

SHORT STRUCTURAL PAPERS

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Acta Cryst. (1973). B29, 1352

Lithium Hexafluorotitanate Dihydrate and Lithium Hexafluorostannate Dihydrate

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(Received 12 January 1973; accepted 21 February 1973)

Abstract. Lithium hexafluorotitanate dihydrate: monoclinic, $C2/m$, $a = 10.294(1)$, $b = 5.934(2)$, $c = 4.8032(5)$ Å, $\beta = 90.13(8)^\circ$; formula $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$, $Z = 2$, $D_m = 2.46(9)$, $D_c = 2.35$. The crystals were prepared by crystallization of commercial Li_2TiF_6 from 40% aqueous HF. The structure was refined by least-squares methods to give a weighted $R_2 = 0.10$ for 463 photographically measured structure factors. The structure consists of a hexagonal close-packed array ($c = \text{hexagonal axis}$) of fluorine and water molecules with lithium and titanium in distorted octahedral interstices (mean $\text{Ti-F} = 1.94$, $\text{Li-F} = 2.18$, $\text{Li-O} = 2.05$ Å). A hydrogen-bonding scheme is proposed. Lithium hexafluorostannate dihydrate: monoclinic, $C2/m$, $a = 9.818(3)$, $b = 6.101(2)$, $c = 4.7270(6)$ Å, $\beta = 90.96(8)^\circ$; formula $\text{Li}_2\text{SnF}_6 \cdot 2\text{H}_2\text{O}$, $Z = 2$, $D_m = 3.40(9)$, $D_c = 3.26$. The crystals were prepared by crystallization of commercial Li_2SnF_6 from 40% aqueous HF. The structure was refined by least-squares methods to give a weighted $R_2 = 0.078$ for 336 photographically measured structure factors. The crystal is isostructural with $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$ with mean $\text{Sn-F} = 1.97$, $\text{Li-F} = 2.08$ and $\text{Li-O} = 2.06$ Å.

Introduction. The structure of $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$ was solved using the Patterson function and chemical considerations. The systematic absence are: hkl , $h+k = 2n+1$, and a centre of symmetry was assumed only after refinement in space group $C2$ indicated that it was present. Intensities for 463 of a possible 600 reflections to $d = 0.8$ Å were measured with a microdensitometer from equi-inclination integrated Weissenberg photographs (Ni filtered $\text{Cu K}\alpha$ radiation) of layers $h0l$, $h1l$, $h2l$, $h3l$, $h,h+k,l$ with $k = 0, 3, 4, 6$ and integrated precession photographs (Zr filtered $\text{Mo K}\alpha$ radiation) of the layer $hk0$ using a crystal $0.75 \times 0.65 \times 0.70$ mm. All intensities were corrected for Lorentz and polarization effects. Measurements made with $\text{Cu K}\alpha$ radiation were corrected for absorption assuming that the crystal was spherical ($R = 0.36$ mm, $\mu = 5.84$ mm $^{-1}$). The structure was refined by least squares using the locally written program *CUDLS* to give $R_2 = 0.10$ (Cruickshank weighting scheme). Hydrogen atoms were not found or included in the calculation. Scattering factors for Li^+ , Ti^{4+} , F^- and O^{2-} were taken from *International Tables for X-ray Crystallography* (1962). The coordinates are given in Table 1 and observed and calculated structure factors are given by Marseglia (1971b).

The structure of $\text{Li}_2\text{SnF}_6 \cdot 2\text{H}_2\text{O}$ was determined from 336 of a possible 460 reflexions with $d > 0.86$ Å meas-

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Table 1. Atomic coordinates for $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$

The temperature factors (U) are the mean square displacement in units of 10^{-3} Å 2 .

| | x | y | z | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|------|---------------|---------------|---------------|----------|----------|----------|----------|----------|----------|
| Ti | 0 | 0 | 0 | 19 (1) | 17 (1) | 20 (1) | 0 | 2 (1) | 0 |
| F(1) | 0.0852 (3) | 0.2203 (6) | 0.2232 (7) | 33 (2) | 30 (2) | 32 (1) | -2 (1) | 1 (1) | -1 (1) |
| F(2) | -0.1576 (4) | 0 | 0.2313 (10) | 28 (2) | 27 (2) | 32 (2) | 0 | 8 (2) | 0 |
| O | 0.3434 (6) | 0 | 0.2861 (12) | 22 (3) | 21 (3) | 29 (3) | 0 | 6 (2) | 0 |
| Li | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 71 (12) | 47 (10) | 48 (9) | 18 (10) | -9 (9) | -28 (8) |

Table 2. Atomic coordinates for $\text{Li}_2\text{SnF}_6 \cdot 2\text{H}_2\text{O}$

The temperature factors (U) are the mean square displacements in units of 10^{-3} Å 2 .

| | x | y | z | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|------|---------------|---------------|---------------|----------|----------|----------|----------|----------|----------|
| Sn | 0 | 0 | 0 | 9 (1) | 6 (1) | 10 (1) | 0 | 1 (3) | 0 |
| F(1) | 0.0875 (5) | 0.2297 (9) | 0.2297 (9) | 21 (3) | 25 (3) | 15 (2) | -2 (2) | -4 (2) | -7 (2) |
| F(2) | -0.1624 (6) | 0 | 0.2440 (15) | 20 (3) | 27 (4) | 19 (3) | 0 | 5 (3) | 0 |
| O | 0.3414 (8) | 0 | 0.2794 (17) | 17 (4) | 22 (4) | 14 (3) | 0 | 4 (3) | 0 |
| Li | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 31 (11) | 41 (13) | 15 (8) | -3 (10) | -2 (8) | -8 (8) |

ured with a microdensitometer from equininclination integrated Weissenberg photographs (Ni filtered Cu $K\alpha$ radiation) of layers with $l=0$ to 4 and integrated precession photographs (Zr filtered Mo $K\alpha$ radiation) of layers with $h=0$ to 4 and $k=0$ to 2 taken of a crystal $0.04 \times 0.04 \times 0.09$ mm. All intensities were corrected for Lorentz and polarization effects but not absorption (maximum variation in $I=2\%$, $\mu(\text{Cu } K\alpha)=7.2 \text{ mm}^{-1}$, $\mu(\text{Mo } K\alpha)=0.87 \text{ mm}^{-1}$). The systematic absences are hkl , $h+k=2n+1$. The structure was assumed to be similar to that of $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$ and was refined by least squares to give $R_2=0.078$ (Cruickshank weighting scheme). Hydrogen atoms were neither observed nor included in the calculation. Scattering curves for Li^+ , Sn^{4+} , F^- and O^{2-} were taken from *International Tables for X-ray Crystallography* (1962). Atomic coordinates are given in Table 2 and the observed and calculated structure factors are given by Marseglia (1971a).

Discussion. Fig. 1 shows how the structure of $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$ is composed of rows of edge sharing $\text{LiF}_4(\text{OH}_2)_2$ octahedra running along **b**. These are linked into a three dimensional network by corner sharing with TiF_6 octahedra which are tetragonally distorted, the farther axial F(2) being bonded to two Li and the closer equatorial F(1) being bonded only to one Li. Bond distances and angles are given in Table 3. Although the hydrogen atoms were not found their position can be inferred by the requirement of tetrahedral

Table 3. Bond lengths (\AA) and angles ($^\circ$) in $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$

| | | | |
|---------|--------------------------|--------------|--------------------|
| Ti-F(1) | 1.903 (3) ($\times 4$) | F(1)-Ti-F(1) | 93.2 (1), 86.8 (1) |
| Ti-F(2) | 1.968 (4) ($\times 2$) | F(1)-Ti-F(2) | 93.5 (1), 86.5 (1) |
| Li-F(1) | 2.160 (3) ($\times 2$) | F(1)-Li-F(2) | 91.9 (2), 88.1 (2) |
| Li-F(2) | 2.186 (3) ($\times 2$) | F(1)-Li-O | 90.1 (2), 89.9 (2) |
| Li-O | 2.046 (4) ($\times 2$) | F(2)-Li-O | 90.5 (2), 89.5 (2) |
| | | Li-O-Li | 93.0 (2) |

Possible hydrogen bonds

| | | | |
|-----------|------|-----------|----------------|
| O-H(1)... | F(1) | 3.007 (6) | ($\times 2$) |
| O-H(2)... | F(1) | 3.048 (6) | ($\times 2$) |
| O-H(2)... | F(2) | 3.133 (8) | |

Table 4. Bond strengths in $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$

| | Ti | Li | H(1) | H(2) | Sum |
|------|----------------------|--------------------------------------|----------------------|----------------------|------|
| F(1) | 0.70 ($\times 4$)† | 0.13 ($\times 2$)† | 0.10 ($\times 2$)† | ($\times 2$)* 0.07 | 1.00 |
| F(2) | 0.60 ($\times 2$)† | ($\times 2$)* 0.13 ($\times 2$)† | | 0.07 | 0.93 |
| O | | ($\times 2$)* 0.19 ($\times 2$)† | 0.80 | 0.80 | 1.98 |
| Sum | 4.00 | 0.90 | 1.00 | 1.01 | |

Parameters used in the calculation of the bond strengths (s)

| | s_0 | R_0 | N |
|------|-------|-------|-------|
| Ti-F | 0.667 | 1.925 | 4.5 |
| Li-F | 0.5 | 1.547 | 4.0 |
| Li-O | 1.0 | 1.378 | 4.165 |

where $s=s_0(R/R_0)^{-N}$ (see Brown & Shannon, 1973)
H bond strengths are estimated

* Multiplicity around anion
† Multiplicity around cation

coordination of oxygen by Li and H. Such an arrangement leads to one bifurcated and one trifurcated H bond as shown in Fig. 1. This arrangement is confirmed by the fact that the sums of the bond strengths (s) calculated using the equation of Brown & Shannon (1973), $s=s_0(R/R_0)^{-N}$, are very close to the valences (Table 4).

The principal difference in $\text{Li}_2\text{SnF}_6 \cdot 2\text{H}_2\text{O}$ lies in the significantly smaller distortion shown by the SnF_6 octa-

Table 5. Bond lengths (\AA) and angles ($^\circ$) in $\text{Li}_2\text{SnF}_6 \cdot 2\text{H}_2\text{O}$

| | | | |
|---------|--------------------------|--------------|--------------------|
| Sn-F(1) | 1.962 (5) ($\times 4$) | F(1)-Sn-F(1) | 91.2 (2), 88.8 (2) |
| Sn-F(2) | 1.983 (6) ($\times 2$) | F(1)-Sn-F(2) | 91.5 (2), 88.5 (2) |
| Li-F(1) | 2.031 (5) ($\times 2$) | F(1)-Li-F(2) | 90.4 (2), 89.6 (2) |
| Li-F(2) | 2.137 (5) ($\times 2$) | F(1)-Li-O | 91.1 (3), 88.9 (3) |
| Li-O | 2.062 (5) ($\times 2$) | F(2)-Li-O | 93.4 (2), 86.6 (2) |
| | | Li-O-Li | 95.4 (3) |

Possible hydrogen bonds

| | | | |
|-----------|------|------------|----------------|
| O-H(1)... | F(1) | 2.938 (8) | ($\times 2$) |
| O-H(2)... | F(1) | 3.009 (8) | ($\times 2$) |
| O-H(2)... | F(2) | 3.011 (10) | |

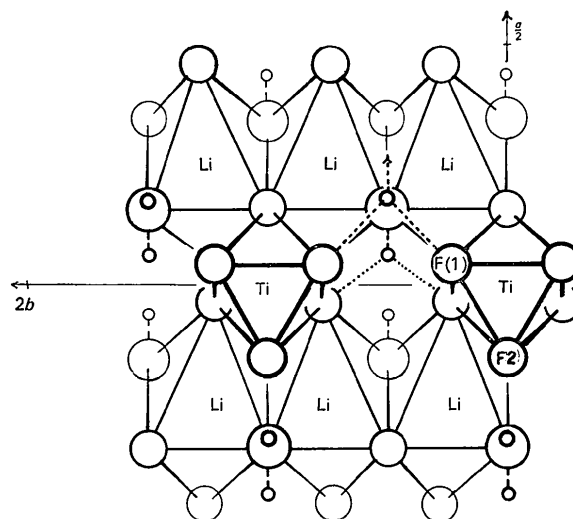


Fig. 1. The arrangement of $\text{LiF}_4(\text{OH}_2)_2$ and TiF_6 octahedra in $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$. The proposed hydrogen-bonding scheme is shown around one of the water molecules.

Table 6. Bond strengths in $\text{Li}_2\text{SnF}_6 \cdot 2\text{H}_2\text{O}$

| | Sn | Li | H(1) | H(2) | Sum |
|------|----------------------|--|----------------------|---------------------|------|
| F(1) | 0.68 ($\times 4$)† | 0.17 ($\times 2$)† | 0.09 ($\times 2$)† | 0.06 ($\times 2$) | 1.00 |
| F(2) | 0.64 ($\times 2$)† | ($\times 2$) [*] 0.14 ($\times 2$)† | | 0.06 | 0.98 |
| O | | 0.18 ($\times 2$)† | 0.81 | 0.81 | 1.98 |
| Sum | 4.00 | 0.98 | 0.99 | 0.99 | |

Bond strengths (s) calculated after Brown & Shannon (1973) using the parameters

| | s_0 | R_0 | N |
|------|-------|-------|-------|
| Sn-F | 0.667 | 1.969 | 6.3 |
| Li-F | 0.5 | 1.547 | 4.0 |
| Li-O | 1.0 | 1.378 | 4.165 |

in the equation $s = s_0(R/R_0)^{-N}$. Hydrogen bond strengths estimated.

* Multiplicity around anion.

† Multiplicity around cation.

hedron compared with the TiF_6 octahedron and the correspondingly larger distortion in the environment of Li (see Table 5). A bond strength calculation (Table 6) indicates that the hydrogen bonding scheme is probably similar to that in the Ti compound.

This research was supported by a grant from the National Research Council of Canada who also awarded one of us (EAM) a scholarship.

References

- BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst. A* **29**, 266–282.
International Tables for X-ray Crystallography (1962). Vol. 3, Table 3.3.1. Birmingham: Kynoch Press.
 MARSEGLIA, E. A. (1971*a*). Ph.D. Thesis, McMaster Univ., pp. 26–28.
 MARSEGLIA, E. A. (1971*b*). Ph.D. Thesis, McMaster Univ., pp. 32–35.

Acta Cryst. (1973). **B29**, 1354

L- α -Glycerolphosphorylethanolamine Monohydrate

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(Received 11 Decemaber 1972; accepted 11 February 1973)

Abstract. $\text{C}_5\text{H}_{14}\text{O}_6\text{NP} \cdot \text{H}_2\text{O}$, monoclinic, space group $P2_1$ with $a=9.566$ (5), $b=7.324$ (5), $c=7.657$ (5) Å, $\beta=106.72$ (2)°; $d_{\text{meas}}=1.51$, $d_{\text{calc}}=1.507$ g cm⁻³ for $Z=2$; $\mu(\text{Cu } K\alpha)=25.6$ cm⁻¹. The absolute configuration has been confirmed from the intensities of 710 Bijvoet pairs hkl and $h\bar{k}l$, using the Cu $K\alpha$ anomalous scattering of phosphorus and oxygen atoms. Bond lengths and angles are reported with e.s.d.'s of about 0.004 Å and 0.3°.

Experimental. A suitable crystal was selected from a sample of L- α -glycerolphosphorylethanolamine monohydrate (hereafter GPE·H₂O), which was prepared by

Baer & Stancer (1953) and was kindly supplied by Professor Baer of the University of Toronto. In order

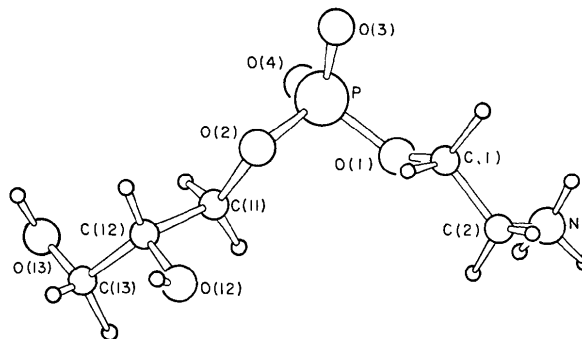


Fig. 1. The atomic nomenclature, conformation, and absolute configuration for the L- α -GPE zwitterion.

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