

The Crystal Structure of Sodium Pentafluorooxoniate(2-), Na₂[NbF₅O]

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Crystals of Na₂[NbF₅O] are orthorhombic, space group *Pcnb* (No. 60), with $a=5.089(1)$ Å, $b=5.512(1)$ Å, $c=18.207(4)$ Å and $Z=4$. The structure was solved and refined from single-crystal X-ray diffractometer data to a final R_F -value of 0.027. The pentafluorooxoniate(2-) ions are slightly distorted octahedra with edge lengths in the range 2.588(3)–2.826(3) Å. The configuration around the sodium ions are very distorted octahedra (edge lengths 2.588(3)–3.742(4) Å). The niobium atom, the oxygen atom and one fluorine atom are disordered. The structure has a close resemblance with that of Fe₂WO₆, the prototype of the so-called tri- α -PbO₂ type.

Bond lengths within the [NbF₅O]²⁻ anion are: Nb–O 1.765(2) Å, Nb–F_{trans} 2.095(2) Å and Nb–F_{eq} 1.925(2)–1.974(2) Å. Coordination distances to the sodium ions are 2.221(3)–2.447(3) Å.

A number of fluoroperoxo complexes of pentavalent niobium, mainly with sodium as cation, have been studied at this department.^{1–5} Fluorooxonates are formed as intermediates in the preparation of such compounds and it seemed natural to investigate the former, many of which can be isolated from aqueous solutions or from melts.⁶ The structures of two fluorooxonates have already been published.^{7,8} One of these, (C₉H₈NO)₂[NbF₅O]·2H₂O, contains a disorderedly orientated octahedral anion.⁷ In the other, α -Na₃[NbF₆O], the arrangement of the ligands in the anion is somewhat distorted pentagonal bipyramidal.⁸ This contradicts the mono-capped octahedral configuration proposed by Williams *et al.* for the [NbF₆O]³⁻ ion in K₃[NbF₆O],⁹ which appears as an example of that

geometry in certain textbooks (see, *e.g.* Ref. 10). In the present work the structure of Na₂[NbF₅O] is reported; it is neither isomorphous with Li₂NbF₅O,¹¹ nor with K₂[NbF₅O].¹²

EXPERIMENTAL

Preparation. 10.0 g niobium(V) oxide and 9.5 g sodium fluoride were dissolved in 60 ml of boiling 38 % hydrofluoric acid in a platinum crucible. The excess of hydrofluoric acid was expelled by repeated addition of water and subsequent evaporation almost to dryness. One of the crystals picked out from the crystalline crust thus obtained was found suitable for the X-ray work; most others were intergrown.

X-ray method. Intensities were recorded at 18 °C with a SYNTEX P2₁ automatic four-circle single-crystal X-ray diffractometer using graphite-monochromatized MoK α radiation and a parallel-epipedic crystal with the dimensions 0.06×0.09×0.09 mm. The ω -2 θ scan method was used and the 2 θ scan speed was allowed to vary between 2.3 and 20.0 °/min depending on the intensity of the measured reflexion. Data were collected for both hkl and $hk\bar{l}$ reflexions for $3.5^\circ \leq 2\theta \leq 80.0^\circ$. Two test reflexions, measured after each forty-eighth reflexion, showed no significant difference in intensity during the data collection. A profile analysis based on the Lehmann-Larsen method¹³ was applied to the 96-step profile collected for each reflexion.

A total of 2978 reflexions were measured. After averaging hkl and $hk\bar{l}$ reflexions 874 independent reflexions with $I \geq 3\sigma(I)$ were obtained. The intensities were corrected for Lorentz and polarization effects. Since a rather small crystal was used absorption correction was not considered necessary.

The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

CRYSTAL DATA

Sodium pentafluorooxonioate(2-),
 $\text{Na}_2[\text{NbF}_5\text{O}]$; F.W.=249.88 Space group *Pcnb*
 (No. 60; non-standard setting).

Positions: $8d \pm(x, y, z)$; $\pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$;
 $\pm(\frac{1}{2}+x, \bar{y}, \frac{1}{2}-z)$; $\pm(\bar{x}, \frac{1}{2}-y, z)$

$4c \pm(0, \frac{1}{4}, z)$; $\pm(\frac{1}{2}, \frac{1}{4}, \frac{1}{2}+z)$

$a=5.089(1) \text{ \AA}$, $b=5.512(1) \text{ \AA}$, $c=18.207(4) \text{ \AA}$,
 $V=510.7(2) \text{ \AA}^3$, $Z=4$, $D_c=3.250 \text{ g cm}^{-3}$,
 $\mu(\text{MoK}\alpha)=2.51 \text{ mm}^{-1}$

STRUCTURE DETERMINATION

Space considerations alone suggested that niobium occupied the four-fold site $4c$ of space group *Pcnb* with $z=0.12$. This was confirmed by a Patterson summation from which $z_{\text{Nb}}=0.1111$ was obtained. The complete structure was then solved by electron density calculations and refined by the least-squares method. With isotropic thermal parameters the R -value became 0.080 ($R=\Sigma|F_o|-|F_c|/\Sigma|F_o|$) and with anisotropic thermal parameters 0.033. All the fluorine atoms and

the oxygen atom were found to occupy three general eight-fold positions $8d$, denoted F1–F3. As an ordered structure presupposes the oxygen atom to occupy a four-fold site the oxygen atom and at least one fluorine atom in the asymmetric unit could not be distinguished in this model. At this stage the niobium-ligand distances obtained were: Nb–F1 1.846(3), Nb–F2 2.021(3) and Nb–F3 1.948(3) Å, respectively. Since the Nb–O distance was supposed to be considerably shorter than the Nb–F distances and since the electron density difference map was negative at F1 (the atomic form factor of fluorine was used for the ligands) there was strong evidence for F1 to be half fluorine and half oxygen. A model with F1 and O in two different, half-occupied, and well-separated positions $8d$ was refined. Within the limits of experimental errors the resulting positions of F1 and O were indistinguishable. The sodium and ligand atoms showed only minor anisotropy (Table 1b). The niobium atom, however, had a considerably larger thermal motion in the direction Nb–(F1,O). Since this seemed to be without physical meaning the assumption was made that the niobium atom is situated at a short distance from the two-fold rotation axis through $(0, \frac{1}{4}, z)$. Such a model, with niobium in site $8d$ with half-occupancy, was

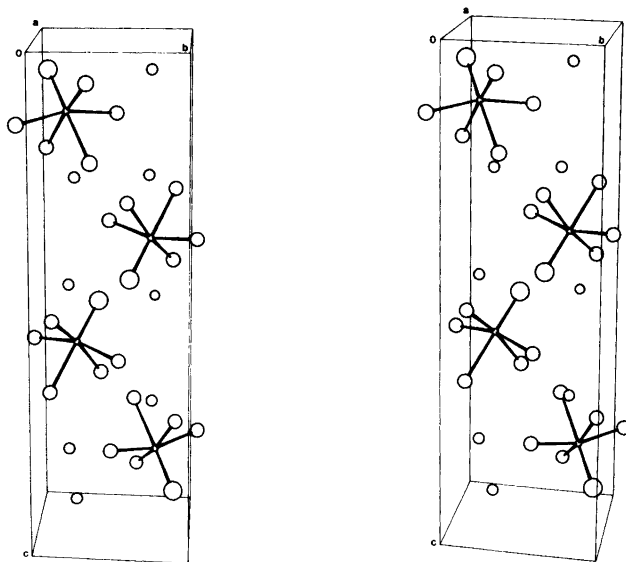


Fig. 1. Stereoscopic drawing of the unit cell of $\text{Na}_2[\text{NbF}_5\text{O}]$.

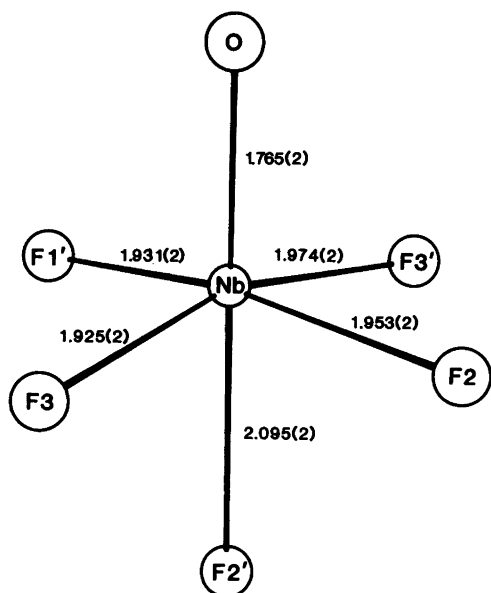


Fig. 2. The anion [NbF₅O]²⁻.

tested. Refinement led to a niobium position 0.112(1) Å from the two-fold rotation axis; the niobium atom then showed only minor anisotropy (Table 1b). Starting from a position either closer to or more remote from the two-fold axis led to the same result. The *R*-value then was 0.027. The weighting scheme $w = (a + |F_o| + c|F_o|^2)^{-1}$ with $a = 50$ and $c = 0.0001$ was used.¹⁴ The scattering factors for Nb, Na⁺, F and O were taken from Ref. 15 as were the dispersion corrections. An electron density difference synthesis calculated after the final cycle of refinement showed no peak higher than 0.8 e Å⁻³. Calculations were carried out on an IBM 3033 computer using the crystallographic programmes described in Ref. 16. A list of observed and calculated structure factors are available from the author on request.

RESULTS AND DISCUSSION

Positional and thermal parameters are given in Table 1, distances and angles within the anion in Table 2, and coordination distances to sodium ions in Table 3. A stereoscopic drawing of the unit cell is shown in Fig. 1 and the anion in Fig. 2.

Table 1a. Fractional atomic coordinates and B_{eq} for Na₂[NbF₅O]. Space group *Pcnb*, *Z*=4.
 $B_{eq} = \frac{4}{3} \sum_i \beta_{ij} a_i \cdot a_j$.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/\text{Å}^2$
Nb	8d ^a	0.02054(9)	0.24279(20)	0.11059(2)	0.93(2)
Na1	4c	0	¼	0.44385(11)	1.72(3)
Na2	4c	½	¼	0.27205(10)	1.71(2)
O, F1 ^b	8d	0.2337(4)	0.1158(4)	0.04451(12)	1.66(3)
F2	8d	0.2080(5)	0.0999(4)	0.19357(12)	2.02(3)
F3	8d	0.2099(4)	0.5415(4)	0.12482(11)	1.69(3)

^a Half occupied. ^b Half O, half F.

Table 1b. Anisotropic thermal parameters U_{ij} for Na₂[NbF₅O]. The expression used is $\exp[-2\pi^2 (U_{11}h^2a^{*2} + \dots + U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	0.0098(7)	0.0136(2)	0.0122(1)	-0.002(2)	-0.0000(3)	-0.0000(9)
Na1	0.0200(7)	0.0210(7)	0.0243(7)	0.006(2)	0	0
Na2	0.0238(7)	0.0190(7)	0.0222(7)	-0.009(2)	0	0
F1	0.0188(8)	0.0232(9)	0.0212(8)	0.006(2)	0.007(2)	-0.004(2)
F2	0.0266(9)	0.0252(9)	0.0249(8)	-0.010(2)	0.026(2)	0.018(2)
F3	0.0232(8)	0.0168(7)	0.0243(8)	-0.016(2)	0.007(2)	-0.006(1)

Table 2. Distances (Å) and angles (°) in the $[\text{NbF}_5\text{O}]^{2-}$ ion. A prime indicates the generated position ($x, \frac{1}{2}-y, z$).

Distance		Angle	
Nb—O	1.765(2)	O—Nb—F1'	98.5(1)
Nb—F1'	1.931(2)	O—Nb—F2'	175.8(1)
Nb—F2	1.953(2)	O—Nb—F2	93.8(1)
Nb—F2'	2.095(2)	O—Nb—F3	97.1(1)
Nb—F3	1.925(2)	O—Nb—F3'	98.0(1)
Nb—F3'	1.974(2)	F1'—Nb—F2'	84.8(1)
O...F1'	2.802(5)	F1'—Nb—F2	166.5(1)
O...F2	2.718(3)	F1'—Nb—F3	94.2(1)
O...F3	2.767(3)	F1'—Nb—F3'	90.2(1)
O...F3'	2.826(3)	F2'—Nb—F2	83.1(1)
F1'...F2'	2.718(3)	F2'—Nb—F3	80.0(1)
F1'...F3	2.826(3)	F2'—Nb—F3'	84.5(1)
F1'...F3'	2.767(3)	F2—Nb—F3	89.8(1)
F2...F2'	2.687(5)	F2—Nb—F3'	82.4(1)
F2...F3	2.737(3)	F3—Nb—F3'	163.4(1)
F2...F3'	2.588(3)		
F2'...F3	2.588(3)		
F2'...F3'	2.737(3)		

Table 3. Coordination distances (Å) to the sodium ions.

Na1...F3 ($\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$)	2.250(2)
Na1...O, F1 ($\frac{1}{2}-x, y, \frac{1}{2}+z$)	2.396(3)
Na1...O, F1 ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$)	2.438(2)
Na2...F2 (x, y, z)	2.221(3)
Na2...F2 ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$)	2.288(2)
Na2...F3 ($\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$)	2.447(3)

Table 4. Displacements (Å) of the atoms from certain least-squares planes^a in the $[\text{NbF}_5\text{O}]^{2-}$ ion. A prime indicates the generated position ($\bar{x}, \frac{1}{2}-y, z$). Defining atoms are

Plane	Defining atoms
Plane I	O, F2, F2' and F1'
Plane II	O, F3, F2' and F3'
Plane III	F1', F3, F2 and F3'

Atom	Plane I	Plane II	Plane III
Nb	0.027	0.080	0.234
O	0.073	0.025	1.998
F1'	-0.073	1.998	0.025
F2	-0.073	-1.859	0.028
F2'	0.073	0.028	-1.859
F3	1.929	-0.028	-0.026
F3'	-1.929	-0.026	-0.028

^a The angles between the planes I and II, I and III, and II and III are 90.9, 89.1 and 89.5°, respectively.

The crystals of $\text{Na}_2[\text{NbF}_5\text{O}]$ are built up of sodium ions and discrete pentafluoro-oxoniobate(2-) ions held together by ionic forces. The oxygen atom and the five fluorine atoms occupy three general 8-fold positions 8d. The oxygen atom O thus cannot have an ordered location, but the structure analysis has shown that the oxygen atom and the fluorine atom F1 probably occupy a common position. O is then located in one of the two equivalent positions related by the two-fold axis through $(0, \frac{1}{4}, z)$ and F1 in the other and *vice versa*. The complex anion is thus orientated in either of two equally probable ways. The structure resembles that of Fe_2WO_6 , the prototype of the so-called tri- α - PbO_2 type.^{17,18} A recent example of that type is $\text{Na}_2\text{WO}_2\text{F}_4$,¹⁹ which seems to be ordered, contrary to $\text{Na}_2[\text{NbF}_5\text{O}]$. The ligands have a slightly distorted octahedral configuration in the anion with the niobium atom displaced 0.234 Å from the equatorial plane towards the oxygen atom (Table 4). In $\text{N}_2\text{H}_6[\text{NbF}_5\text{O}] \cdot \text{H}_2\text{O}$,²⁰ in which the anion is very similar to that in the present investigation, the corresponding distance was found to be 0.27 Å. As a consequence of this displacement the angle O—Nb—F_{equatorial} is larger than 90°, being on the average 97(2)° in $\text{Na}_2[\text{NbF}_5\text{O}]$ and 101(1)° in $\text{N}_2\text{H}_6[\text{NbF}_5\text{O}] \cdot \text{H}_2\text{O}$.

The Nb—F_{equatorial} bond distances,

1.925(2)–1.974(2) Å, are shorter than the Nb–F_{apical} bond distance, being 2.095(2) Å in the present investigation and 2.21(2) Å in N₂H₆[NbF₅O]·H₂O.²⁰ They are also shorter than Nb–F_{equatorial} bond distances observed in the pentagonal planes in a number of pentafluoroperoxoniobates (1.97–2.05 Å),^{1–4} and in α-Na₃[NbF₆O] (2.016–2.050 Å),⁸ but compare well, however, with the values 1.93(2) and 1.96(2) Å found in N₂H₆[NbF₅O]·H₂O. In K₂[NbF₅O] as short Nb–F_{equatorial} bond distances as 1.84 Å were observed.¹² In the latter compound an Nb=O distance of 1.68(3) Å was observed, while the corresponding distance is 1.765(2) Å in Na₂[NbF₅O] and 1.75(2) Å in N₂H₆[NbF₅O]·H₂O. The Nb=O distance is on the average 1.71±0.02 Å, calculated from data for N₂H₆[NbF₅O]·H₂O,²⁰ K₂[NbF₅O],¹² [NbCl₂O(OC₂H₅)(C₁₀H₈N₂)],²¹ [(C₆H₅)₄As]₂[Nb(NCS)₅O],²¹ and (NH₄)₃[Nb(C₂O₄)₃O]·H₂O.^{22,23} In α-Na₃[NbF₆O] the Nb=O bond length is 1.738(3) Å.⁸ The F···F and F···O distances between nearest neighbours in the [NbF₅O]²⁻ ion range between 2.588(3) and 2.826(3) Å, comparable to the corresponding distances, 2.68(3)–2.83(3) Å, in N₂H₆[NbF₅O]·H₂O. The [NbF₅O]²⁻ ions in Na₂[NbF₅O] and N₂H₆[NbF₅O]·H₂O are, therefore, rather similar, the largest discrepancy, 0.12 Å, being between the Nb–F_{apical} bond distances. This difference might be a consequence of the hydrogen bonding in N₂H₆[NbF₅O]·H₂O. In both compounds the anions have approximately C_{4v} symmetry, while the deviation from this symmetry is considerably larger in K₂[NbF₅O].

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