Mauer, in the press). The bond distances observed in coordinated imidazole are in substantial agreement with those found for corresponding bonds in coordinated biimidazole. Related pairs agree to within two standard deviations of the imidazole bond distances. The observed distances in the imidazole ring, moreover, are in close agreement with the values calculated by Dewar & Gleicher (1966) and with those found by Lundberg (1966) in diimidazolezinc(II) dichloride. The shortest observed and calculated distances in the imidazole ring is between atoms involved in the classical C–N double bond.

Table 5. *Distances from the ring atoms to the least-squares planes of the imidazole ring*

The equation of the plane in direct space is given by $PX+QY+RZ=S$ ($P=11{\cdot}385$, $Q=-5{\cdot}0896$, $R=5{\cdot}6823$ and $S=0{\cdot}16597$).

N(1)	0·00574 Å
N(2)	0·00593
C(1)	−0·00742
C(2)	−0·00221
C(3)	−0·00204

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The Crystal Structure of $NaNbO_2F_2$

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$NaNbO_2F_2$, a new niobium oxide fluoride, is monoclinic, with $a=8{\cdot}063$, $b=5{\cdot}405$, $c=7{\cdot}626$ Å, $\beta=101{\cdot}70°$, space group $P2_1/c$. The structure, refined by the least-squares method, contains layers of corner-sharing NbO_4F_2 octahedra. The structure of the layers with the composition $(NbO_2F_2)_n^{n-}$ is related to the PdF_3 structure type. The structure of $NaNbO_2F_2$ is also related to the α-PbO_2 structure type. The anion arrangement is probably ordered.

Introduction

The substitution of F^- for O^{2-} in niobium oxides has been useful in making compounds of simple and predictable structures, which can serve as model substances for the study of the principles of synthesis, non-stoichiometry, and possible mechanisms of reaction (Andersson, 1967). Preparative and structural studies have been made on the $NaNbO_3$–Nb_2O_5, $NaNbO_3$–Nb_2O_5–H_2O and NaF–Nb_2O_5 systems. The present paper reports the crystal structure of $NaNbO_2F_2$, a new compound which has been prepared in the NaF–NbO_2F system.

Experimental

Heating a mixture of NaF and NbO_2F in the mole ratio 1:1 in a sealed platinum capsule for one day at 600 °C resulted in a product consisting of colourless plate-shaped crystals. Single-crystal X-ray studies showed the crystals to be of monoclinic symmetry and the crystallographic constants are given in Table 1. The Hägg–Guinier powder pattern is given in Table 2. The *h*0*l*, *h*1*l*, *h*2*l* and *h*3*l* reflexions 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, $0{\cdot}05 \times 0{\cdot}04 \times 0{\cdot}02$ mm, no absorption corrections were considered necessary. All calculations were performed on an IBM 7090 computer, with the *Crystal Structure Calculations System, X-ray* 63 (Stewart & High, 1964). The Nb^{5+} scattering curve used was derived from the tables of Thomas & Umeda (1957). For Na^+ and O^{2-} the scattering curves given by Freeman (1959) and Suzuki (1960) were used. The F^- scattering curve was taken from *International Tables for X-ray Crystallography* (1962).

Table 1. *Crystallographic data for* $NaNbO_2F_2$

Symmetry: monoclinic.
Unit-cell dimensions: $a = 8{\cdot}013 \pm 0{\cdot}002$ Å
$b = 5{\cdot}405 \pm 0{\cdot}002$
$c = 7{\cdot}626 \pm 0{\cdot}002$
$\beta = 101{\cdot}70 \pm 0{\cdot}05°$

Systematically absent reflexions
$h0l$, $l \neq 2n$
$0k0$, $k \neq 2n$

Space group $P2_1/c$
$Z = 4$

Structure determination

Approximate niobium coordinates were obtained from the Patterson projection on to (010). From the single-crystal data some similarities of this structure and the structure of α-PbO_2 were recognized, and with the use of this information, it was easy to derive approximate positions for the anions as well as for the sodium atoms. The first electron density projection on to (010) showed all the atoms in the expected positions. For all the atoms the 4(*e*) position in space group $P2_1/c$ was chosen, and the data were processed by a full-matrix least-squares refinement. The very strong 110, 210, 120, 130, 012, 222, 320 and 230 reflexions were omitted in the calculations. Of the four anions two (1 and 2) are shared between two Nb and one Na, and the other two (3 and 4) between one Nb and three Na. It was considered well worth trying an ordered arrangement of the anions in a least-squares refinement. Atoms

Table 2. *Powder pattern of* $NaNbO_2F_2$ (Cu $K\alpha_1$)

Intensity	$\sin^2\theta$ (obs)	*hkl*	$\sin^2\theta$ (calc)
m	0·00959	100	0·00965
vst	0·03000	110	0·02997
w	0·03859	200	0·03862
w+	0·04264	002	0·04264
m	0·04387	$10\bar{2}$	0·04389
vst	0·05901	210	0·05893
vst	0·06302	012	0·06295
vw	0·06412	$11\bar{2}$	0·06420
w	0·06443	$20\bar{2}$	0·06446
st	0·08098	112	0·08100
		020	0·08124
w	0·08474	$21\bar{2}$	0·08477
vw	0·08699	300	0·08690
w	0·09083	120	0·09089
vw	0·09804	202	0·09806
m	0·10573	$31\bar{1}$	0·10527
		$12\bar{1}$	0·10575

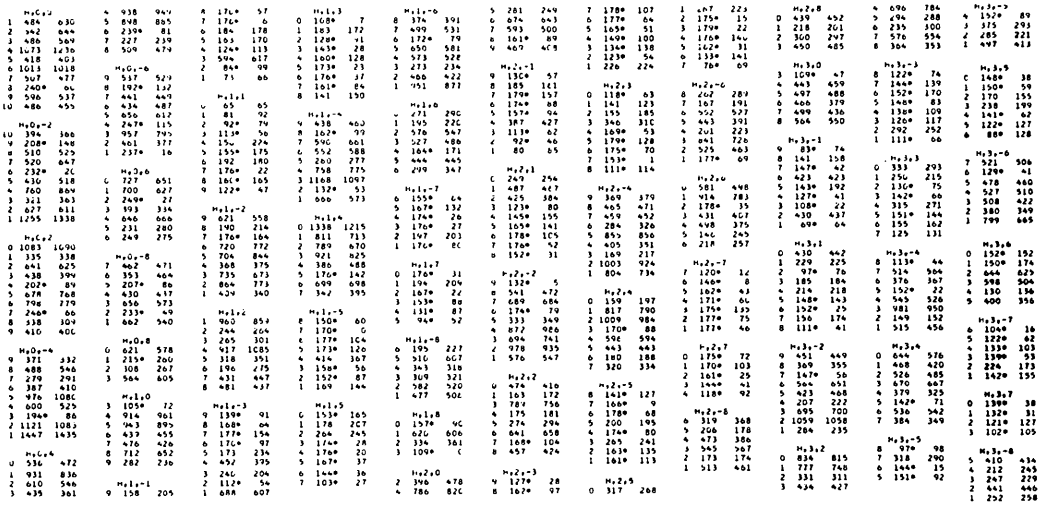
Table 3. *Fractional atomic parameters*

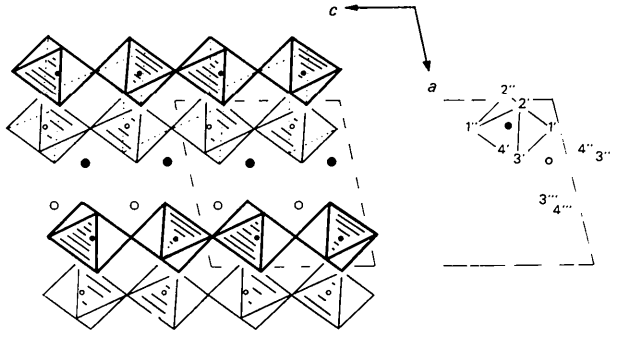
Space group $P2_1/c$. All atoms in the general position 4 (*e*).

		Alt. 1. All atoms treated as oxygens	Alt. 2. Ordered arrangement of oxygen and fluorine	Coordinates for atoms in an ideal, hexagonal close-packed arrangement
Nb	*x*	0·1555 ± 2	0·1554 ± 2	0·1875
	y	0·2654 ± 5	0·2655 ± 5	0·2500
	z	0·3177 ± 2	0·3176 ± 2	0·3125
	B	1·14 ± 5	1·10 ± 5	
Na	*x*	0·3679 ± 11	0·3685 ± 11	0·3125
	y	0·7741 ± 26	0·7750 ± 25	0·7500
	z	0·1187 ± 13	0·1187 ± 12	0·1875
	B	2·47 ± 18	2·42 ± 17	
O(1)	*x*	0·1705 ± 18	0·1721 ± 17	0·1875
	y	0·1591 ± 42	0·1561 ± 39	0·1250
	z	0·0533 ± 19	0·0545 ± 19	0·0625
	B	1·39 ± 30	1·34 ± 29	
O(2)	*x*	0·0333 ± 19	0·0351 ± 18	0·0625
	y	0·5571 ± 41	0·5546 ± 38	0·6250
	z	0·2066 ± 20	0·2084 ± 19	0·1875
	B	1·38 ± 27	1·24 ± 24	
O(3)	*x*	0·3750 ± 16	0·3760 ± 15	0·4375
	y	0·4497 ± 36	0·4513 ± 33	0·3750
	z	0·3143 ± 16	0·3142 ± 16	0·3125
	B	0·53 ± 23	1·86 ± 24	
O(4)	*x*	0·3164 ± 16	0·3166 ± 16	0·3125
	y	0·9835 ± 38	0·9827 ± 34	0·8750
	z	0·3775 ± 19	0·3793 ± 18	0·4375
	B	0·95 ± 26	2·16 ± 26	
F(3)			0·3760 ± 15	0·4375
			0·4513 ± 33	0·3750
			0·3142 ± 16	0·3125
			1·86 ± 24	
F(4)			0·3166 ± 16	0·3125
			0·9827 ± 34	0·8750
			0·3793 ± 18	0·4375
			2·16 ± 26	

Table 4. *Observed and calculated structure factors*

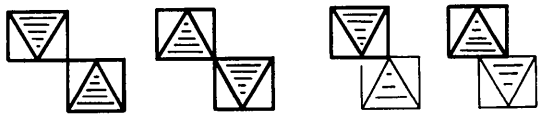
For unobserved reflexions (indicated by an asterisk) mod F_o is the estimated threshold value.





$NaNbO_2F_2$

Fig. 1. The crystal structure of $NaNbO_2F_2$. The filled and the open circles are niobium (small) and sodium (large) atoms at approximate heights of $\frac{3}{4}$ and $\frac{1}{4}$ respectively.



Corner sharing

Edge sharing

Fig. 2. Some different ways of joining octahedra when the projection axis is ~5 Å, corresponding to **a**+**b** in the hexagonal close packed arrangement of atoms.

numbered 1 and 2 were assumed to be oxygens and 3 and 4 to be fluorines. The least-squares refinement with a disordered arrangement of the anions gave an R index of 8·9%, while the fully ordered arrangement gave 8·5%. The ordered arrangement also improved the temperature factors and the standard deviations, which together with the coordinates for the two alternatives are compared in Table 3. In Table 4 a comparison is given between the observed structure factors and those calculated from the ordered arrangement. Interatomic distances are given in Table 5.

Table 5. *Interatomic distances*

Nb octahedron	
Nb–O(1)^{I}	2·12
Nb–O(1)^{II}	1·83
Nb–O(2)^{I}	1·93
Nb–O(2)^{II}	1·88
Nb–F(3)^{I}	2·04
Nb–F(4)^{I}	1·99
O(1)^{I} –O(2)^{I}	2·79
O(1)^{I} –O(2)^{II}	2·76
O(1)^{I} –F(3)^{I}	2·79
O(1)^{I} –F(4)^{I}	2·68
O(1)^{II}–O(2)^{I}	2·88
O(1)^{II}–O(2)^{II}	2·80
O(1)^{II}–F(3)^{I}	2·76
O(1)^{II}–F(4)^{I}	2·76
O(2)^{I} –O(2)^{II}	2·86
O(2)^{I} –F(3)^{I}	2·74
O(2)^{II}–F(4)^{I}	2·79
F(3)^{I}—F(4)^{I}	2·65
Na	
Na–O(1)^{I}	2·58
Na–O(2)^{I}	3·13
Na–F(3)^{I}	2·29
Na–F(3)^{II}	2·77
Na–F(3)^{III}	2·22
Na–F(4)^{I}	2·39
Na–F(4)^{II}	2·27
Na–F(4)^{III}	2·98

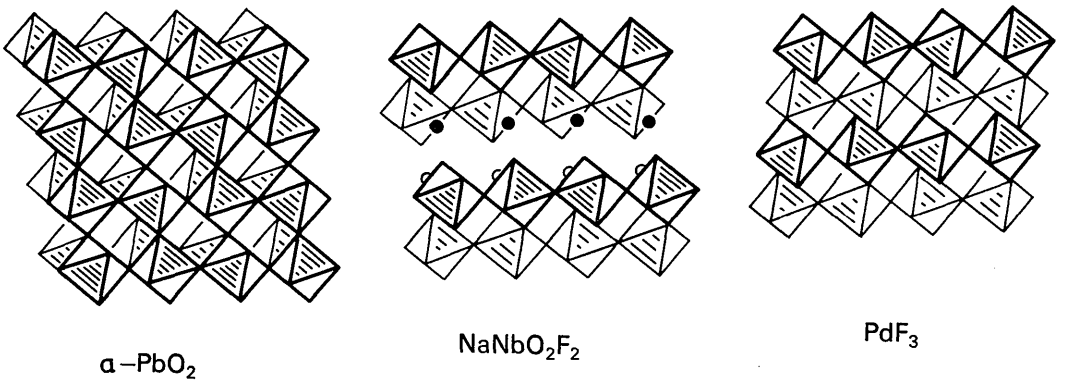


Fig. 3. The relationships between the α-PbO_2, $NaNbO_2F_2$ and PdF_3 structure types. The drawings of the structures are idealized.

Description of the structure

The structure is shown in Fig. 1. The niobium atom has four nearest oxygen neighbours at an average distance of 1·94 Å, and two nearest fluorine neighbours at an average of 2·015 Å. Within this octahedron the average oxygen–oxygen distance is 2·82 Å, the corresponding value for oxygen–fluorine is 2·75 Å and for fluorine–fluorine 2·65 Å. The configuration of the anions around sodium can be described in two different ways. F_3^{I}, F_3^{II}, F_3^{III}, F_4^{I}, F_4^{II} and F_4^{III} form a trigonal prism and on the outside of this there is an oxygen atom O_1^{I}, which completes the sevenfold coordination of sodium. On the other hand, sodium can also be described as being situated in a distorted octahedron of O_1^{I}, O_2^{I}, F_3^{I}, F_3^{III}, F_4^{I} and F_4^{II}. The sodium–fluorine distances within this octahedron are 2·26, 2·23, 2·36 and 2·22 Å with an average of 2·30 Å. The errors for the Nb–(O,F), Na–(O,F) and (O,F)–(O,F) distances are 0·015, 0·020 and 0·025 Å respectively.

The anion arrangement of this structure is approximately hexagonally close-packed. The ideal coordinates for atoms in such an arrangement are given in Table 3. The relationships between the real monoclinic cell of $NaNbO_2F_2$ and the hexagonal are:

$$\begin{aligned} \mathbf{a} &= 2\mathbf{a}_{hex} + \mathbf{c}_{hex} \\ \mathbf{b} &= \mathbf{a}_{hex} + \mathbf{b}_{hex} \\ \mathbf{c} &= -2\mathbf{a}_{hex} + \mathbf{c}_{hex} \, . \end{aligned}$$

Some different ways of joining octahedra formed by a hexagonal close-packed arrangement of anions are given in Fig. 2. The projection axis is the same as the *b* axis of $NaNbO_2F_2$.

If sodium is situated in an octahedron formed by the hexagonal close-packed arrangement of anions, the structure can be described as an ordered α-PbO_2 structure. The cation ordering, different from that of columbite, is described in an idealized drawing in Fig. 3.

Another way of describing this structure is to relate it to the PdF_3 structure type (Hepworth, Jack, Peacock & Westland, 1957), which is demonstrated in Fig. 3. Here it can be seen that blocks of the PdF_3 structure type form layers in the $NaNbO_2F_2$ structure. The composition of these layers is $(NbO_2F_2)_n^{n-}$, and they are held together by the sodium ions. The niobium anion octahedra all share corners. The ordering of the fluorine and oxygen atoms found is quite natural, with the fluorine atoms bridging the sodium ions and the layers.

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