Journal of Fluorine Chemistry, 42 (1989) 41–50

Received February 1, 1988, accepted June 17, 1988

CRYSTALLINE Li_3ThF_7 : X-RAY DIFFRACTION AND NMR STUDIES

Sandra Helena PULCINELLI
Universidade de Sao Paulo, Faculdade de Ciencias Farmaceuticas de Ribeirao Preto, Via do Café, s/n°, 14100, Ribeiro Preto, SP (Brazil)

Regina Helena de Almeida SANTOS
Universidade de Sao Paulo, Instituto de Fisica e Quimica de Sao Carlos, C.P. 369, 13560, Sao Carlos, SP (Brazil)

and Jean SENEGAS
Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex (France)

SUMMARY

A crystal structure determination of Li_3ThF_7 has been performed on a tetragonal single crystal by X-ray diffraction : a = 6.200 (1) Å; c = 12.937 (2) Å ; Z = 4 ; P4/ncc. The structure is characterized by layers of monocapped antiprism $|ThF_9|$ polyhedra sharing 4 corners in the a,b plane. The lithium atoms are localized between these layers and bridge $|ThF_9|$ polyhedra along the c-axis. There is a 1:3 disorder of lithium atoms in the Wyckoff sites 8f and 16g.

NMR studies show that the rapid exchange of the lithium ions between non equivalent sites modulates the electric field gradient seen by individual lithium atoms and can explain the behavior of the ^7Li quadrupolar effect observed in crystalline phases. Calculations of the main component of the electric field gradients tensor according to the different sites of the lithium atoms indicate a partial covalent character of the Th-F bond.

INTRODUCTION

Crystalline phase Li_3ThF_7 was synthesised from vitreous phase $Li_{0.75}Th_{0.25}F_{1.75}$ [1] by melting followed by slow cooling. Two different

0022-1139/89/$3 50

prismatic monocrystals were found in which were selected by color, pulverized and examined by polycristalline X-ray diffraction using the Guinier technique. The diffractograms were however the same tetragonal system; a = 6.206 Å , c = 6.470 Å ; Z = 2 ; possible space groups : P4/n or P4/nmm compatible with Harris et al. [2].

It was clear that only one phase has been prepared and that the color of monocrystals were due to the surface aderence effects. Cousson et al., 1977 studying a single crystal by the Weissenberg method suggested the space group P4/nnc with a double c paramaters and Z.

DATA COLLECTION AND CALCULATION

As thorium absorbs X-ray strongly, for this study we chose a single crystal which was submitted to a special treatment to obtain a spherical form [3].

Using the spherical monocrystal (R = 0.0125 cm) in a CAD-4 automatic diffractometer, crystallographic parameters were determined as : a = 6.200 (1) A ; c = 12.937 (2) Å ; V = 497.301 (2) Å ; $d_{obs.}$ = 4.73 (5) g/cm^3 ; $d_{calc.}$ = 4.784 g/cm^3 ; Z = 4 ; tetragonal space group P4/ncc.

X-ray intensities of 2373 reflections (972 with $I > 3\sigma(I)$) were collected using MoKα radiation monochromated using a graphite monocrystal, zigzag mode, $0 \leq \theta \leq 45°$; $0 \leq h \leq 12$; $0 \leq k \leq 12$; $0 \leq l \leq 25$.

Data reduction was carried out using Lorentz, polarization and absorption (μ = 267.93 cm^{-1}) correction by a spherical model [4].
Maximal, minimal and mean transmission coefficients were 5.78 ; 1.59 and 3.77 respectively.

STRUCTURE DETERMINATION AND REFINEMENT

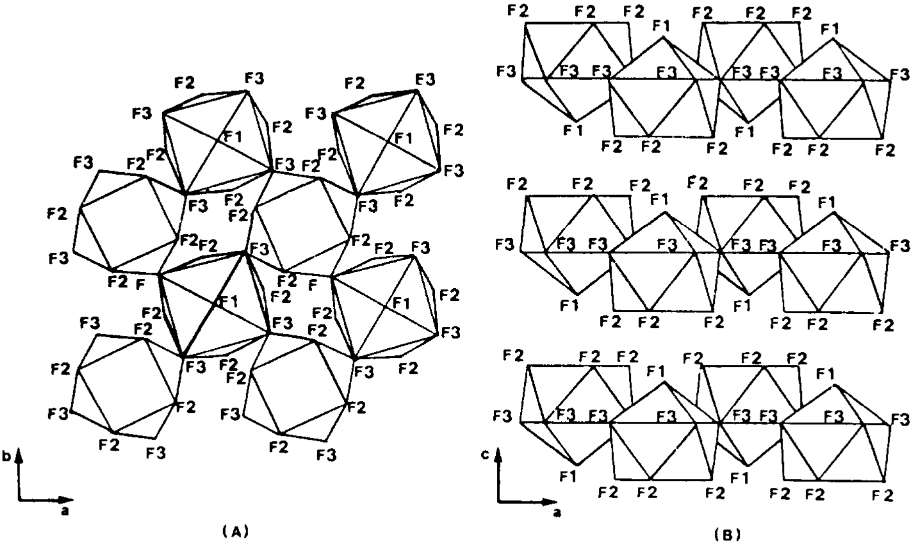
The structure was solved by the Patterson method using the space group P4/ncc with the origin on the center of symmetry. In the map, thorium and one of the fluorine atoms were localized on 4c sites. The positions of the other fluorine atoms were determined by Difference-Fourier Synthesis (on 16g (F2) and 8f (F3) sites), after least square refinement of positional and vibrational parameters for Th and F1 atoms.

Anisotropic temperature parameters were refined and convergency was obtained on R = 0.0492. The lithium atom positions were determined by Difference-Fourier, lying on 8f (Li1) and 16g (Li2) sites. Refinement made with alternately isotropic thermal vibrational parameters and site occupation factors for lithium atoms showed that there is a 1·3 disorder of lithium atoms in the sites 8 f and 16 g.

Final refinement adding crystal size and extinction corrections using weight $w = k/(\sigma(F^2) + c\ F^2)$, with k = 0.2305 and c = 0.00198, showed R_f = 0.0203 and R_w = 0.0227.

RESULTS AND DISCUSSION OF STRUCTURE

The crystalline structure of Li_3ThF_7 is formed by layers of thorium polyhedra $|ThF_9|$. These polyhedra, monocapped antiprisms (9 corners and 13 faces), share 4 corners in the a, b plane. A projection of $|ThF_9|$ polyhedra with fluorine atoms identified, along c and b crystallographic axes is shown in Fig. 1.



(A) (B)

Fig. 1. Projection of $|ThF_9|$ polyhedra with fluorine atoms identified, along c and b crystallographic axes.

Positional and equivalent thermal vibrational parameters for all atoms and occupation factors for lithium atoms are given in Table I.

TABLE I

Positional and equivalent thermal vibrational parameters for all atoms and occupation factors for lithium atoms.

Atom	x/a	y/b	z/c	Biso(Å^2)	Occupation Factor
Th	0.2500(0)	0.2500(0)	0.1899(0)	0.487(6)	
F1	0.2500(0)	0.2500(0)	0.3715(4)	1.2(1)	
F2	0.1620(6)	-0.0382(6)	0.0760(2)	1.30(8)	
F3	0.9347(3)	0.0651(7)	0.2500(0)	1.39(9)	
Li1	-0.037(3)	0.175(3)	0.408(1)	5.3(3)	0.559(3)
Li2	-0.70(1)	1.70(1)	0.2500(0)	7.1(4)	0.197(3)

In Table II are shown the anisotropic thermal vibrational parameters for thorium and fluorine atoms.

Figure 2 shows the evolution of the |ThF_9| polyhedra along the c crystallographic axis. Distances and angles between fluorine atoms in |ThF_9| polyhedra are given in Table III.

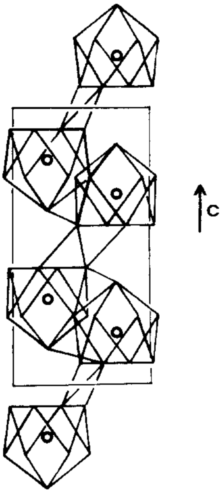


Fig. 2. View of |ThF_9| polyhedra along the c crystallographic axis.

TABLE II

Anisotropic thermal vibrational parameters for thorium and fluorine atoms.

Atom	u_{11} (Å²)	u_{22} (Å²)	u_{33} (Å²)	u_{23} (Å²)	u_{13} (Å²)	u_{12} (Å²)
Th	0.0069(1)	0 0069(1)	0.0047(1)	0.0000(0)	0.0000(0)	0 0000(0)
F1	0.018(2)	0 018(2)	0 011(2)	0.0000(0)	0.0000(0)	0.0000(0)
F2	0.019(1)	0 021(2)	0 010(1)	-0 004(1)	0.0004(1)	-0 004(1)
F3	0 015(1)	0 015(1)	0.022(2)	0 004(6)	-0.004(6)	-0 005(2)

TABLE III

Distances and angles between fluorine atoms in $|ThF_9|$ polyhedra.

Atom			Distance(Å)		Angle(°)
A	B	C	AB	BC	ABC
F3	F1	F3	2.753(5)	2 753(5)	71.03(9)
F2	F2	F2	2 651(7)	2 651(7)	90 00(0)
F2	F2	F3	2.651(7)	2.725(5)	63.31(3)
F2	F3	F3	2.725(5)	3 199(2)	62.18(7)
F1	F3	F3	2.725(5)	3 199(2)	54 48(8)
F2	F3	F2	2 823(4)	2.823(4)	56.80(4)
F2	F3	F3	2.823(4)	3 199(2)	56.08(6)
F3	F3	F3	3 199(2)	3 199(2)	90.00(0)

Using the distances between thorium and fluorine atoms (center and corners of $|ThF_9|$ polyhedra) : d_{Th-F1} = 2.362 (5) Å ; d_{Th-F2} = 2.371 (6) Å ; d_{Th-F3} = 2.399 (4) Å, the bond-valency of thorium was calculated [5] (Σ s = 3.91 uv) comparable with the theoretical value ($s_{theor.}$ = 3.88 uv) and with a coordination number 9 for thorium. The poyhedral distortion calculated is 20.9.

Lithium atoms are localized between layers of $|ThF_9|$ polyhedra and are responsible for holding the structure together. Due to the disorder of site occupation by lithium atoms in this structure there is a superposition of the lithium coordination polyhedra, forbidding the complete determination of its coordination number.

Lithium atoms layers cross the c crystallographic axis at approximately 0, 1/4, 1/2 and 3/4 of z fractional coordinates.

As P4/ncc is a supergroup of P4/nmm, the structure of Li_3ThF_7 determined in this subgroup allow disorder of fluorine atoms F2 and F3, which would adopt a 1/2 occupation factor.

Distances and angles between all the atoms and observed and calculated structure factors are available for the authors.

NUCLEAR MAGNETIC RESONANCE STUDIES

Polycrystalline Li_3ThF_7 was studied by ^{19}F and ^7Li nuclear magnetic resonance as a function of temperature.

No thermal change of absorption line width (17 KHz) of the ^{19}F resonance was observed between 296 and 393 K (Fig.3), showing that the fluorine jump frequency is smaller than this value, i.e., the residence time on a site is greater than 60 μs.

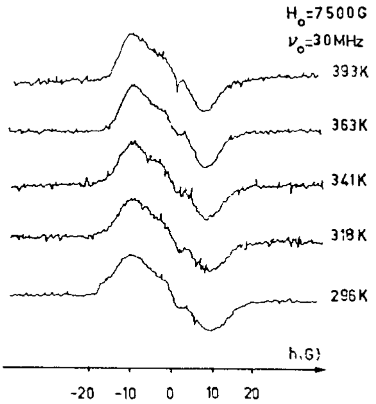


Fig. 3. Thermal change of ^{19}F NMR spectra for polycrystalline Li_3ThF_7.

The thermal evolution of the ^7Li resonance line shape between 273 and 473 K is shown in Figure 4 and it is observed that at 273 K the line, width (8 KHz), does not have a gaussian shape. A continuous line narrowing with increasing temperature is observed. At approximately 333 K two symmetric satellites (quadrupolar splitting, ν_m = 17 KHz) characteristic of the first order quadrupolar effect of ^7Li are observed. The central line narrows up to ΔH_{pp} = 0.2 G (of the same order as for field inhomogeneity). The central line width for a rigid lithium lattice could not be determined experimentally, but the activation energy due to the lithium motions was estimated from its thermal behavior (E_{Li} = 0.15 (3) eV).

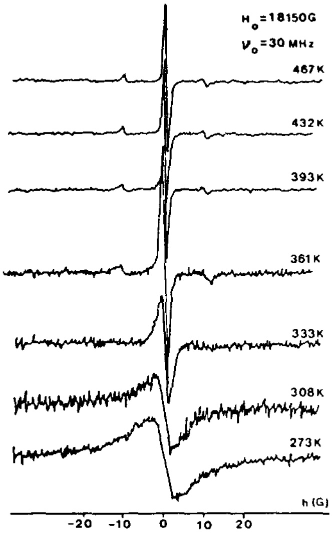


Fig. 4 . Thermal change of ^{7}Li NMR spectra for polycrystalline Li_3ThF_7.

Up to 333 K there are no satellites as can be explained, on the one side by dipolar broadening of the central line, on the other by frequency stretching due to a possible superposition of the quadrupole splitting because of the two non equivalent sites occupied by lithium atoms.

ELECTRIC FIELD GRADIENT CALCULATIONS

The ^{7}Li quadrupolar effect may be explained by the exchange of the Li^+ between non equivalent sites averaging the electric field gradients seen by an individual lithium.

From Li_3ThF_7 structural data, it is possible to calculate the main components of the electric field gradient [6] for each lithium site. These calculations were carried out using the EFG program [7].

As this fluoride is highly ionic, it is reasonable to use a ponctual charge model. The lithium charge was taken as +1 but to allow for a degree of covalency for the Th-F bond calculations were made for different charge values for Th($+4 \geqslant q \geqslant +2.5$) and F($-1 \leqslant q' \leqslant -0.79$), using: $Li^+Th^{+q}F^{-q'}$, $|q'| = (q+3)/7$.

The quadrupolar interaction [8] is :

$$\nu_Q = \frac{3eq}{2I(I-1)h} V_{zz}$$

where Q is the quadrupolar moment and V_{zz} the main component of the electric field gradient tensor. For ^{7}Li (I = 3/2),

$$\nu_Q = 2 \frac{eQ}{h} V_{zz}$$

For polycrystalline samples it is only possible to measure ν_m ($\nu_m = \eta_Q(1 - \eta)$, where η is the assymetric factor defined by:

$$\eta = \frac{|V_{xx} - V_{yy}|}{V_{zz}}$$

with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ limiting η, *i.e.*, $0 \leq \eta \leq 1$.

In the Li_3ThF_7 crystalline structure the 12 lithium atoms occupy two different sites · 9 lithium atoms (Li1) are distributed on 16 g sites, characterised by $\eta \neq 0$, while 3 lithium atoms (Li2) are distributed on 8f sites, characterized by $\eta = 0$ (Table IV).

The observed satellite splitting (ν_m = 19 KHz) at 333 K can be attributed to either Li1 ($\eta \neq 0$) or to Li2 ($\eta = 0$).

On the first hypothesis the quadrupolar interaction seen by the lithium Li1 changes from 56 to 240 KHz depending on the thorium charge ($+4 \geq q \geq +2.5$). The ν_{Q_2} interaction, seen by the lithium Li2, is calculated by ν_{Q2}/ν_{Q1} which is equal to Vzz_2/Vzz_1 between EFG tensor components along z related to Li1 and Li2. This interaction changes, with thorium charge, from 6.2 to 45 KHz.

On the second hypothesis the quadrupolar interaction ν_{Q_2}, seen by Li2 is constant and equal to 19 KHz ($\eta = 0$) , meanwhile ν_{Q_1}, seen by Li1 changes from 173 to 100 KHz and $\nu_{Q_1}(1 - \eta)$ from 58 to 8 KHz with changes in thorium charge.

It can be seen that, for a likely formal charge of approximately +3 for thorium, the quadrupolar splitting for lithiums Li1 and Li2 are close for both hypotheses. The thermal change of the lithium resonance spectra can be explained on both hypotheses.

So, up to 273 K lithium atoms are fixed, *i.e.*, their jump frequency is less than 8 KHz. Between 273 and 333 K the line narrowing observed is due to local motions, *i.e.* between the Li1 sites (9 Li1/16 sites) and between the Li2 sites (3 Li2/8 sites). Above 333 K a rapid exchange between lithiums in different sites averages the electric field gradients. The jump frequency is about 18 KHz and the satellites disappear.

TABLE IV

Main axis of the electric field gradient tensor, assymetric factor, coupling constants and quadrupolar splitting for the lithium atoms Li1 and Li2 in Li_3ThF_7.

atom	atomic positions			Th charge	EFG tensor, main components			assymmetrical factor	Hypothesis 1		Hypothesis 2	
									quadrupolar interaction	theoretical quadrupolar splitting	quadrupolar interaction	theoretical quadrupolar splitting
	x	y	z	q^+	V_{xx}	V_{yy}	V_{zz}	η	ν_Q (KHz)	$\nu_Q(1-\eta)$ (KHz)	ν_Q (KHz)	$\nu_Q(1-\eta)$ (KHz)
Li1 (16g)	-0 0372	0 1748	0.4077	4 0	0.1378	0.6775	-0.8152	0.662	56	19	173	58
				3.5	0.1000	0.6667	-0.7667	0.739	73	19	146	38
				3.0	0.0629	0.6559	-0.7188	0.825	108	$\boxed{19}$	119	$\boxed{21}$
				2.5	0.0265	0.6452	-0.6717	0.921	240	19	100	8
Li2 (8f)	-0.6978	0.6978	0.2500	4.0	0 0448	0.0448	-0.0897	0.0	6.2	6.2	19	19
				3.5	0.0511	0.0511	-0.1022	0.0	9.7	9.7	19	19
				3.0	0.0574	0.0574	-0.1148	0.0	17	$\boxed{17}$	19	$\boxed{19}$
				2.5	0.0637	0.0637	-0.1273	0.0	45	45	19	19

CONCLUSIONS

The crystal structure of Li_3ThF_7, characterized by $|ThF_9|$ polyhedral layers, is the main reason for the lithium atoms mobility. With increasing temperature lithium structural disorder is favoured and the increasing lithium mobility with rised temperature is in good agreement with the 1.3 disorder of lithium atoms in the Wyckoff sites 8f and 16g.

A plausible formal charge +3 obtained for the thorium atoms from electric field gradient calculations indicates partial covalent character for the Th-F bonds.

The rapid exchange of the lithium ions between non equivalent sites modulates the electric field gradient seen by individual lithiums and can explain the behaviour of the ^7Li quadrupolar effect.

ACKNOWLEDGEMENT

One of us (S.H.P.) thanks the CNPq (Conselho Nacional de Desenvolvimento Cientifico et Technologico, Brasil) for a support provided by a grant n° 300201/84-QU.

REFERENCES

1 S.H. Pulcinelli and J. Sénégas, J. Fluorine Chem., 38 (1988) 375.
2 L.A. Harris, G.D. White and R.E. Thoma, J. Phys. Chem., 63, (1959) 1974.
3 C. Lariucci, G. Santarini, Private communication (1986).
4 SAC EXE, 'Structure Determination Package', USA (1982).
5 I.D. Brown and R.D. Shannon, Acta Cryst., 266 (1973).
6 H. Eyring, J.L. Walter and G.E. Kimball, 'Quantum Chemistry', Wiley, London (1960).
7 J. Pannetier, 'Programme EFGDIR', Université de Rennes, France (1967).
8 J.M. Crettez, E. Coquet, J. Pannetier, J. Bonillot and M. Durand Le Floch, J. Sol. State Chem., 56 (1985) 133.