ACTA CHEMICA SCANDINAVICA 19 (1965) 2285–2290

The Crystal Structure of $NaNb_6O_{15}F$ and $NaNb_6O_{15}OH$

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$NaNb_6O_{15}F$ was prepared by heating NaF and Nb_2O_5; $NaNb_6O_{15}OH$ was prepared by heating $NaNbO_3$ and Nb_2O_5 in supercritical water. The two compounds are isomorphous and their crystal structure has been determined using single-crystal methods. The space group is *Amm*2 and the unit cell dimensions are:

$NaNb_6O_{15}F$:	$a = 3.949$ Å,	$b = 10.192$ Å,	$c = 14.721$ Å
$NaNb_6O_{15}OH$:	$a = 3.955$ Å,	$b = 10.186$ Å,	$c = 14.753$ Å

The structure contains building blocks which have one pentagonal bipyramid sharing edges with a ring of octahedra. These blocks are joined to each other by having corners in common.

In the system $NaNbO_3$-Nb_2O_5-H_2O a sodium niobium oxide hydroxide of the composition $NaNb_6O_{15}OH$ was formed at high pressure and temperature.[1] The crystals were very fibrous and similar in their shape to $K_2Ti_6O_{13}$ fibres as reported by Berry *et al.*[2] The fibres of $NaNb_6O_{15}OH$ gave rather poor single-crystal data and in order to get crystals more suitable for X-ray diffraction analysis, the corresponding oxide fluoride, $NaNb_6O_{15}F$, was synthesized.

The crystal structure of the two isomorphous compounds will now be reported.

EXPERIMENTAL

$NaNb_6O_{15}OH$ was made by heating $NaNbO_3$ and Nb_2O_5 in the mole ratio 1:2.5 with 20—30 weight % of water for three days in sealed gold or platinum capsules at a temperature of 600°C and a pressure of 2000 atm. The material obtained was very fibrous and although it gave a very good X-ray powder pattern, the single-crystal data obtained were of rather poor quality. Heating a mixture of NaF and Nb_2O_5 in the mole ratio 1:3 in a sealed platinum capsule for two days at 1100°C resulted in a product consisting of beautiful rod-shaped crystals. From the single-crystal data obtained of the oxide hydroxide and the oxide fluoride, it could be decided that the two compounds were isomorphous and this was also fully supported by the comparison of their X-ray powder patterns.

The 0*kl*, 1*kl*, and 2*kl* reflections for $NaNb_6O_{15}F$ were registered on multiple films by the integrating Weissenberg method using Cu$K\alpha$ radiation, and were measured by means of a calibrated film strip. Because of the small crystal used, 0.1 × 0.01 × 0.005 mm, no absorption corrections were considered necessary. The single-crystal X-ray studies showed

Table 1. Crystallographic constants for $NaNb_6O_{15}F$ and $NaNb_6O_{15}OH$.

Unit-cell dimensions:

$NaNb_6O_{15}F$	$NaNb_6O_{15}OH$
$a = 3.949$ Å	$a = 3.955$ Å
$b = 10.192$ Å	$b = 10.186$ Å
$c = 14.721$ Å	$c = 14.753$ Å

Systematically absent reflexions: hkl with $k + l = 2n$
Possible space groups: $C222$ (No. 21), $Cmm2$ (No. 35), $Amm2$ (No. 38) and $Cmmm$ (No. 65)

Observed density for $NaNb_6O_{15}OH$:	4.67
Calculated » » » :	4.68
» » » $NaNb_6O_{15}F$:	4.70

$Z = 2$

Table 2. $NaNb_6O_{15}F$ and $NaNb_6O_{15}OH$. Guinier powder patterns of Cu$K\alpha$ radiation.

	$NaNb_6O_{15}F$		
Intensity	$\sin^2\theta$ (obs.)	hkl	$\sin^2\theta$ (calc.)
w	0.00844	011	0.00845
vvw	0.02283	020	0.02284
w	0.03036	013	0.03035
vst	0.03804	100	0.03803
m	0.04379	004	0.04381
w	0.04647	111	0.04648
vvw	0.04892	102	0.04898
st	0.05415	031	0.05414
vvw	0.06088	120	0.06087
st	0.06657	024	0.06665
w	0.06835	113	0.06832
vvw	0.07181	122	0.07183
m	0.07412	015	0.07416
m	0.07603	033	0.07604
m	0.08184	104	0.08184
st	0.09213	131	0.09217
m	0.10466	124	0.10468

	$NaNb_6O_{15}OH$		
Intensity	$\sin^2\theta$ (obs.)	hkl	$\sin^2\theta$ (calc.)
w	0.00849	011	0.00844
vvw	0.02283	020	0.02287
w	0.03030	013	0.03025
vst	0.03794	100	0.03792
m	0.04369	004	0.04362
w	0.04631	111	0.04636
vvw	0.04889	102	0.04882
st	0.05418	031	0.05419
vvw	0.06067	120	0.06079
st	0.06653	024	0.06649
w	0.06810	113	0.06817
vvw	0.07161	122	0.07169
m	0.07382	015	0.07387
m	0.07590	033	0.07599
m	0.08165	104	0.08154
st	0.09199	131	0.09211
m	0.10450	124	0.10443

the crystals to be of orthorhombic symmetry and the crystallographic constants are given in Table 1. The powder patterns of the two compounds are given in Table 2.

Random occupancy of the anion sites was assumed and because of the small difference in scattering between the two elements, one F^- was simply treated as if it was one O^{2-}.

STRUCTURE DETERMINATION

Visual inspection showed the $0kl$ and $2kl$ intensities to be identical. The $1kl$ intensities were very similar to the corresponding ones in the $0kl$ and $2kl$ layers. This indicates that all the niobium atoms are situated in one plane, perpendicular to the a-axis. From the Patterson projection, calculated along the projection [100], a metal atom arrangement could be derived which consisted of one niobium surrounded by five other niobium atoms in the form of a rather regular pentagon. The distances between the central atom and the other five varied between 3.1—3.4 Å. If oxygen bridging was assumed to be present in these five distances, a unit could be derived which consisted of one pentagonal bipyramid sharing edges with a ring of five octahedra. The structure was now assumed to consist of such building blocks and various ways of joining them were investigated. One of the models fitted one of the space group alternatives ($Amm2$), the composition and also the unit-cell dimensions. This trial structure was tested by means of structure factor calculations. A very good general agreement was obtained and the $0kl$, $1kl$, and $2kl$ data were now used in several least-squares cycles using the Åsbrink-Brändén program written for the computer FACIT. The least-squares procedure stopped at an R-factor of 0.058. Atomic coordinates with standard deviations and temperature factors are given in Table 3.

Table 3. Fractional atomic parameters. Space group $Amm2$.

Atom	Point position	x	y	z	B
Nb(1)	2(a)	0	0	0	0.10 ± 0.10
Nb(2)	2(a)	0	0	0.2142 ± 0.0005	0.60 ± 0.12
Nb(3)	4(d)	0	0.3186 ± 0.0005	0.0620 ± 0.0004	0.60 ± 0.07
Nb(4)	4(d)	0	0.3153 ± 0.0005	0.3154 ± 0.0003	0.40 ± 0.07
Na	2(b)	½	0	0.404 ± 0.004	3.9 ± 1.2
O(1)	2(b)	½	0	0	1.4 ± 1.2
O(2)	2(b)	½	0	0.226 ± 0.004	0.7 ± 1.1
O(3)	4(e)	½	0.324 ± 0.004	0.050 ± 0.002	−0.2 ± 0.6
O(4)	4(e)	½	0.323 ± 0.003	0.307 ± 0.002	−0.2 ± 0.5
O(5)	4(d)	0	0.119 ± 0.003	0.105 ± 0.003	−0.1 ± 0.6
O(6)	4(d)	0	0.133 ± 0.003	0.311 ± 0.002	−0.1 ± 0.6
O(7)	4(d)	0	0.305 ± 0.003	0.447 ± 0.002	−0.9 ± 0.5
O(8)	4(d)	0	0.351 ± 0.003	0.178 ± 0.002	−0.7 ± 0.5
O(9)	2(a)	0	½	0.356 ± 0.005	1.8 ± 1.3
O(10)	2(a)	0	0	0.159 ± 0.002	−1.4 ± 0.6

Table 4. Interatomic distances.

Nb(1) pentagonal bipyramid

	Number	Length	Stand. deviation
Nb(1) – O(1)(≡ F)	2	1.97 Å	0.01
Nb(1) – O(5)	2	1.96	0.05
Nb(1) – O(7)	2	2.13	0.04
Nb(1) – O(9)	1	2.12	0.07
O(5) – O(5)	1	2.43	0.15
O(5) – O(7)	2	2.44	0.06
O(7) – O(9)	2	2.40	0.05
O(1) – O(5)	4	2.79	0.05
O(1) – O(7)	4	2.90	0.04
O(1) – O(9)	2	2.89	0.07
Nb(2) octahedron			
Nb(2) – O(2)	2	1.98 Å	0.01
Nb(2) – O(5)	2	2.02	0.05
Nb(2) – O(6)	2	1.96	0.04
O(2) – O(5)	4	2.93	0.08
O(2) – O(6)	4	2.70	0.07
O(5) – O(6)	2	3.03	0.08
O(5) – O(5)	1	2.43	0.15
O(6) – O(6)	1	2.71	0.12
Nb(3) octahedron			
Nb(3) – O(3)	2	1.98	0.01
Nb(3) – O(5)	1	2.13	0.05
Nb(3) – O(7)	1	2.11	0.04
Nb(3) – O(8)	1	1.75	0.04
Nb(3) – O(10)	1	1.96	0.01
O(3) – O(5)	2	2.98	0.05
O(3) – O(7)	2	2.82	0.05
O(3) – O(8)	2	2.74	0.05
O(3) – O(10)	2	2.71	0.05
O(5) – O(7)	1	2.44	0.06
O(5) – O(8)	1	2.60	0.06
O(7) – O(10)	1	3.28	0.06
O(8) – O(10)	1	2.80	0.05
Nb(4) octahedron			
Nb(4) – O(4)	2	1.98	0.01
Nb(4) – O(6)	1	1.86	0.04
Nb(4) – O(7)	1	1.94	0.04
Nb(4) – O(8)	1	2.05	0.04
Nb(4) – O(9)	1	1.98	0.07
O(4) – O(6)	2	2.77	0.06
O(4) – O(7)	2	2.86	0.05
O(4) – O(8)	2	2.75	0.05
O(4) – O(9)	2	2.77	0.08
O(6) – O(7)	1	2.67	0.05
O(6) – O(8)	1	2.96	0.05
O(7) – O(9)	1	2.40	0.05
O(8) – O(9)	1	3.02	0.08

(Table 4 cont.)

	Na		
Na — O(2)	1	2.62	0.09
Na — O(3)	2	2.80	0.07
Na — O(6)	4	2.76	0.08
Na — O(10)	2	2.59	0.08
	Nb—Nb		
Nb(1) — Nb(2)	1	3.153	0.005
Nb(1) — Nb(3)	2	3.373	0.005
Nb(1) — Nb(4)	2	3.306	0.005

DISCUSSION

The structure of $NaNb_6O_{15}F$ and $NaNb_6O_{15}OH$ is illustrated in Fig 1. Interatomic distances with their estimated standard deviations are given in Table 4. The structure consists of building block units of one pentagonal bipyramid surrounded by five octahedra as shown in Fig 2. In the structure these units are joined by corner sharing. During the determination and refinement of the structure the fluorine atoms were treated as oxygens and also were assumed to be disordered on the anion sites. However, in the structure of ScOF, as determined by Holmberg,[3] the fluorine and oxygen atoms are ordered. This was convincingly shown by least-squares methods and was also in agreement with Pauling's second principle.[4] If $\sum s_i$ (the sum of the strength of the electrostatic atom valence bonds) is calculated according to Pauling for the different anion positions in the $NaNb_6O_{15}F$ stucture, the smallest positive potential is obtained for the anion position which is situated between two

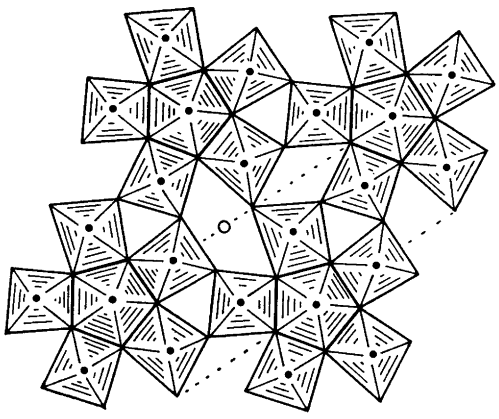

Fig. 1. The crystal structure of $NaNb_6O_{15}F$ and $NaNb_6O_{15}OH$.

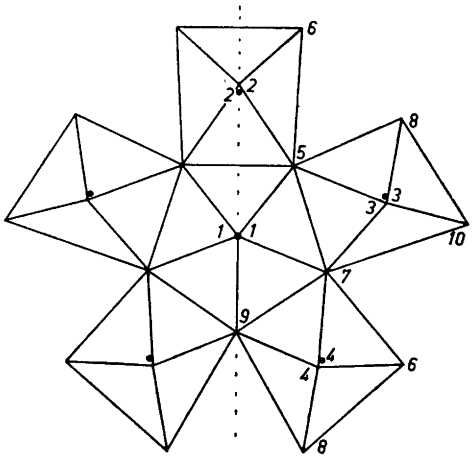

Fig. 2. Building block unit of $NaNb_6O_{15}F$ or $NaNb_6O_{15}OH$. Filled circles are Nb atoms. The mirror plane is indicated by dotted line.

pentagonal bipyramids. This position, which is $\frac{1}{2},0,0$, has thus been tentatively chosen for the fluorine and the OH in $NaNb_6O_{15}F$ and $NaNb_6O_{15}OH$.

The NbO_5F_2 pentagonal bipyramid is very regular as is shown in Fig. 2. The five anion-anion distances corresponding to edge sharing between the pentagonal bipyramid and the octahedra are all 2.42 ± 0.02 Å. The remaining anion-anion distances within the pentagonal bipyramid are 2.84 ± 0.06 Å. The mean value for metal-anion distances in the octahedra is 1.98 Å. The corresponding value for α-Nb_2O_5, as determined by Gatehouse and Wadsley,[5] is 1.99 and for $NaNbO_{13}O_{33}$[6] it is 2.00 Å. The mean value for the metal-anion distances in the pentagonal bipyramid is 2.03 Å.

The sodium atom is situated in a trigonal prism of oxygens. Three additional oxygen atoms are bonded through the three rectangular prism faces. This is similar to what has been observed for sodium in $Na_2Ti_3O_7$[7] and in $Na_{2-x}V_6O_{15}$.[8]

A building block of this kind has been found in several structures, and the use of it as a structure-forming unit will soon be reviewed.[9]

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Received August 20, 1965.