

## Crystal Structure of $\text{Th}_6\text{F}_{24} \cdot \text{H}_2\text{O}$

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### Abstract

The crystal structure of  $\text{Th}_6\text{F}_{24} \cdot \text{H}_2\text{O}$  was solved by a three-dimensional X-ray study. Crystal data are: space group  $I4/m$ ,  $Z = 2$ ,  $a = 9.194$  (3),  $c = 11.553$  (4) Å,  $V = 976.57$  Å<sup>3</sup>,  $D_m = 6.31$  (5),  $D_c = 6.35$  Mg m<sup>-3</sup>. The final  $R$  value is 0.061 for 745 reflexions. This compound was falsely known as  $\text{LiTh}_4\text{F}_{17}$ . In fact, no lithium is present and this compound is a new variety of thorium tetrafluoride.

### Introduction

In connexion with a more general study of fluorides of the actinides, we have been particularly interested in the crystal growth of phases appearing in the binary system  $\text{LiF}-\text{ThF}_4$ .

We have developed a new method of growing crystals which has enabled us to synthesize  $\text{LiTh}_4\text{F}_{17}$  as single crystals. However, the preliminary crystal structure analysis led us to question the stoichiometry of this compound. We believed there to be an incompatibility between the number of formula units per unit cell and the space group obtained for the stoichiometry of this compound. Analogous compounds may also be synthesized for uranium, neptunium and plutonium. We therefore thought it important to determine its crystal structure and, from this, its formula.

### Experimental

Single crystals were obtained using a flux-growth method (Cousson, Pagès, Cousseins & Védrine, 1977), and appear in the form of prisms with rectangular bases.

Lattice parameters and systematic absences were determined by a preliminary study of single crystals with Weissenberg and precession photographs and then of powder on a focusing goniometer.

The Laue group  $4/m$  with  $hkl$  present for  $h + k + l = 2n$  indicated the space group to be  $I4/m$ ,  $I4$  or  $I\bar{4}$ .

The density of the crystals was measured by pycnometry in *o*-xylene; it led to  $Z = 3$  in the case of the formula  $\text{LiTh}_4\text{F}_{17}$ , and to  $Z = 12$  for  $\text{ThF}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

The absence of Li was confirmed by fast- $\gamma$ -ray spectroscopy. With the help of Dr B. Borderie we created a set-up which enabled us to determine the Li/F ratio using fast- $\gamma$ -ray spectroscopy of the single crystal used for intensity measurement (Borderie, Pinault & Barrandon, 1977). The ratio obtained was less than one Li atom to every 100 F atoms. In fact, the measurement in this case becomes a measurement of the background. Since this method is very sensitive, especially for lithium, we can conclude that no lithium was present in the single crystal.

The single crystal used (of dimensions  $0.048 \times 0.059 \times 0.122$  mm) was a prism elongated along the [001] axis.

Measurements were made with the Nonius CAD-4 four-circle diffractometer of the Centre de Mesures Physiques de Clermont Ferrand. Data-collection conditions were: Mo  $K\alpha$  radiation with graphite monochromator,  $\omega-2\theta$  scan,  $\theta_{\text{max}} = 40^\circ$ , scan range:  $(1 + 0.35 \tan \theta)^\circ$ . We worked with the bisect mode. 1712 reflexions were recorded. The intensities of three standard reflexions were checked hourly and the orientation was checked after every hundred reflexions (standard reflexions: 600, 060, 006). The relative

Table 1. Atomic positional parameters ( $\times 10^4$ ) and isotropic temperature factors

	Position	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Th(1)	8( <i>h</i> )	1841 (2)	3842 (1)	0	1.3
Th(2)	4( <i>e</i> )	0	0	2097 (1)	1.3
H <sub>2</sub> O	2( <i>a</i> )	0	0	0	5.7
F(1)	8( <i>g</i> )	0	$\frac{1}{2}$	1126 (22)	1.7
F(2)	8( <i>h</i> )	3643 (26)	2060 (39)	0	2.9
F(3)	16( <i>i</i> )	919 (20)	2103 (19)	1242 (15)	2.1
F(4)	16( <i>i</i> )	2030 (20)	639 (22)	3248 (18)	2.8

standard deviation on the control marks is 0.018. After Lorentz-polarization corrections, 846 positive reflexions remained, of which 776 were independent. Maximum indices were 16 for  $h$  and  $k$ , and 20 for  $l$ .

The linear absorption coefficient for Mo  $K\alpha$  is  $53.1 \text{ mm}^{-1}$ . Absorption corrections were made using de Meleunaer and Tompa's analytical method (Ahmed, 1974) with the program *AGNOST*.

### Structure determination and refinement

The packing was determined by classical methods. A three-dimensional Patterson map yielded the positions of the Th atoms. A difference Fourier synthesis was carried out using these data and enabled all the F atoms to be located. An expansion of the observed structure factors in a Fourier series was also carried out, after they had been multiplied by a filter function (Tournarie, 1964).

All refinement calculations were made using the program *AFFINE*, which is a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The scattering factors used are those given in *International Tables for X-ray Crystallography* (1974). Anomalous dispersion was taken into account.

This structure was refined in the space group  $I4/m$ . A set of three-dimensional refinements was made on the heavy atoms only and corrected in three different cycles the  $k$  scale factor, the coordinates and the individual anisotropic thermal parameters. The evolution of the calculations is matched by the variation of the two agreement coefficients:  $R = \sum (|F_o| - k|F_c|) / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$  where  $F_o$  and  $F_c$  are the observed and calculated structure factors,  $k$  is the scale factor and  $w$  is a statistical weight given to each  $F_o$ .

A second series of refinements was made on the Th and F atoms, giving each an individual isotropic then an anisotropic temperature factor.

Omitting the 31 weakest reflexions, we obtained  $R = 0.061$  and  $R_w = 0.077$  for the 745 remaining reflexions.

Finally, 12 Th atoms and 50 F atoms were located in this space group, which is incompatible with the electrostatic neutrality. The packing is such that the presence of Li in this structure is impossible, apart from which the absence of Li has been confirmed by fast- $\gamma$ -ray spectroscopy. We have therefore been led to consider the formula  $(48\text{F}^- + 2X)$ ,  $X$  being a neutral entity. The electron density of this entity is close to that of a F atom.

This entity could be either a hydrogen fluoride molecule or a water molecule. Since single crystals were prepared in chloride solutions, and although the compounds were degassed under high vacuum, it seems more probable that a water molecule may have been trapped. This water molecule could have entered the

structure when we washed and separated the crystals from the flux with very hot water.

### Discussion

Atomic parameters are listed in Table 1, and interatomic distances in Table 2.\* Fig. 1 is an ideal projection of the structure on the  $xy0$  plane. The structure contains two independent Th atoms. Th(1) has eight-coordination; its coordination polyhedron is a trigonal bipyramid. There are pyramids on two of the rectangular faces, formed by F(2) atoms. The triangular base is formed by the F(1) atom, located at the 8(g) site, and by the F(3) and F(4) atoms which are not located at any particular site. The last two form the base of the antiprism in which the Th(2) atoms are located.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34440 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* ( $\text{\AA}$ )

	Number at this distance		Number at this distance		
Th(1)-F(3)	2	2.31 (2)	F(1)-F(4)	2	2.88 (2)
Th(1)-F(2)	1	2.32 (2)	F(1)-F(1)	1	3.18 (5)
Th(1)-F(4)	2	2.32 (2)	F(2)-F(4)	2	2.86 (3)
Th(1)-F(2)	1	2.33 (3)	F(2)-F(3)	2	2.88 (3)
Th(1)-F(1)	2	2.38 (1)	F(2)-F(4)	2	2.99 (3)
Th(2)-F(3)	4	2.33 (2)	F(2)-F(3)	2	3.40 (4)
Th(2)-F(4)	4	2.37 (2)	F(3)-F(4)	1	2.73 (3)
Th(2)-H <sub>2</sub> O	1	2.422 (3)	F(3)-F(4)	2	2.87 (3)
H <sub>2</sub> O-F(3)	8	2.55 (2)	F(3)-F(3)	1	2.87 (3)
F(1)-F(1)	1	2.60 (5)	F(3)-F(3)	2	2.98 (3)
F(1)-F(2)	2	2.61 (3)	F(4)-F(4)	2	2.77 (3)
F(1)-F(3)	2	2.80 (2)			

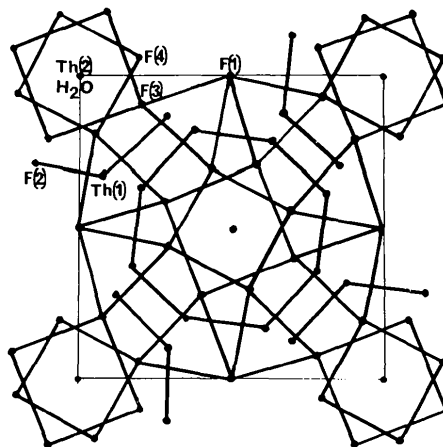


Fig. 1. Ideal projection of the structure on to the (001) plane.

The Th(1) and F(2) atoms are located in the same type of crystallographic site. They are therefore situated in the  $xy0$  and  $xy\frac{1}{2}$  planes. The Th(1) polyhedra are linked together by F(2) atoms forming rings in those two planes. These rings are made up of four Th polyhedra linked by four F(2) atoms. Also two adjacent rings in the same planes are linked together by a F(1) edge. This gives a two-dimensional aspect to the structure. Inside each ring, the F(3) and F(4) corners of the polyhedra each form a cube. These cubes form infinite spirals along the  $c$  axis. This piling up creates antiprisms between the cubes, in which the Th(2) atoms are located. The cubes formed by the F(3) atoms are smaller than those formed by the F(4) atoms, but since they alternate in the chains the antiprisms are identical. Each F(3) cube contains the neutral entity. The presence of the Th(2) atom in the antiprism gives a three-dimensional aspect to the structure.

Taking no account of the neutral entity, the Th(2) atom also has eight-coordination. Each F atom is linked to two Th atoms; therefore, electrostatically speaking, its charge is always  $-1$ . This compound,  $\text{Th}_6\text{F}_{24} \cdot \text{H}_2\text{O}$ , was falsely known as  $\text{LiTh}_4\text{F}_{17}$ . Because of the three-dimensional aspect of this structure and its

ionic character, it is the most stable of all compounds encountered in the  $\text{LiF}-\text{ThF}_4$  system. Analogous compounds have been obtained for uranium, neptunium and plutonium. Although there is no lithium present in the structure, we feel certain that its presence is necessary for the preparation of the compounds. The neutral entity, however, might not be indispensable to the structure. A neutron diffraction analysis should determine whether it is  $\text{H}_2\text{O}$  or  $\text{HF}$ .

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