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Crystal structure of Li₂Th₅F₂₂·LiOH

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Abstract

The crystal structure of Li₂Th₅F₂₂.LiOH, $M_r = 1616 \cdot 02$, was solved by Patterson and difference syntheses, and refined by least-squares methods. Crystal data are: space group $P42_12$, $Z = 2$, $a = 11 \cdot 307$, $c = 6 \cdot 390$ (2) Å, $D_m = 6 \cdot 33$ (5), $D_x = 6 \cdot 57$ Mg m⁻³, $V = 816 \cdot 95$ Å³. The final R value is $0 \cdot 032$ for 561 reflexions. The formula of the single crystal used to measure the intensities was determined using fast γ-ray spectroscopy. This compound was falsely known as LiTh₂F₉.

Introduction

A new method of growing crystals enabled us to synthesize LiTh₂F₉ as single crystals. The preliminary crystal structure analysis showed an incompatibility between the number of formula units per unit cell and the space group obtained. This led us to question the formula of this compound. Therefore, we undertook its complete crystal structure analysis.

Experimental

Single crystals were obtained using the flux-growth method and appeared as colourless prisms.

Lattice parameters and systematic absences ($hk0$ with $h + k = 2n$) were determined by a preliminary study of single crystals with Weissenberg and precession photographs and then of powder on a focusing goniometer. Cu $K\bar{\alpha}$ and Mo $K\bar{\alpha}$ radiations were used.

The density of the crystals, measured by picnometry in *o*-xylene, led to $Z = 2$ for the formula Li₂Th₅F₂₂.LiOH, instead of $Z = 5$ for LiTh₂F₉ (Cousson, Pagès, Cousseins & Védrine, 1977).

With the help of Dr B. Borderie we created a set up which enabled us to determine the Li/F ratio using fast γ-ray spectroscopy of the single crystal used for intensity measurement (Borderie, Pinault & Barrandon, 1977). The detection limits obtained for a sample of niobium were as follows: approximately 1 p.p.m. for the light elements Li and F.

The single crystal used (of dimensions 0·038 × 0·035 × 0·164 mm) was a square 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 $K\bar{\alpha}$ radiation with a graphite monochromator, ω–2θ scan, $\theta_{max} = 40°$, scan range: $(1 + 0 \cdot 35 \tan \theta)°$. 1445 reflexions were recorded of which 864 were unobserved. This high number of unobserved reflexions indicates an I sublattice. The intensities of three standard reflexions were checked hourly and the orientation after every hundred reflexions (standard reflexions: 600, 060, 0,0,10). The relative standard deviation is 0·02. Maximum indices are 20 for h and k, and 11 for l. The linear absorption coefficient

for Mo $K\bar{\alpha}$ is 50·7 mm^{-1}. Absorption corrections were made using the de Meleunaer and Tompa analytical method (Ahmed, 1974) with the program *AGNOST*.

Structure determination and refinement

The packing was determined by classical methods. A Patterson map yielded the positions of the Th atoms. These positions are such that the Th atoms cannot be located in space group $P4/nmm$ determined in the preliminary study. We then tried $P4/n$ in which the heavy atoms could be distributed. The ten Th atoms separate into two different sites:

$$2(c) \quad \tfrac{1}{4} \ \tfrac{1}{4} \ z \qquad\qquad z \simeq \tfrac{1}{2}$$
$$8(g) \quad x \ y \ z \quad x \simeq 0·39 \quad y \simeq -0·11 \quad z \simeq -\tfrac{1}{4}.$$

The peculiar values of the $8(g)$ position explain the observed $4/mmm$ Laue group. A series of three-dimensional refinements was made on the heavy atoms only. It corrected in three cycles, respectively, 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 respectively the observed and calculated structure factors and w a statistical weight given to each F_o. The refinements were made from the 581 observed reflexions, uniformly weighted, and led to $R = 0·135$.

A difference Fourier synthesis was made from these data; it did not enable us to locate all the F atoms.

The anisotropic thermal tensors of the heavy atoms are negative. The same phenomenon is observed in space groups $P4$ and $P\bar{4}$. We had to return to space groups of the $4/mmm$ Laue group, with a $P.2_1.$ diffraction symbol. In space group $P42_12$, the Th atoms separate into three independent sites:

$$2(c) \quad 0 \ \tfrac{1}{2} \ z \quad z \simeq \tfrac{1}{4}$$
$$4(e) \quad x \ x \ 0 \quad x \simeq \tfrac{3}{8}$$
$$4(f) \quad x \ x \ \tfrac{1}{2} \quad x \simeq \tfrac{1}{8}.$$

This structure was refined using sub-programs *PATCH* and *RESET*, which take into account the restrictions due to the unusual positions of the Th atoms [$x = y$, $\beta_{11} = \beta_{22}$ and $\beta_{23} = -\beta_{13}$ for the $4(e)$ and $4(f)$ sites, and $\beta_{11} = \beta_{22}$ for the $2(c)$ site]. This refinement led to $R = 0·069$. The thermal parameters show no further peculiarities. At this stage, a difference Fourier synthesis yielded the positions of all the F atoms. A second series of refinements was made on the Th and the eight independent F atoms, which led to $R = 0·040$.

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 by the series were specified through maps with very small steps. Since no correction for primary and secondary extinction was made, we omitted the six reflexions most affected by this systematic error. Leaving the Th and F atoms fixed, we then introduced the Li atoms and varied k (the scale factor), the lithium z coordinate and then its isotropic temperature factor. Finally, after leaving out the 14 weakest reflexions, for the 561 remaining reflexions we obtained $R = 0·032$ and $R_w = 0·039$.*

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. Although the space group is not centro-symmetric, the absolute configuration could not be determined, because of the centrosymmetrical distribution of the heavy atoms. Finally, ten Th, four Li and 46 F atoms were located in this space group, which is incompatible with electrostatic neutrality. It is impossible to place two more Li atoms in this space group, so there must be 44 F$^-$ + $2X$ atoms, X being a neutral entity with the same electron density as a F$^-$ ion. Fast γ-ray spectroscopy showed six Li atoms for every 44 F atoms. The experimental value for the ratio Li/F is (Li/F) = 0·049 $\pm$ 0·002, the calculated value for the ratio 3Li/22F is 0·0498. This means that some Li must be present in the neutral entity X, but that there cannot be any more F atoms present. This leads to $X = $ LiOH.

Discussion

Atomic parameters with B_{eq} for each atom are listed in Table 1, and interatomic distances in Table 2. Fig. 1 is an ideal projection on the $xy0$ plane.

There are three independent Th atoms in this structure. The Th(1) and Th(2) atoms have nine-coordination. Their polyhedra are tri-capped trigonal prisms, and share a corner. These polyhedra form infinite zigzag chains along the c axis. They have a pyramid on each of their three rectangular faces, formed by the F(6) and F(7) atoms for one Th atom, and the F(1) and F(4) atoms for the other. The F(2), F(3) and F(5) atoms form the bases of these trigonal polyhedra, and the F(5) atom is the common corner. The F(2) and F(3) atoms make up the base of the octahedral cavities which hold the Li atoms. These Li octahedra are linked together by their F(6) and F(7) corners and form

Table 1. *Atom positional parameters* ($\times 10^4$ *for* Th, $\times 10^3$ *for* Li, F *and* OH) *and isotropic temperature factors*

	Position	x	y	z	B ($\mathring{A}^2$)
Li	4(d)	0 (0)	0 (0)	242 (45)	5·6 (1·3)
Th(1)	4(f)	1434 (2)	1434 (2)	$\frac{1}{2}$ (0)	0·5
Th(2)	4(e)	3552 (2)	3552 (2)	0 (0)	0·3
Th(3)	2(c)	0 (0)	$\frac{1}{2}$ (0)	2754 (4)	0·5
F(1)	8(g)	153 (3)	408 (2)	52 (3)	1·5
F(2)	8(g)	325 (3)	506 (4)	251 (3)	2·5
F(3)	8(g)	198 (2)	−9 (4)	248 (3)	1·8
F(4)	8(g)	84 (3)	355 (3)	448 (3)	1·7
F(5)	8(g)	265 (3)	234 (4)	239 (3)	1·7
F(6)	2(a)	0 (0)	0 (0)	0 (0)	1·8
F(7)	2(b)	0 (0)	0 (0)	$\frac{1}{2}$ (0)	3·1
OH	2(c)	0 (0)	$\frac{1}{2}$ (0)	−297 (5)	7·0

Table 2. *Interatomic distances* ($\mathring{A}$)

	Number at this distance			Number at this distance	
Li–F(6)	1	1·5 (3)	F(3)–F(4)	1	2·83 (3)
Li–F(7)	1	1·6 (3)	F(3)–F(5)	1	2·85 (6)
Li–F(2)	2	1·98 (3)	F(4)–F(4)	2	2·68 (4)
Li–F(3)	2	2·24 (2)	F(4)–F(5)	1	2·80 (4)
Li–Th(2)	2	2·8 (2)	F(4)–F(5)	1	2·81 (4)
Li–Th(1)	2	2·8 (2)	F(5)–F(5)	1	3·09 (3)
F(1)–F(2)	1	2·58 (4)	F(6)–F(7)	2	3·195 (2)
F(1)–F(5)	1	2·62 (4)	OH–F(4)	4	2·498 (35)
F(1)–F(5)	1	2·63 (3)	OH–F(1)	4	3·008 (35)
F(1)–F(4)	1	2·71 (3)	OH–F(3)	4	3·43 (2)
F(1)–F(3)	1	2·73 (3)	Th(1)–F(2)	2	2·25 (3)
F(1)–F(1)	2	2·85 (4)	Th(1)–F(7)	1	2·293 (4)
F(1)–F(4)	1	3·22 (3)	Th(1)–F(5)	2	2·39 (3)
F(1)–F(2)	1	3·36 (4)	Th(1)–F(3)	2	2·44 (3)
F(2)–F(7)	1	2·54 (3)	Th(1)–F(4)	2	2·51 (3)
F(2)–F(6)	1	2·55 (3)	Th(2)–F(3)	2	2·29 (3)
F(2)–F(4)	1	2·55 (4)	Th(2)–F(5)	2	2·291 (3)
F(2)–F(3)	1	2·97 (5)	Th(2)–F(6)	1	2·316 (3)
F(2)–F(5)	1	3·00 (5)	Th(2)–F(2)	2	2·36 (3)
F(2)–F(5)	1	3·01 (5)	Th(2)–F(1)	2	2·39 (3)
F(2)–F(5)	1	3·14 (6)	Th(3)–F(4)	4	2·19 (3)
F(2)–F(3)	1	3·20 (3)	Th(3)–F(1)	4	2·47 (3)
F(2)–F(3)	1	3·22 (3)	Th(3)–OH	1	2·73 (3)
F(3)–F(5)	1	2·67 (5)			
F(3)–F(6)	1	2·74 (2)			
F(3)–F(7)	1	2·76 (2)			

infinite chains parallel to the c axis. The F(1) and F(4) atoms form a square antiprism which encloses the Th(3) atom. The antiprisms are not linked to each other.

The LiOH neutral entity occupies the same type of site as Th(3). In the LiOH structure the Li atom has tetrahedral coordination (Ernst, 1933), and the OH⁻ ion is located in a site of $4mm$ symmetry, above a
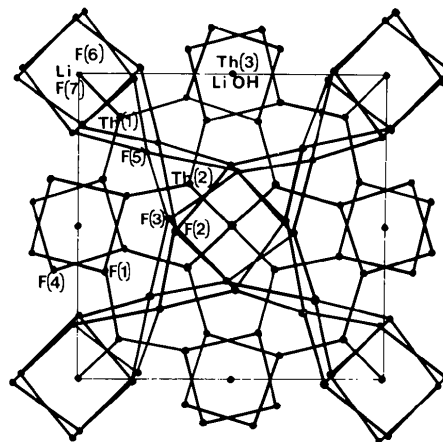

Fig. 1. Projection of the structure of $Li_2Th_5F_{22}.LiOH$ on to the (001) plane.

square with Li atoms at the corners. In this case, the symmetry of the site of the neutral entity is a quaternary axis. We can assume that the OH⁻ ion is located on the quaternary axis and that it is also above a square, the corners of which are Li ions. However, in this case there is only one Li atom. To simulate a square under it, the OH⁻ ion must be delocalized. Using X-rays we determined the position of the O atom of the neutral entity but we could not locate the Li atom. It was observed that the O atom is closer to F(4) than to F(1). It is also closer to the Th(3) atom of its own cell than to that of the cell above it.

Because of the asymmetric position of the OH⁻ ion with respect to the Th atoms it seems more probable that the Li atom is located near F(1). A neutron diffraction analysis should yield the position of the Li atom.

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