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The Crystal Structure of $LiNb_6O_{15}F$

MONICA LUNDBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The crystal structure of $LiNb_6O_{15}F$ has been determined from threedimensional single-crystal data. The orthorhombic unit-cell dimensions are:

$$a = 16.635 \text{ Å}; \; b = 3.964 \text{ Å}; \; c = 8.888 \text{ Å}$$

The space group is *Pmma*. The structure can be described as being built up of blocks containing one pentagonal bipyramid sharing edges with five octahedra. These building blocks are joined together by having corners in common.

The results of a phase analysis of the system $LiF\text{-}Nb_2O_5$ were reported in a recent publication.[1] Two oxide fluoride phases were found, *viz.* $LiNb_6O_{15}F$ and $LiF{\cdot}10-12Nb_2O_5$. The crystal structure of the former has now been determined and will be described below.

EXPERIMENTAL

The compound $LiNb_6O_{15}F$ was prepared by heating a mixture of LiF (Baker's Analyzed, 99.89 %) and α-Nb_2O_5 (Kawecki, 99.99 %), in the mole ratio 1:3, in a sealed platinum tube at 1200°C for two days applying a technique developed by Roth.[2] The product consisted of colourless, rod-shaped crystals up to 0.5 mm in length. The single-crystal X-ray examination showed the crystals to be of orthorhombic symmetry. From the indexed Guinier X-ray powder pattern, given in Table 1, the following unit-cell dimensions were derived:

$$a = 16.635 \text{ Å}; \; b = 3.964 \text{ Å}; \; c = 8.888 \text{ Å}$$

The crystal was rotated about the rod axis and the *h*0*l*, *h*1*l*, and *h*2*l* reflections were collected in an integrating Weissenberg camera using filtered Cu*K* radiation. The crystal was 0.19 mm in length and had the cross section edges 0.03 and 0.01 mm. The reflections were registered by the multiple-film technique and visually estimated by means of a standard scale. The data were corrected for absorption using a program written by Werner [3] for the computer FACIT EDB.

STRUCTURE DETERMINATION

The calculated density 4.67 g/cm³ with two formula units $LiNb_6O_{15}F$ per unit cell, agrees well with the observed density, 4.62 g/cm³. The only sys-

Table 1. Guinier X-ray powder pattern of $LiNb_6O_{15}F$, internally calibrated with KCl.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
w	0.00751	001	0.00751
m	0.00858	200	0.00858
w	0.00969	101	0.00968
w	0.02680	301	0.02680
w	0.03004	002	0.03004
w	0.03217	102	0.03218
vst	0.03775	010	0.03774
w	0.03862	202	0.03862
st	0.04184	401	0.04181
w	0.04631	210	0.04632
st	0.04933	302	0.04934
st	0.06112	501	0.06111
vw	0.06446	311	0.06454
vw	0.06776	012	0,06778
m	0,06972	103	0.06973
m	0.07616	203	0.07617
m	0.07716	600	0.07718
m	0.07955	411	0.07955
w	0.08363	502	0.08364
w	0.08467	601	0.08469
st	0.08709	312	0.08708
m	0.09883	511	0.09885
w	0.10199	412	0.10208
m	0.10731	602	0.10722
st	0.15091	020	0.15096

tematically absent reflections are $hk0$, when h is odd. This is characteristic of the space groups $P2_1ma$ (No. 26), $Pm2a$ (No. 28), and $Pmma$ (No. 51).

The $h0l$, $h1l$, and $h2l$ layer lines, with due regard for observational errors and for the effects of thermal motion, were found to be very similar. This

Table 2. Atomic parameters in $LiNb_6O_{15}F$. Space group *Pmma*.

Atom	Position	x	y	z	B	σB
2 Nb_1	2(e)	¼	0	0.6874 ± 0.0004	0.49	0.07
4 Nb_2	4(i)	0.1305 ± 0.00016	0	0.3973 ± 0.0003	0.54	0.05
4 Nb_3	4(i)	0.0593 ± 0.00017	0	0.8146 ± 0.0003	0.52	0.05
2 Nb_4	2(e)	¼	0	0.0578 ± 0.0005	0.69	0.07
2 O_1	2(e)	¼	0	0.4582 ± 0.0042	1.3	0.7
4 O_2	4(i)	0.1309 ± 0.0013	0	0.6149 ± 0.0023	0.3	0.4
4 O_3	4(i)	0.1744 ± 0.0013	0	0.8823 ± 0.0022	0	0.4
2 O_4(≡F)	2(f)	¼	½	0.6922 ± 0.0032	0.2	0.6
4 O_5	4(i)	0.1636 ± 0.0014	0	0.1963 ± 0.0023	0.5	0.4
4 O_6	4(i)	0.0206 ± 0.0018	0	0.3386 ± 0.0030	1.2	0.5
4 O_7	4(j)	0.1286 ± 0.0016	½	0.3998 ± 0.0029	1.5	0.5
2 O_8	2(a)	0	0	0	1.2	1.0
4 O_9	4(j)	0.0583 ± 0.0016	½	0.8170 ± 0.0027	1.0	0.5
2 O_{10}	2(f)	¼	½	0.0524 ± 0.0043	1.5	0.7

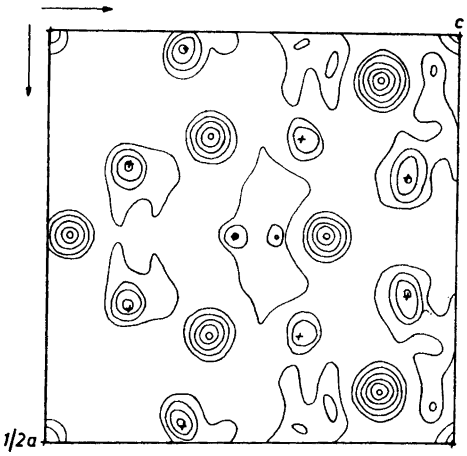

Fig. 1. Electron density projection along [010]. The figure is on an arbitrary scale and only every third contour is drawn for the niobium peak.

suggests that all the niobium atoms are situated in one plane, and rather likely a mirror plane, perpendicular to the *b*-axis. The space group with the highest symmetry, *Pmma*, comprises the following point positions in such planes of symmetry:

$4(j)\ m$ $x,\frac{1}{2},z\ ;\ \bar{x},\frac{1}{2},\bar{z}\ ;\ \frac{1}{2}+x,\frac{1}{2},\bar{z}\ ;\ \frac{1}{2}-x,\frac{1}{2},z.$
$4(i)\ m$ $x,0,z\ ;\ \bar{x},0,\bar{z}\ ;\ \frac{1}{2}+x,0,\bar{z}\ ;\ \frac{1}{2}-x,0,z.$
$2(f)\ mm$ $\frac{1}{4},\frac{1}{2},z\ ;\ \frac{3}{4},\frac{1}{2},\bar{z}.$
$2(e)\ mm$ $\frac{1}{4},0,z\ ;\ \frac{3}{4},0,\bar{z}.$
$2(d)\ 2/m$ $0,\frac{1}{2},\frac{1}{2}\ ;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}.$
$2(c)\ 2/m$ $0,0,\frac{1}{2}\ ;\ \frac{1}{2},0,\frac{1}{2}.$
$2(b)\ 2/m$ $0,\frac{1}{2},0\ ;\ \frac{1}{2},\frac{1}{2},0.$
$2(a)\ 2/m$ $0,0,0\ ;\ \frac{1}{2},0,0.$

Using the Patterson projection along [010], eight niobium atoms were placed in two 4(*i*) positions and the other four niobium atoms in two 2(*e*) positions. The corresponding electron density projection (Fig. 1) showed all the heavy atoms in the expected positions.

In addition to the high niobium atom maxima the electron density projection was found to contain several lower ones likely to correspond to non-metal atoms (*cf.* Fig. 1). The distribution of these minor peaks is a fivefold one around one of the metal atoms of one of the 2(*e*) positions and roughly square around the other niobium atoms. This suggested that the non-metal coordination around the former is a pentagonal bipyramid with non-metal atoms, not disclosed in the map overlapping the niobium atoms. The arrangement around all the other metal atoms would by analogy be an octahedron of anions. In this way sixteen anion atoms were placed in four 4(*i*) positions, two in 2(*e*) and two in 2(*a*), all at the same *y* level as the metal atoms. The twelve top

anions of the polyhedra were placed in two (4*j*) and two 2(*f*) positions with x and z parameters equal to those of the metal atoms.

This trial structure was refined by means of successive F_o-F_c Fourier summations until the reliability factor R was 0.135. The final F_o-F_c summation led to no shifts of the atoms and the general shape of this synthesis was fairly smooth.

Assuming *Pmma* to be the correct space group, 409 independent reflections from *h*0*l*, *h*1*l*, and *h*2*l* were finally refined by the least-squares method using the Åsbrink and Brändén [4] program written for FACIT. The refinement was stopped when the shifts of the positional parameters were less than 0.5 % of the standard deviations. The R factor was then 0.091.

During the determination and refinement of the structure all the non-metal atoms were given the form factor of an oxygen, which very nearly corresponds to a random distribution of oxygen and fluorine on the anion sites. No account was taken of the arrangement of the two lithium atoms in the unit cell.

Atomic coordinates and temperature factors with their standard deviations are given in Table 2. The comparison between observed and calculated structure factors is presented in Table 3.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $LiNb_6O_{15}F$ illustrated in Fig. 2 can be described as a polygonal network which contains identical building blocks each consisting of one pentagonal bipyramid sharing edges with five octahedra. The building blocks are joined together with corners in common in the *b*-direction as well as in the *ac*-plane. The *b*-axis of the unit-cell corresponds to the space-diagonal of the polyhedra.

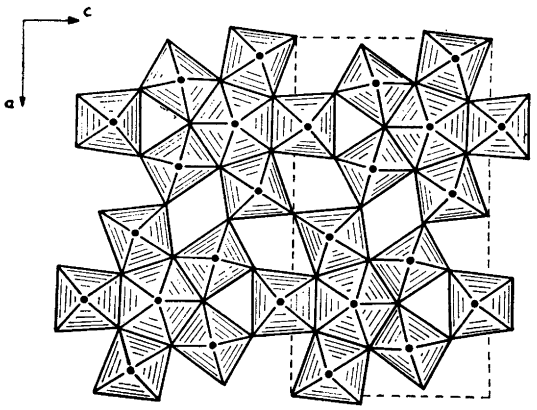

Fig. 2. The crystal structure of $LiNb_6O_{15}F$.

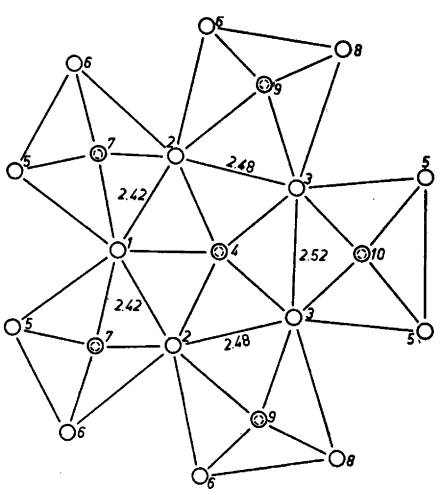

Fig. 3. The pentagonally bipyramidal coordination in $LiNb_6O_{15}F$. Nb_1 is situated in the center of the polyhedron. Small circle represents niobium, large circle represents oxygen.

Table 3. Observed and calculated F-values.

h k l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}
2 0 0	—	63	6 0 3	< 26	4
4 0 0	20	14	7 0 3	155	138
6 0 0	187	147	8 0 3	302	267
8 0 0	192	158	9 0 3	165	157
10 0 0	288	271	10 0 3	< 33	16
12 0 0	< 34	5	11 0 3	60	49
14 0 0	< 37	16	12 0 3	36	42
16 0 0	244	238	13 0 3	53	54
18 0 0	48	42	14 0 3	84	73
20 0 0	26	29	15 0 3	92	89
0 0 1	—	29	16 0 3	< 37	14
1 0 1	37	35	17 0 3	102	114
2 0 1	< 14	9	18 0 3	113	132
3 0 1	33	28	0 0 4	143	149
4 0 1	205	178	1 0 4	24	29
5 0 1	266	242	2 0 4	< 25	4
6 0 1	75	65	3 0 4	79	92
7 0 1	58	53	4 0 4	131	142
8 0 1	163	151	5 0 4	172	191
9 0 1	71	65	6 0 4	50	42
10 0 1	30	30	7 0 4	98	96
11 0 1	153	141	8 0 4	81	75
12 0 1	121	113	9 0 4	66	71
13 0 1	36	21	10 0 4	35	29
14 0 1	37	41	11 0 4	76	74
15 0 1	84	80	12 0 4	91	88
16 0 1	< 38	8	13 0 4	65	54
17 0 1	< 36	12	14 0 4	38	32
18 0 1	53	58	15 0 4	36	31
19 0 1	< 30	17	16 0 4	49	58
20 0 1	54	69	17 0 4	32	29
0 0 2	61	67	18 0 4	28	28
1 0 2	38	47	19 0 4	37	47
2 0 2	84	92	0 0 5	169	179
3 0 2	277	294	1 0 5	114	113
4 0 2	28	30	2 0 5	140	150
5 0 2	93	80	3 0 5	41	45
6 0 2	43	47	4 0 5	184	195
7 0 2	113	104	5 0 5	107	122
8 0 2	170	140	6 0 5	32	35
9 0 2	< 29	5	7 0 5	58	53
10 0 2	73	62	8 0 5	34	36
11 0 2	57	57	9 0 5	50	48
12 0 2	< 35	8	10 0 5	52	52
13 0 2	201	193	11 0 5	115	106
14 0 2	< 38	15	12 0 5	139	155
15 0 2	< 38	7	13 0 5	< 38	21
16 0 2	< 37	21	14 0 5	115	128
17 0 2	< 36	22	15 0 5	77	81
18 0 2	51	58	16 0 5	68	81
0 0 3	20	20	17 0 5	40	41
1 0 3	149	187	18 0 5	45	60
2 0 3	120	155	0 0 6	32	25
3 0 3	22	22	1 0 6	130	118
4 0 3	65	64	2 0 6	73	75
5 0 3	69	73	3 0 6	102	103

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
4	0	6	107	114	1	0	10	31	31
5	0	6	60	53	2	0	10	31	25
6	0	6	50	58	3	0	10	99	91
7	0	6	111	112	4	0	10	87	78
8	0	6	130	126	5	0	10	28	23
9	0	6	115	121	6	0	10	< 28	4
10	0	6	38	40	7	0	10	66	64
11	0	6	< 38	8	2	1	0	49	40
12	0	6	52	56	4	1	0	< 18	7
13	0	6	71	78	6	1	0	85	79
14	0	6	< 34	3	8	1	0	115	113
15	0	6	31	33	10	1	0	196	202
16	0	6	< 28	9	12	1	0	< 31	8
17	0	6	55	76	14	1	0	< 33	9
0	0	7	36	34	16	1	0	170	188
1	0	7	102	94	18	1	0	40	37
2	0	7	< 36	5	0	1	1	14	20
3	0	7	134	120	1	1	1	24	20
4	0	7	37	35	2	1	1	< 13	6
5	0	7	37	45	3	1	1	27	19
6	0	7	37	33	4	1	1	112	111
7	0	7	38	28	5	1	1	151	152
8	0	7	38	24	6	1	1	49	39
9	0	7	65	58	7	1	1	34	31
10	0	7	37	35	8	1	1	119	111
11	0	7	36	42	9	1	1	60	52
12	0	7	< 35	18	10	1	1	< 27	16
13	0	7	141	127	11	1	1	113	102
14	0	7	< 30	9	12	1	1	95	89
15	0	7	58	72	13	1	1	32	18
0	0	8	136	129	14	1	1	33	35
1	0	8	53	56	15	1	1	66	64
2	0	8	< 38	21	16	1	1	< 33	6
3	0	8	< 38	27	17	1	1	< 31	11
4	0	8	151	131	18	1	1	44	50
5	0	8	65	64	19	1	1	< 25	17
6	0	8	152	142	20	1	1	47	58
7	0	8	52	51	0	1	2	43	43
8	0	8	36	36	1	1	2	26	29
9	0	8	70	56	2	1	2	51	60
10	0	8	135	129	3	1	2	158	183
11	0	8	< 32	22	4	1	2	< 18	13
12	0	8	84	79	5	1	2	54	50
13	0	8	46	43	6	1	2	22	29
14	0	8	56	46	7	1	2	85	79
0	0	9	118	119	8	1	2	114	102
1	0	9	< 37	24	9	1	2	< 27	5
2	0	9	< 37	1	10	1	2	53	45
3	0	9	< 37	2	11	1	2	42	41
4	0	9	71	57	12	1	2	< 32	5
5	0	9	156	137	13	1	2	139	146
6	0	9	48	41	14	1	2	< 33	13
7	0	9	< 34	11	15	1	2	< 33	3
8	0	9	55	50	16	1	2	< 32	14
9	0	9	< 31	9	17	1	2	< 30	21
10	0	9	71	71	18	1	2	43	49
11	0	9	71	82	0	1	3	18	17
0	0	10	130	121	1	1	3	85	113

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
2	1	3	68	89	2	1	6	66	58
3	1	3	< 20	13	3	1	6	79	75
4	1	3	42	46	4	1	6	91	87
5	1	3	59	57	5	1	6	44	47
6	1	3	< 24	1	6	1	6	44	43
7	1	3	105	98	7	1	6	82	80
8	1	3	189	198	8	1	6	95	95
9	1	3	119	115	9	1	6	96	93
10	1	3	< 30	14	10	1	6	< 33	26
11	1	3	44	39	11	1	6	< 33	5
12	1	3	32	27	12	1	6	45	45
13	1	3	46	45	13	1	6	61	62
14	1	3	57	53	14	1	6	< 29	2
15	1	3	65	67	15	1	6	26	24
16	1	3	< 31	11	16	1	6	< 23	5
17	1	3	84	93	17	1	6	53	60
18	1	3	97	107	0	1	7	45	34
0	1	4	100	111	1	1	7	72	69
1	1	4	22	22	2	1	7	< 32	2
2	1	4	< 23	4	3	1	7	97	91
3	1	4	62	67	4	1	7	32	27
4	1	4	97	104	5	1	7	33	35
5	1	4	124	139	6	1	7	33	29
6	1	4	37	34	7	1	7	33	24
7	1	4	65	66	8	1	7	33	15
8	1	4	61	59	9	1	7	46	45
9	1	4	52	52	10	1	7	32	32
10	1	4	31	25	11	1	7	31	33
11	1	4	56	53	12	1	7	< 29	16
12	1	4	66	69	13	1	7	111	106
13	1	4	33	41	14	1	7	< 25	9
14	1	4	32	26	15	1	7	53	56
15	1	4	31	27	0	1	8	112	96
16	1	4	41	48	1	1	8	57	45
17	1	4	27	19	2	1	8	< 33	16
18	1	4	23	27	3	1	8	< 33	22
19	1	4	28	39	4	1	8	125	105
0	1	5	120	133	5	1	8	56	48
1	1	5	84	83	6	1	8	129	113
2	1	5	103	107	7	1	8	45	40
3	1	5	46	39	8	1	8	31	32
4	1	5	128	146	9	1	8	51	45
5	1	5	89	90	10	1	8	119	102
6	1	5	29	28	11	1	8	< 27	15
7	1	5	30	43	12	1	8	73	66
8	1	5	31	23	13	1	8	37	37
9	1	5	32	36	14	1	8	30	38
10	1	5	32	45	0	1	9	110	93
11	1	5	90	86	1	1	9	< 32	15
12	1	5	112	121	2	1	9	< 32	1
13	1	5	< 33	19	3	1	9	< 31	6
14	1	5	103	106	4	1	9	52	51
15	1	5	65	66	5	1	9	122	109
16	1	5	68	66	6	1	9	41	32
17	1	5	33	33	7	1	9	< 28	10
18	1	5	35	45	8	1	9	49	43
0	1	6	29	20	0	1	10	101	98
1	1	6	95	88	1	1	10	26	28

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
2	1	10	25	22	5	2	3	53	50
3	1	10	79	73	6	2	3	< 22	4
4	1	10	77	68	7	2	3	117	109
5	1	10	24	18	8	2	3	228	217
6	1	10	< 23	6	9	2	3	133	130
7	1	10	62	54	10	2	3	< 27	11
2	2	0	49	45	11	2	3	51	42
4	2	0	< 18	10	12	2	3	28	38
6	2	0	147	125	13	2	3	39	48
8	2	0	134	121	14	2	3	59	65
10	2	0	228	223	15	2	3	71	79
12	2	0	< 27	3	16	2	3	< 75	12
14	2	0	< 28	14	17	2	3	93	101
16	2	0	190	210	18	2	3	98	127
18	2	0	32	37	0	2	4	105	114
0	2	1	14	21	1	2	4	21	20
1	2	1	28	27	2	2	4	< 22	3
2	2	1	12	8	3	2	4	74	73
3	2	1	26	20	4	2	4	106	111
4	2	1	149	133	5	2	4	143	152
5	2	1	220	188	6	2	4	34	32
6	2	1	61	56	7	2	4	93	80
7	2	1	46	44	8	2	4	55	64
8	2	1	135	118	9	2	4	63	62
9	2	1	50	50	10	2	4	27	25
10	2	1	25	25	11	2	4	64	65
11	2	1	131	120	12	2	4	69	76
12	2	1	98	94	13	2	4	53	48
13	2	1	27	16	14	2	4	36	29
14	2	1	39	35	15	2	4	24	27
15	2	1	75	70	16	2	4	37	52
16	2	1	< 25	8	17	2	4	18	28
17	2	1	< 22	11	18	2	4	18	27
18	2	1	46	52	0	2	5	139	145
0	2	2	39	52	1	2	5	93	90
1	2	2	32	35	2	2	5	124	123
2	2	2	62	67	3	2	5	35	36
3	2	2	225	225	4	2	5	154	160
4	2	2	17	28	5	2	5	99	103
5	2	2	70	68	6	2	5	26	28
6	2	2	43	41	7	2	5	38	43
7	2	2	90	76	8	2	5	27	32
8	2	2	130	110	9	2	5	44	41
9	2	2	< 25	5	10	2	5	44	45
10	2	2	54	52	11	2	5	90	91
11	2	2	50	47	12	2	5	127	136
12	2	2	< 28	8	13	2	5	< 25	19
13	2	2	163	169	14	2	5	125	114
14	2	2	< 27	13	15	2	5	70	71
15	2	2	< 26	6	16	2	5	66	75
16	2	2	< 25	20	0	2	6	26	20
17	2	2	< 22	20	1	2	6	107	98
18	2	2	44	53	2	2	6	59	61
0	2	3	< 18	15	3	2	6	91	87
1	2	3	132	148	4	2	6	95	95
2	2	3	116	131	5	2	6	39	45
3	2	3	19	21	6	2	6	51	52
4	2	3	40	45	7	2	6	95	99

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
8	2	6	117	110	3	2	8	26	25
9	2	6	103	106	4	2	8	133	115
10	2	6	42	36	5	2	8	65	56
11	2	6	< 26	7	6	2	8	151	125
12	2	6	42	50	7	2	8	45	45
13	2	6	73	70	8	2	8	36	33
14	2	6	< 21	3	9	2	8	57	50
15	2	6	34	31	10	2	8	125	115
0	2	7	27	29	11	2	8	< 18	20
1	2	7	93	84	12	2	8	31	43
2	2	7	< 28	5	0	2	9	115	106
3	2	7	114	103	1	2	9	23	22
4	2	7	27	30	2	2	9	< 23	1
5	2	7	39	40	3	2	9	< 23	2
6	2	7	27	29	4	2	9	66	51
7	2	7	27	25	5	2	9	139	123
8	2	7	26	21	6	2	9	32	36
9	2	7	47	53	7	2	9	< 20	9
10	2	7	34	31	8	2	9	46	47
11	2	7	39	38	0	2	10	121	116
12	2	7	< 21	16	1	2	10	27	29
13	2	7	111	117	2	2	10	26	23
0	2	8	126	113	3	2	10	82	88
1	2	8	50	49	4	2	10	75	76
2	2	8	26	16					

The pentagonal bipyramid is quite regular as is shown in Fig. 3. The five anion-anion distances corresponding to edge sharing between the octahedra and the pentagonal bipyramid are all rather short, varying between 2.42 and 2.52 Å. The remaining anion-anion distances within the pentagonal bipyramid are 2.87—2.89 Å. The distances between the non-metal atoms of the octahedra range from 2.55 to 3.08 Å. The metal-anion distances in the pentagonal bipyramid (1.98—2.14 Å) have a mean value of 2.06 Å while the corresponding distances of the three crystallographically different types of octahedra are 1.87—2.06 Å, 1.90—2.14Å, and 1.89—2.01 Å, with mean values of 1.95, 1.99, and 1.96 Å, respectively. These values agree well with the average niobium-oxygen distance of 1.99 Å reported for the octahedra of α-Nb_2O_5.[5]

Sevenfold coordination has earlier been found for niobium in the NbF_7^{2-} ion,[6] in $NbOF_6^{3-}$ ion,[7] in $NaNb_3O_8$, [8] and also in 0.4 Nb_2O_5—0.6WO_3. [9,10]

In the structure of ScOF, as determined by Holmberg,[11] the fluorine and oxygen atoms have been found to be ordered. This was shown by a least-squares refinement of the structure. It is obviously in agreement with Pauling's Electrostatic Valence Principle.[12] If $\sum s_i$ (the sum of the strength of the electrostatic valence bonds) is calculated according to Pauling for the different twofold anion positions in $LiNb_6O_{15}F$, the lowest positive potential is obtained for the anion position which is shared between two pentagonal bipyramids in the point position 2(f) and has the coordinates $\frac{1}{4},\frac{1}{2},0.69$.

Table 4. Interatomic distances in a building block of the $LiNb_6O_{15}F$ structure (Fig. 3).

		Mean value
2 Nb_1 — Nb_2	3.26 ± 0.001	
2 Nb_1 — Nb_3	3.37 ± 0.001	
1 Nb_1 — Nb_4	3.29 ± 0.001	
1 Nb_1 — O_1	2.04 ± 0.04	
2 Nb_1 — O_2	2.08 ± 0.03	2.06
2 Nb_1 — O_3	2.14 ± 0.02	
2 Nb_1 — O_4 (≡ F)	1.98 ± 0.001	
1 Nb_2 — O_1	2.06 ± 0.01	
1 Nb_2 — O_2	1.93 ± 0.03	
1 Nb_2 — O_5	1.87 ± 0.03	1.95
1 Nb_2 — O_6	1.90 ± 0.03	
2 Nb_2 — O_7	1.98 ± 0.001	
1 Nb_3 — O_2	2.14 ± 0.03	
1 Nb_3 — O_3	2.01 ± 0.03	
1 Nb_3 — O_6	1.90 ± 0.03	1.99
1 Nb_3 — O_8	1.92 ± 0.003	
2 Nb_3 — O_9	1.98 ± 0.001	
2 Nb_4 — O_3	2.01 ± 0.02	
2 Nb_4 — O_5	1.89 ± 0.03	1.96
2 Nb_4 — O_{10}	1.98 ± 0.001	
2 O_1 — O_2	2.42 ± 0.03	
2 O_2 — O_3	2.48 ± 0.03	
1 O_3 — O_3	2.52 ± 0.05	
2 O_1 — O_4 (≡ F)	2.87 ± 0.001	
4 O_2 — O_4 (≡ F)	2.89 ± 0.03	
4 O_3 — O_4 (≡ F)	2.89 ± 0.02	
1 O_1 — O_5	2.74 ± 0.04	
2 O_1 — O_7	2.88 ± 0.03	
1 O_2 — O_6	3.07 ± 0.04	
2 O_2 — O_7	2.75 ± 0.03	
1 O_5 — O_6	2.69 ± 0.04	
2 O_5 — O_7	2.75 ± 0.03	
2 O_6 — O_7	2.73 ± 0.03	
1 O_2 — O_6	2.55 ± 0.04	
2 O_2 — O_9	2.93 ± 0.03	
1 O_3 — O_8	3.08 ± 0.03	
2 O_3 — O_9	2.83 ± 0.03	
1 O_6 — O_8	3.03 ± 0.03	
2 O_6 — O_9	2.75 ± 0.03	
2 O_8 — O_9	2.74 ± 0.02	
2 O_3 — O_5	2.80 ± 0.03	
4 O_3 — O_{10}	2.79 ± 0.03	
1 O_5 — O_5	2.88 ± 0.05	
4 O_5 — O_{10}	2.76 ± 0.03	

As for the arrangement of the lithium atoms, two possible positions in the unit-cell, 2(*d*) or 4(*j*) with the approximate coordinates 0.08,½,0.10, present themselves as likely ones. The 4(*j*) position requires a random distribution of the two lithium atoms. Both positions would give rise to six to eight lithium-anion contacts at distances ranging from 2.5 to 3.0 Å.

The same type of building blocks, as are present in $LiNb_6O_{15}F$, *viz.* one pentagonal bipyramid sharing edges with five octahedra, has previously been found in the structures of $W_{18}O_{49}$,[13,14] $Mo_{17}O_{47}$,[14,15] and Mo_5O_{14}.[14,16] The building blocks in $W_{18}O_{49}$ and $Mo_{17}O_{47}$ are, however, joined together both by corners and by edges. Also in contrast to $LiNb_6O_{15}F$ all these binary compounds contain additional octahedra, which are not coupled to the pentagonal bipyramid.

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