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The Crystal Structure of Lithium Hydrazinium Fluoroberyllate

BY M. R. ANDERSON, I. D. BROWN AND S. VILMINOT*

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada

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Abstract. At room temperature crystals of lithium hydrazinium fluoroberyllate, $\text{Li}(\text{N}_2\text{H}_5)\text{BeF}_4$, are orthorhombic, space group $Pna2_1$, with $a=9.811$ (4), $b=8.880$ (8), and $c=5.139$ (4) Å, $Z=4$. The structure was refined by least squares with X-ray diffractometer measurements to give an $R(\text{weighted})=0.039$. The

lithium and beryllium atoms are at the centres of corner-sharing fluorine tetrahedra. The hydrazinium ions lie in channels in the resultant framework so as to form infinite hydrogen-bonded chains along the [001] screw axes. The average Li-F and Be-F bond distances are 1.853 and 1.546 Å respectively. Unlike the corresponding sulphate whose N-H...O bonds are single, this structure has single, bifurcated and trifurcated N-H...F bonds.

* On leave from Laboratoire de Chimie Minérale, E.R.A. 314, Chimie des Matériaux, Faculté des Sciences, Place Eugène Bataillon, 34060 Montpellier, France.

Table 1. *Crystal data for* $\text{Li}(\text{N}_2\text{H}_5)\text{BeF}_4$ *and* $\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$

Estimated standard deviations are in parentheses.

System Space group	Li(N ₂ H ₅)BeF ₄		Li(N ₂ H ₅)SO ₄
	This work Orthorhombic <i>Pna</i> 2 ₁	Tedenac <i>et al.</i> (1971) Orthorhombic <i>Pna</i> 2 ₁	Anderson & Brown (1972) Orthorhombic <i>Pna</i> 2 ₁
<i>a</i>	9.811 (4) Å	9.820 (5) Å	9.929 (5) Å
<i>b</i>	8.880 (8)	8.896 (5)	8.973 (3)
<i>c</i>	5.139 (4)	5.142 (5)	5.181 (2)
<i>V</i>	447.7 (6) Å ³	449.2 (8) Å ³	461.6 (6) Å ³
<i>D</i> _{calc}	1.854 g cm ⁻³	1.848 g cm ⁻³	1.958 g cm ⁻³
<i>Z</i>	4	4	4
Absorption coefficient for Mo <i>K</i> α	2.50 cm ⁻¹		6.03 cm ⁻¹
Systematic absences			
0 <i>kl</i>	$k+l=2n+1$		
<i>h</i> 0 <i>l</i>	$h=2n+1$		

Table 2. *Parameters derived from the final least-squares refinement*

The expressions used for the temperature factors are:

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hlc^*a^*)]$$

and

$$\exp \left[-2\pi^2 U \left(\frac{2 \sin \theta}{\lambda} \right)^2 \right].$$

Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Li	0.322 (1)	0.436 (1)	0.251 (2)	0.019 (2)	0.023 (3)	0.021 (3)	-0.001 (2)	-0.004 (3)	-0.002 (3)
N(1)	0.0225 (4)	0.4116 (4)	0.7455†	0.033 (2)	0.028 (2)	0.034 (2)	-0.007 (1)	0.000 (2)	0.004 (2)
N(2)	0.4422 (3)	0.2228 (4)	0.742 (1)	0.027 (1)	0.026 (1)	0.026 (2)	0.002 (1)	0.001 (2)	0.004 (2)
Be	0.1584 (4)	0.1270 (5)	0.248 (1)	0.015 (1)	0.020 (2)	0.016 (2)	-0.001 (1)	-0.002 (2)	-0.001 (2)
F(1)	0.1958 (2)	0.1051 (2)	0.540 (1)	0.035 (1)	0.025 (1)	0.018 (1)	-0.003 (1)	-0.004 (1)	0.002 (1)
F(2)	0.0002 (2)	0.1433 (3)	0.231 (1)	0.016 (1)	0.040 (1)	0.031 (1)	-0.003 (1)	-0.001 (1)	0.006 (1)
F(3)	0.2249 (2)	0.2701 (2)	0.141 (1)	0.029 (1)	0.023 (1)	0.026 (1)	-0.010 (1)	0.000 (1)	0.003 (1)
F(4)	0.2983 (2)	0.4881 (2)	0.591 (1)	0.036 (1)	0.025 (1)	0.022 (1)	-0.006 (1)	0.004 (1)	-0.008 (1)
H(1)	0.097 (6)	0.389 (6)	0.803 (17)	0.049 (19)					
H(2)	0.011 (5)	0.463 (5)	0.598 (11)	0.013 (12)					
H(3)	0.362 (4)	0.192 (5)	0.690 (12)	0.018 (13)					
H(4)	0.450 (7)	0.259 (8)	0.908 (15)	0.033 (20)					
H(5)	0.472 (6)	0.296 (7)	0.614 (16)	0.025 (19)					

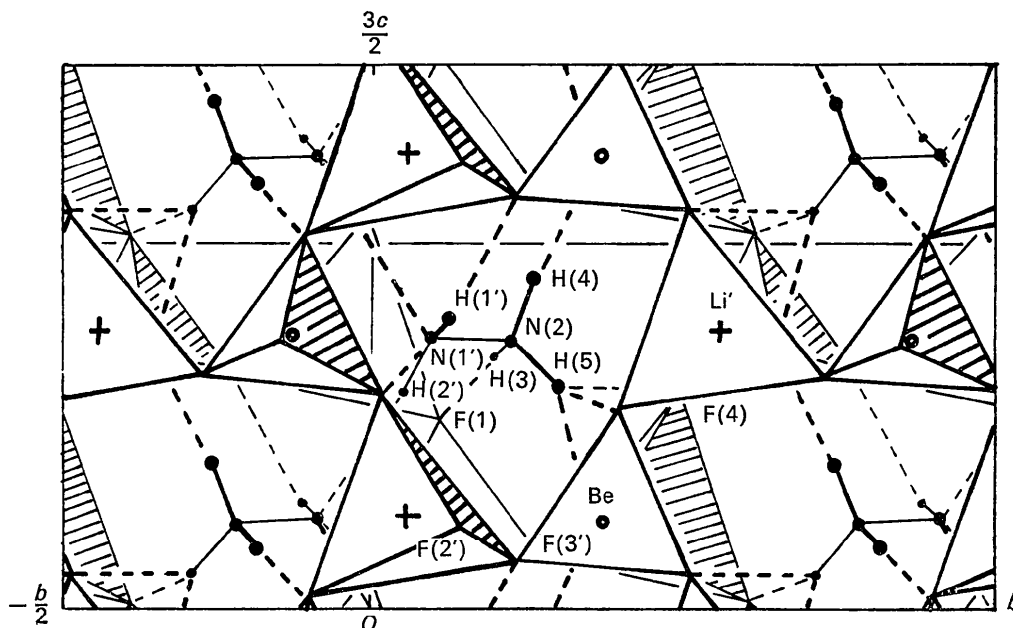
† This parameter was used to define the origin and was not refined.

Introduction. Lithium hydrazinium fluoroberyllate was prepared by the action of $(\text{N}_2\text{H}_6)\text{BeF}_4$ on Li_2CO_3 and crystals were grown by evaporation from an aqueous solution (Tedenac, Vilminot, Cot, Norbert & Maurin, 1971). X-ray diffraction measurements were made at room temperature on a single crystal with dimensions $0.13 \times 0.13 \times 0.2$ mm on a Syntex four-circle automatic diffractometer. Graphite-monochromated $\text{Mo K}\alpha$ radiation was used, $\lambda = 0.71069$ Å. The lattice parameters (Table 1) were refined by a least-squares analysis of the 2θ settings of 15 reflexions. The space group, $Pna2_1$, was confirmed by systematic absences observed on precession photographs and the successful refinement of the structure in an acentric cell. The intensities of 700 independent reflexions with $\sin \theta/\lambda \leq 0.704$ Å⁻¹ were measured and corrected for Lorentz and polarization effects but not for absorption.

Lithium hydrazinium fluoroberyllate was assumed to be isostructural with lithium hydrazinium sulphate and the coordinates of Padmanabhan & Balasubramanian (1967) were used as a basis for the refinement. Initial refinement of the heavy atoms with the full-matrix least-squares program *ORFLS* of the XRAY67 programme library system gave an $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$ of 0.076. A difference map was used to locate the hydrogen atoms and, after further refinement with isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for all other atoms, R was reduced to 0.040. Three reflexions showed significant effects of extinction and the final cycles of refinement used the local least-squares program *CUDLS* in which extinction corrected values of F_c , given by $F_c^* = KF_c [1 + 0.88 \times 10^{-6} \times \beta(2\theta)F_c^2]^{-1/2}$ (Larson, 1967), were used. With a Cruickshank weighting scheme (Cruickshank, Pilling, Bujosa, Lovell

Table 3. Bond distances and angles

BeF ₄ tetrahedron	
Be-F(1)	1.557 (9) Å
Be-F(2)	1.561 (4)
Be-F(3)	1.532 (5)
Be-F(4)	1.534 (6)
F(1)-Be-F(2)	107.6 (4)°
F(1)-Be-F(3)	110.5 (4)
F(1)-Be-F(4)	109.9 (3)
F(2)-Be-F(3)	109.0 (3)
F(2)-Be-F(4)	108.6 (3)
F(3)-Be-F(4)	111.1 (4)
LiF ₄ tetrahedron	
Li-F(1)	1.861 (8) Å
Li-F(2)	1.886 (6)
Li-F(3)	1.842 (7)
Li-F(4)	1.825 (10)
F(1)-Li-F(2)	110.8 (4)°
F(1)-Li-F(3)	114.8 (5)
F(1)-Li-F(4)	109.8 (4)
F(2)-Li-F(3)	99.6 (3)
F(2)-Li-F(4)	105.5 (4)
F(3)-Li-F(4)	115.6 (4)
H ₂ N ₅ ion	
N(1)-N(2)	1.431 (5) Å
N(1)-H(1)	0.81 (6)
N(1)-H(2)	0.89 (5)
N(2)-H(3)	0.87 (5)
N(2)-H(4)	0.91 (8)
N(2)-H(5)	0.97 (7)
N(2)-N(1)-H(1)	107 (4)°
N(2)-N(1)-H(2)	110 (3)
H(1)-N(1)-H(2)	123 (6)
N(1)-N(2)-H(3)	104 (3)
N(1)-N(2)-H(4)	104 (4)
N(1)-N(2)-H(5)	114 (4)
H(3)-N(2)-H(4)	118 (6)
H(3)-N(2)-H(5)	105 (5)
H(4)-N(2)-H(5)	112 (6)

Fig. 1. Structure of $\text{Li}(\text{N}_2\text{H}_5)\text{BeF}_4$ projected down a .

& Truter, 1961) the final $R_2 = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$ was 0.039 where $\omega = (0.26 - 0.018|F_o| + 0.00059|F_o|^2)^{-1}$, and unobserved reflexions were given zero weight if $|F_c| < |F_o|$. The final atomic parameters and temperature factors are given in Table 2.*

Description of the structure. $\text{Li}(\text{N}_2\text{H}_5)\text{BeF}_4$ is isostructural with $\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$ (Brown, 1964); but with differences in the hydrogen-bonding arrangement. Views of the structure along *a* and *c* are given in Figs. 1 and 2.

The structure is composed of a framework of corner-sharing LiF_4 and BeF_4 tetrahedra with channels which run along the *c* direction. The hydrazinium ions lie in these channels with the N-N bond perpendicular to the channel. As in the case of the sulphate, the $-\text{NH}_2$ groups are hydrogen bonded into infinite chains. The bond lengths and angles are given in Table 3.

The BeF_4 and LiF_4 tetrahedra are nearly regular with mean Be-F and Li-F bond lengths of 1.546 and 1.853 Å respectively. The bonds from both Be and Li to F(3) and F(4) are significantly shorter than those to F(1) and (2) which each accept a strong single hydrogen bond. In addition each fluorine atom accepts one or two weak bifurcated or trifurcated hydrogen bonds.

N(1), the nitrogen atom of the $-\text{NH}_2$ group, is involved in three hydrogen bonds, twice as a donor and once as an acceptor. The angles of the bonds around both nitrogen atoms do not differ significantly from 109° and the $-\text{NH}_3$ group is staggered with respect to the $-\text{NH}_2$ group and its lone pair.

The N(1) atoms are hydrogen bonded into chains parallel to *c*; the $\text{N}(1)-\text{H}(2)\cdots\text{N}(1')$ distance is 3.043 (4) Å and the angle at H(2) is 178° . These strong

* The list of observed and calculated structure factors can be found in Anderson (1973), and has also been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30161 (6 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Hydrogen bond lengths (Å) and angles (°) and the dihedral angles (°) of the N_2H_5 ion*

D-H...A	D-H	H...A	D-A	D-H...A
N(1)H(1)F(3)	0.81 (6)	2.39 (7)	3.103 (5)	148 (6)
N(1)H(1)F(4)		2.42 (6)	2.902 (5)	119 (6)
N(1)H(2)N(1')	0.89 (5)	2.15 (5)	3.044 (3)	178 (5)
N(2)H(3)F(1)	0.87 (5)	1.96 (5)	2.832 (5)	172 (6)
N(2)H(4)F(2)	0.91 (8)	1.93 (7)	2.834 (8)	168 (5)
N(2)H(5)F(4)	0.97 (7)	2.41 (6)	2.855 (5)	107 (4)
N(2)H(5)F(2)		2.06 (8)	2.941 (8)	150 (6)
N(2)H(5)F(1)		2.40 (6)	3.099 (5)	129 (5)
Plane defined by atoms	Plane defined by atoms	Dihedral angle		
N(1)N(2)H(1)	N(1)N(2)H(2)	-136		
N(1)N(2)H(1)	N(1)N(2)H(2')	94		
N(1)N(2)H(1)	N(1)N(2)H(3)	176		
N(1)N(2)H(3)	N(1)N(2)H(4)	-125		
N(1)N(2)H(3)	N(1)N(2)H(5)	114		

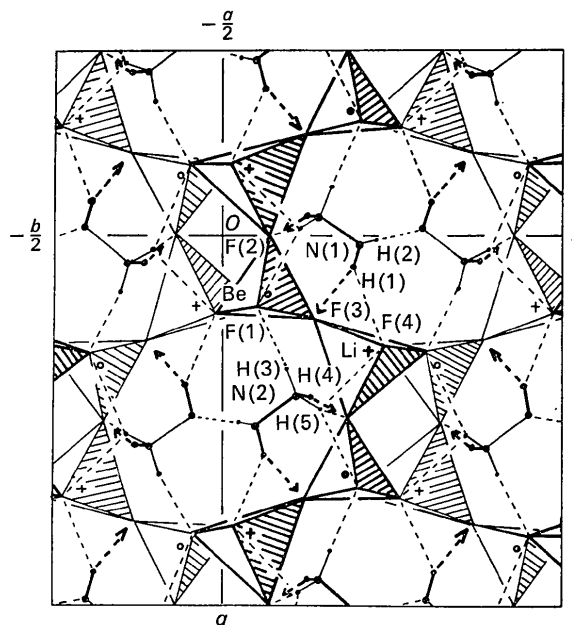


Fig. 2. Structure of $\text{Li}(\text{N}_2\text{H}_5)\text{BeF}_4$ projected down *c*.

bonds cause the N(1)-H(1) donor bond to lie in an unfavourable direction for the formation of a short, linear and hence strong hydrogen bond with any of the fluorine atoms. H(1) thus forms a bifurcated bond with F(3) and F(4).

The staggered configuration of the hydrazinium ion results in both H(3) and H(4) forming strong bonds to F(1) and F(2) respectively but H(5) is positioned so that there is no suitable acceptor for a strong bond. A trifurcated bond is thus formed between H(5) and the three fluorine atoms, F(1), F(2) and F(4). The hydrogen bond lengths and angles are given in Table 4 with the dihedral angles of the N_2H_5 ion.

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