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## The Crystal Structure of $\text{Li}_3\text{ThF}_7$

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The crystal structure  $\text{Li}_3\text{ThF}_7$  has been solved by the Patterson method. Crystal data are: space group  $P4/ncc$ ,  $Z = 4$ ,  $a = 6.206$ ,  $c = 12.940$  Å. The final  $R$  value is 0.031 for 507 observed reflexions. The Th coordination polyhedron is unusual for complex fluoride actinides in that it is a square antiprism with a pyramid on one of the square faces.

### Introduction

In connexion with a more general study of mixed fluorides of the actinides and of the fluorides of the monovalent elements, we felt it appropriate to undertake a complete crystal structure analysis of  $\text{Li}_3\text{ThF}_7$ . The space group and the number of formula units per cell both suggested that the Th atom would occupy a single site and that the compound might show interesting optical properties.

### Experimental

Single crystals have been obtained using the flux growth method (Cousson, Pagès, Cousseins & Vedrine, 1977) and appear in the form of colourless rods and plates.

Lattice parameters and systematic absences were determined by a preliminary study first of single crystals with Weissenberg-camera and precession photographs, then of powder on a focusing goniometer:  $a = 6.206 \pm 0.002$ ,  $c = 12.940 \pm 0.005$  Å;  $h k 0$ ,

$h + k = 2n + 1$ ;  $0kl$ ,  $l = 2n + 1$ ;  $hhl$ ,  $l = 2n + 1$ . Cu  $K\bar{\alpha}$  and Mo  $K\bar{\alpha}$  radiations were used.

The density of the crystals was measured by pycnometry in *o*-xylene, and the value obtained combined with the calculated density leads to  $Z = 4$ .

The 3/7 stoichiometric ratio for Li/F was confirmed by Borderie, Pinault & Barrandon (1977) using fast  $\gamma$ -ray spectrometry.

A single crystal,  $0.002 \times 0.0052 \times 0.0276$  cm, was used for measuring the diffracted intensities with the Nonius CAD-4 four-circle diffractometer of the Centre de Mesures Physiques de Clermont-Ferrand. Data-collection conditions were: Mo  $K\bar{\alpha}$  radiation with graphite monochromator,  $\omega$ - $2\theta$  scan,  $\theta_{\max} = 50^\circ$ , scanning range:  $(1 + 0.35 \tan \theta)^\circ$ , variable scan rate: from 5 to  $1.54^\circ \text{ min}^{-1}$  for more accurate measurements of intensities. We used the sub-program *FLAT*, which optimizes the measurements in the case of plate-shaped crystals. The row normal to this plate is [001]. All 1411 reflexions out to  $2\theta = 100^\circ$  were recorded, 880 of which were unobserved. The intensity of three standard reflexions was checked hourly and the orientation every 100 reflexions (standard reflexions:

600; 060; 0,0,10). The relative standard deviation is 0.02. After Lorentz-polarization correction, 531 positive reflexions remain. Maximum indices are 13 for  $h$  and  $k$ , 27 for  $l$ .

The linear absorption coefficient for Mo  $K\alpha$  is 344  $\text{cm}^{-1}$ . Absorption corrections were made with de Meulenaer and Tompa's analytical method, with the program *AGNOST* (Ahmed, 1974).

### Structure determination and refinement

Packing was determined by classical methods. A Patterson map yielded the positions of the Th atoms. With this data, a Fourier difference synthesis determined the positions of all F atoms. An expansion of the observed structure factors in a Fourier series was carried out after they were multiplied by a filter function (Tournarie, 1964). Positions of the Li atoms located with the series were specified through maps with very close steps for  $(x, y, 0)$  and  $(x, y, \frac{1}{4})$ .

The structure was refined by iterative least-squares adjustment with *AFFINE*, a modification of the Busing, Martin & Levy (1962) computer program. The scattering factors used were those given in *International Tables for X-ray Crystallography* (1974). For Th and F, anomalous dispersion was taken into account. With a series of three-dimensional refinements on the heavy atoms only, the  $K$  scale factor, the coordinates and the individual isotropic temperature factors were successively corrected, in three different cycles.

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, respectively, the observed and calculated structure factors,  $K$  is the scale factor and  $w$  a statistical weight given to each  $F_o$ . A second series of refinements was made on the Th and F atoms, each given an individual isotropic temperature factor, then anisotropic factors. Since no correction of the primary and secondary extinctions was made, we omitted the two reflexions (110, 220) which were most affected, at low  $\theta$ , by this systematic error. We then introduced the Li atoms and, after leaving out the 22 weakest planes, obtained  $R = 0.031$  and  $R_w = 0.04$  for the remaining 507 reflexions.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33334 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances*

	Number at this distance	Distance (Å)	$\sigma$ (Å)
Li(1)-F(2)	4	1.750	0.008
Li(2)-F(3)	1	1.726	0.064
Li(2)-F(3)	2	1.935	0.035
Li(2)-Li(2)	1	2.031	0.125
Li(2)-F(2)	2	2.320	0.011
Li(2)-Th	2	2.613	0.028
Th-F(2)	4	2.357	0.008
Th-F(1)	1	2.383	0.017
Th-F(3)	4	2.395	0.003
F(1)-F(3)	4	2.767	0.010
F(1)-F(2)	4	2.945	0.008
F(1)-F(2)	4	3.234	0.015
F(2)-F(2)	2	2.634	0.011
F(2)-F(3)	1	2.699	0.010
F(2)-F(3)	1	2.822	0.009
F(2)-F(2)	2	2.853	0.013
F(2)-F(2)	1	2.867	0.015
F(2)-F(2)	1	2.870	0.015
F(2)-F(3)	1	3.340	0.011
F(3)-F(3)	4	3.198	0.004
F(3)-F(3)	1	3.295	0.026

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

Position	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )	
Th	4(c)	2500 (0)	2500 (0)	1890 (1)	0.5
Li(1)	4(b)	2500 (0)	7500 (0)	0 (0)	7.2 (1.6)
Li(2)	8(f)	6343 (149)	-6343 (149)	7500 (0)	9.8 (1.4)
F(1)	4(c)	2500 (0)	2500 (0)	3732 (16)	1.7
F(2)	16(g)	1610 (14)	-366 (15)	775 (7)	1.2
F(3)	8(f)	623 (18)	-623 (18)	7500 (0)	1.5

Table 2. *Anisotropic thermal parameters ( $\times 10^4$ ) in the form:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$*

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Th	31 (1)	31 (1)	7 (0)	0 (0)	0 (0)	0 (0)
F(1)	151 (23)	151 (23)	8 (1)	0 (0)	0 (0)	0 (0)
F(2)	81 (12)	81 (13)	16 (3)	-12 (11)	-6 (5)	-13 (5)
F(3)	77 (14)	77 (14)	31 (4)	-11 (18)	6 (7)	-6 (7)

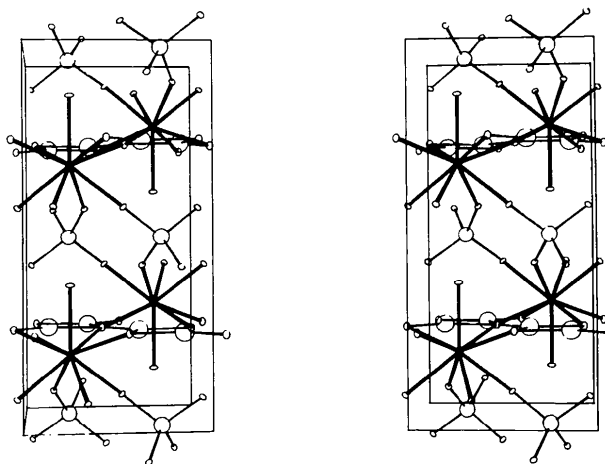


Fig. 1. Stereoscopic view of the packing.

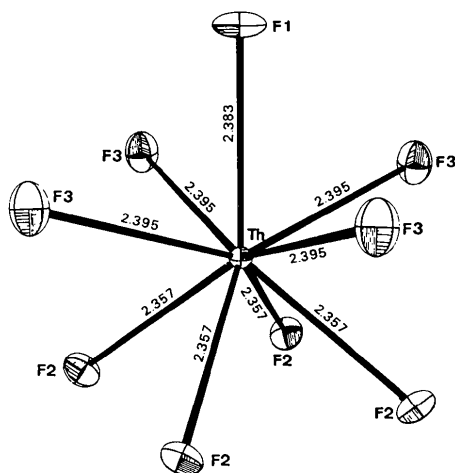


Fig. 2. Thorium polyhedron.

### Discussion

Atomic parameters are listed in Table 1, thermal parameters in Table 2 and interatomic distances in Table 3. Computer program *ORTEP* (Johnson, 1965) was used to draw Figs. 1 and 2, representing a stereoscopic view of the packing and the Th polyhedron. Thermal motions are represented by 50% probability ellipsoids.

The Th polyhedron is a square antiprism. It has a pyramid on one of the square faces because of F(1), which is located, like the Th atom, on the quaternary axis. This F atom is attached to no other cation. The structure can be described as a head-to-tail stacking of these antiprisms along the quaternary axis.

The  $(x, y, \frac{1}{4})$  and  $(x, y, \frac{3}{4})$  planes are F(3) and Li(2) layers. These atoms are located on the same crystallographic  $8(f)$  site. Each F(3) atom is linked to two Th atoms and three Li(2) atoms. F(3) atoms form the base of the pyramid of the Th polyhedron. These polyhedra

share a corner [F(3)] and form infinite chains parallel to the  $[110]$  and  $[\bar{1}\bar{1}0]$  directions. The two remaining rhombic cavities hold two Li(2) atoms each. The 2.03 Å Li(2)–Li(2) distance indicates that this atom has a coordination of three. The distance to the two other closest neighbours [F(2) atoms] is 2.32 Å.

The F(2) atoms enclose tetrahedral cavities which are occupied by Li(1). Therefore, each F(2) anion is linked to a Th atom and to a Li ion.

### Conclusion

The Th coordination polyhedron is unusual for complex fluoride actinides in that it is a square antiprism with a pyramid on one of the square faces. The three-coordination of Li(2) – due to the distribution in a single plane of this cation and the F(3) atoms – is also unprecedented.

Finally, it should be noted that the heavy atom is located in a single crystallographic site (point group of symmetry: quaternary axis). This compound is therefore an interesting matrix for receiving  $M^{4+}$  ions with the  $5f^q$  electronic structure.

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