marginally better overall  $\chi^2$  for the latter model, despite the identical profile fit; the  $\chi^2$  value takes into account a better fit to the geometrical restraints.

Fig. 3. Final Rietveld plot using the (*syn*, *syn*) template model.Fig. 4. Structure of the F<sub>28</sub> cage showing position of one orientation of the template moiety for: (a) (*syn*, *anti*) model and (b) (*syn*, *syn*) model.Fig. 5. Comparison of the filled F<sub>28</sub> cages showing all possible orientations of the disordered template from: (a) from the (*syn*, *anti*) model and (b) the (*syn*, *syn*) model.

#### 4. Discussion

Courbion and co-workers [12] were the first to report this framework structure type, in  $(\text{H}_3\text{O})[\text{Yb}_3\text{F}_{10}] \cdot \text{H}_2\text{O}$ , and gave an elegant description of this and related complex structures based on simple geometrical stackings of giant polyhedra [15]. Subsequently [17], they prepared a range of derivatives for the smaller lanthanides ( $\text{Er}^{3+}$ – $\text{Lu}^{3+}$ , and  $\text{Y}^{3+}$ ). The large alkali metal cation derivatives could be prepared by direct reaction, whereas  $\text{Li}^+$  and  $\text{Na}^+$  derivatives could only be isolated via ion exchange. In each case zeolitic water was found, with reversible dehydration being observed.

This compound is only the second example of an yttrium (or lanthanide) fluoride incorporating an organic template.  $[\text{C}_2\text{N}_2\text{H}_{10}]_{0.5}[\text{Y}_2\text{F}_7]^{11}$  and  $[\text{C}_3\text{N}_2\text{H}_{12}]_{0.5}[\text{Y}_3\text{F}_{10}]$  both display three-dimensionally connected framework structures, though of a very different nature. Further work is in progress to explore a wider range of organic templates, and also to incorporate photo-active lanthanide cations in order to probe the luminescence properties of this family.

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