

The Crystal Structure of Sodium Pentafluoroperoxoniate(V) Monohydrate, $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$

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Crystals of $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$ are orthorhombic, space group *Pbcm*, with $a=7.588(3)$ Å, $b=10.318(4)$ Å, $c=8.185(2)$ Å, $V=640.8(4)$ Å³ and $Z=4$. The structure was solved from 685 reflexions collected by the Weissenberg film method using $\text{CuK}\alpha$ radiation. The refinement was based on 2121 observed, independent reflexions obtained with a SYNTEX single crystal X-ray diffractometer, using $\text{MoK}\alpha$ radiation. Least-squares refinement of the structural parameters yielded a final *R*-value of 0.039 (0.098 with film data).

In the pentafluoroperoxoniate(V) anion niobium is surrounded by a pentagonal bipyramidal arrangement of ligands, the peroxy group and three fluorine atoms forming the equatorial plane and the two remaining fluorine atoms the apices. The niobium atom is slightly (0.026 Å) displaced from the pentagonal plane. The symmetry of the anion is almost C_{2v} . Bond distances are; Nb–O 1.928(4) Å, O–O 1.476(7) Å, Nb–F_{apical} 1.906(4) and 1.938(4) Å and Nb–F_{equatorial} 1.976(3) and 2.037(4) Å, respectively.

In connection with work on peroxy complexes at this department, attention has been focused on the structures of fluoroperoxonates. A number of fluoroperoxonates exist¹ and the fluoroperoxonate system may be as complex although only a few compounds have yet been reported. A preliminary synthesis followed the method given by Balke and Smith for $3\text{NaF}\cdot\text{NbO}_2\text{F}_3\cdot\text{H}_2\text{O}$.² From the crystalline mass obtained, three crystallographically different compounds could be isolated, none of which had the stoichiometry indicated above. According to crystal structure studies they have the formulae $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$,^{3,4} $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$,^{3,5} and $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot 2\text{H}_2\text{O}$,^{3,5} the first compound being described in this paper.

EXPERIMENTAL

Preparation. For the photographic method the preparational method given by Balke and Smith was used.² Both sodium and potassium fluoroperoxonates were synthesised. For the crystallographic work the sodium salts were more suitable, since they formed welldeveloped crystals while the potassium salts crystallised as thin flakes. For the diffractometer work crystals were obtained using a slightly modified method in which sodium fluoride was used instead of sodium carbonate. In all preparations $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$ was obtained only in minute quantities. The major product was $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot 2\text{H}_2\text{O}$ and/or $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$ which separated out first from the solution while $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$ was obtained at a later stage of the crystallisation process, probably due to transformation of part of $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot 2\text{H}_2\text{O}$. No chemical analysis was therefore performed on $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$.

X-Ray methods. X-Ray powder photographs were obtained by the Guinier-Hägg method ($\text{CuK}\alpha$ -radiation) using $\text{Pb}(\text{NO}_3)_2$ ($a=7.8566$ Å at 21 °C) as an internal standard. Observed lines in the powder photograph of $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$ are given in Table 1. For the single crystal work multiple film equi-inclination Weissenberg photographs were taken at room temperature on a Nonius integrating camera (the crystal rotating about [001], layer lines 0–7, $\text{CuK}\alpha$ -radiation). 685 independent reflexions were registered from a rod-shaped crystal with dimensions $0.056 \times 0.072 \times 0.34$ mm. The intensities were corrected for Lorentz, polarization and absorption effects but not for extinction.

Intensity data for the refinement were recorded at room temperature with a SYNTEX $P2_1$ automatic single crystal X-ray diffractometer, using a crystal with dimensions $0.186 \times 0.210 \times 0.327$ mm. The X-ray intensities were measured by the ω - 2θ scan

Table 1. Observed lines in the powder photograph of $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$ at room temperature registered with $\text{CuK}\alpha$ radiation, using lead nitrate $a=7.8566 \text{ \AA}$) as internal standard.

d_o	d_c	hkl	I_o	d_o	d_c	hkl	I_o
7.564	7.560	1 0 0	m	1.8593	1.8596	4 1 0	w
6.078	6.099	1 1 0	m	1.8201	1.8197	3 3 2	s
5.159	5.159	0 2 0	s	1.8126	1.8131	4 1 1	vw
4.892	4.885	1 1 1	vs	1.7954	1.7955	2 0 4	w
4.361	4.361	0 2 1	m	1.7890	1.7891	1 5 2	s
4.256	4.261	1 2 0	vw	1.7750	1.7750	4 2 0	vw
4.082	4.080	0 0 2	s	1.7677	1.7682	2 5 1	vw
3.781	3.781	2 0 0	w	1.7348	1.7345	4 2 1	m
3.393	3.391	1 1 2	s	1.7192	1.7195	0 6 0	m
3.255	3.255	2 1 1	vw	1.7151	1.7153	4 0 2	vw
3.199	3.200	0 2 2	s	1.7087	1.7092	1 3 4	s
3.128	3.130	1 3 0	vs	1.6957	1.6957	2 2 4	s
3.050	3.050	2 2 0	m	1.6823	1.6826	0 6 1	vw
2.8565	2.8567	2 2 1	w	1.6764	1.6774	2 4 3	m
2.6802	2.6783	2 1 2	w	1.6567	1.6567	4 3 0	vw
2.5787	2.5793	0 4 0	w	1.6489	1.6490	3 4 2	vw
2.5426	2.5441	2 3 0	w	1.6273	1.6277	4 2 2	w
2.5213	2.5206	3 0 0	vw	1.5967	1.5967	3 5 0	m
2.4835	2.4843	1 1 3	m	1.5910	1.5916	2 3 4	vw
2.4576	2.4593	0 4 1	w	1.5762	1.5766	1 1 5	m
2.4496	2.4486	3 1 0	m	1.5662	1.5674	3 1 4	m
2.4409	{ 2.4423	{ 2 2 2	w	1.5554	1.5561	0 2 5	m
	{ 2.4412	{ 1 4 0	w	1.5368	1.5373	2 6 1	m
2.4056	{ 2.4062	{ 0 2 3	w	1.5158	1.5158	3 2 4	vw
2.3453	2.3453	3 1 1	vw	1.4871	{ 1.4869	{ 3 5 2	m
2.1583	2.1592	2 1 3	vw		{ 1.4866	{ 4 2 3	
2.0996	2.0996	3 1 2	vw	1.4825	1.4829	2 1 5	vw
2.0940	2.0949	1 4 2	w		{ 1.4736	{ 2 4 4	
2.0617	2.0617	2 4 1	m	1.4730	{ 1.4719	{ 5 1 1	vw
2.0395	2.0402	0 0 4	m	1.4615	1.4614	2 6 2	m
2.0333	2.0330	3 3 0	w	1.4533	1.4535	0 6 3	w
1.9908	1.9907	1 5 0	m	1.4397	1.4401	3 3 4	w
1.9691	1.9697	1 0 4	w	1.4294	1.4289	5 2 1	vw
1.9346	1.9348	1 1 4	m	1.4245	1.4248	1 5 4	s
1.8964	1.8972	0 2 4	vw	1.3795	1.3792	0 4 5	w
1.8887	1.8887	2 4 2	m	1.3738	1.3743	4 1 4	w
1.8706	1.8717	0 4 3	m	1.3635	1.3635	1 7 2	vw

technique using graphite-monochromated $\text{MoK}\alpha$ radiation ($2\theta \leq 90^\circ$). A reflexion measured after each twenty-fifth reflexion showed no significant difference in intensity during the collection of the data. The 2θ scan speed was varied between 1.5 and $8^\circ/\text{min}$ and a 96-step profile was recorded for each reflexion. The Lehmann-Larsen method was used for background correction.⁶ A total of 3019 independent reflexions were measured. Of these, 2121 having $I_o \geq 3\sigma(I_o)$, were regarded as being observed and were used in the subsequent calculations. Corrections were made for Lorentz, polarisation and absorption effects. For the absorption correction

the crystal was divided into a $6 \times 6 \times 6$ grid. The transmission factor varied between 0.65 and 0.71. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 13 reflexions.

Computing methods. Calculations were carried out on an IBM 360/65 computer at Göteborg Universities' Computing Centre using the crystallographic programs described in Ref. 7. The atomic scattering factors for Na^+ , Nb, F and O were taken from the *International Tables for X-Ray Crystallography, Vol. III*, as was the dispersion correction applied to Nb.

CRYSTAL DATA

$\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$	
Unit cell	Orthorhombic with $a = 7.588(3) \text{ \AA}$ [7.562] $b = 10.318(4) \text{ \AA}$ [10.317] $c = 8.185(2) \text{ \AA}$ [8.161] $V = 640.8 (4) \text{ \AA}^3$ [636.7] $Z = 4$
Formula weight	$M_r = 283.89$
Density	$D_c = 2.943 \text{ g cm}^{-3}$
Systematic absences	$0kl$ for $k = 2n + 1$ $h0l$ for $l = 2n + 1$
Space group	$Pbcm$ (No. 57) (or $Pbc2_1$ (No. 29))
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 20.4 \text{ cm}^{-1}$ $\mu(\text{CuK}\alpha) = 184 \text{ cm}^{-1}$

Values in brackets refer to powder diffraction data. The errors given are σ .

A list of observed and calculated structure factors is available from the author upon request.

STRUCTURE DETERMINATION

The structure was solved from film data (at that time no automatic single crystal X-ray diffractometer was available at the department). From the Patterson function it could be concluded that the niobium atoms occupy the positions $4d$ of space group $Pbcm$ with $x \approx 0.25$ and $y \approx 0.06$. From a series of Fourier calculations the other atomic positions were deduced, consistent with the formula $\text{Na}_2[\text{NbF}_5(\text{O}_2)]$. Least-squares refinement of positional and isotropic temperature parameters yielded an R -value of 0.123.

An electron density maximum at $(0.65, \frac{1}{4}, 0)$ with a peak height half of that of an oxygen peak still persisted in a difference map. This was taken to be due to a water molecule. On including this and refining positional and isotropic temperature parameters as well as an overall scale factor the R -value dropped to 0.105. The water oxygen atoms were then assumed to occupy the positions $4c$ with $x = 0.654$. The observed extension of the water oxygen peak in the Fourier maps – in the difference map the peak was well resolved into two peaks 0.8 \AA apart – was interpreted as being due to disorder, the parameters obtained being average ones.

An alternative description, used subsequently, is based on the assumption that the water oxygen atoms statistically occupy half-filled positions $8e$.

This gave a final R -value of 0.098 for the film data set. The positional parameters obtained are given in Table 2.

Refinement of the structural parameters based on diffractometer data was performed at a later date. An overall scale factor, positional and anisotropic thermal parameters and an isotropic extinction coefficient were refined using a full matrix least-squares procedure. A final R -value of 0.039 was obtained with the parameters given in Table 2. The maximum peak height in a subsequent difference map was 2 e/\AA^3 which is less than 10% of the height of a fluorine peak. The results obtained by the two methods agree to within 3σ and they indicate that the choice of space group $Pbcm$ is reasonable.

DISCUSSION

The crystals of sodium pentafluoroperoxoniobate(V) monohydrate consist of sodium ions, pentafluoroperoxoniobate(V) ions and water of crystallization. The content of the unit cell is shown in Fig. 1 and the anion in Fig. 2. Bond distances and angles are given in Table 3, and coordination distances to the sodium ions in Table 4.

$[\text{NbF}_5(\text{O}_2)]^{2-}$ has a pentagonal bipyramidal arrangement of ligands, as shown in Fig. 2, a configuration observed in several transition metal peroxo complexes (see, e.g., Refs. 8–10). The anion has a crystallographic mirror plane in which Nb, F1, F2 and F3 are situated. The point group is therefore C_s . The distances from the least-squares plane through F2, F4, F4', O1 and O1' to the atoms Nb, F2, F4, O1, F1 and F3 are 0.026, -0.046 , 0.040, -0.018 , -1.899 and 1.914 \AA , respectively. The line joining F1 and F3 forms an angle of 89.5° with the pentagonal plane. The intersection between the mirror plane and the pentagonal plane is, therefore, approximately a two-fold proper rotation axis. Hence, the point group is almost C_{2v} .

The niobium atom is displaced 0.026 \AA from the equatorial plane. Such displacement is usually observed for transition metal peroxo compounds, when, as in this case, the apical positions are occupied by identical ligands. In those cases when the apical atoms are different, or are differently coordinated, the central atom is, in most cases, displaced by 0.2 – 0.5 \AA (see Table 6 in Ref. 9).

The equatorial Nb–F bond distances, 1.976 – 2.037 \AA , are somewhat longer than the apical ones, 1.906 – 1.938 \AA . This compares well with the corresponding distances in $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$,⁵ in

Table 2a. Atomic coordinates, expressed as fractions of the cell edges, for $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$. The numbers in parentheses are the standard deviations. Figures within brackets refer to film data. The extinction coefficient is $0.39(3) \times 10^4 \text{ s}$.

Atom	Position	x	y	z
Nb	4d	0.22944(6) [0.2292(2)]	0.06249(3) [0.0621(2)]	1/4 [1/4]
Na 1	4c	0.9543(4) [0.952(1)]	1/4 [1/4]	0 [0]
Na 2	4d	0.2397(4) [0.241(2)]	0.4724(4) [0.470(1)]	1/4 [1/4]
F1	4d	-0.0998(6) [-0.099(2)]	0.4006(3) [0.400(1)]	1/4 [1/4]
F2	4d	-0.0199(5) [-0.026(1)]	0.1355(4) [0.136(1)]	1/4 [1/4]
F3	4d	0.2982(7) [0.300(2)]	0.2401(4) [0.242(2)]	1/4 [1/4]
F4	8e	0.1808(5) [0.182(2)]	0.0797(3) [0.081(1)]	0.0138(3) [0.013(2)]
O1	8e	0.4421(5) [0.442(2)]	-0.0107(4) [-0.015(1)]	0.1598(4) [0.163(2)]
O2	8e ^a	0.655(1) [0.651(2)]	0.224(1) [0.224(3)]	0.035(2) [0.042(3)]

^a Half-filled.

Table 2b. Anisotropic temperature parameters β_{ij} and their standard deviations. The expression used is $\exp -(\beta_{11}h^2 + \dots + 2\beta_{23}kl)$. The *B*-values obtained by the film method for the atoms Nb to O2 are in order 1.64(6), 3.3(2), 3.6(2), 2.8(3), 2.3(3), 3.8(2), 3.9(2), 5.0(3) and 8(1).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb	0.00646(9)	0.00276(3)	0.00351(4)	0.00047(3)	0	0
Na1	0.0123(5)	0.0069(3)	0.0097(4)	0	0	0.0038(3)
Na2	0.0107(5)	0.0111(4)	0.0060(3)	0.0038(3)	0	0
F1	0.0121(7)	0.0032(2)	0.0101(5)	0.0014(3)	0	0
F2	0.0089(6)	0.0047(3)	0.0070(4)	0.0017(3)	0	0
F3	0.0163(9)	0.0037(3)	0.0125(7)	-0.0013(4)	0	0
F4	0.0124(5)	0.0080(3)	0.0041(2)	0.0008(3)	-0.0003(3)	0.0001(2)
O1	0.0115(7)	0.0098(4)	0.0082(4)	0.0038(4)	0.0011(4)	-0.0001(3)
O2	0.008(1)	0.009(1)	0.022(3)	-0.000(1)	0.002(1)	-0.004(1)

which they are 1.975–2.019 and 1.906–1.936 Å, respectively. In $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ the equatorial plane takes one of two possible orientations, caused by the peroxo group being statistically oriented along two mutually perpendicular direc-

tions.⁵ Only one of the fluorine atoms is situated in the pentagonal plane in either orientation, the Nb–F distance being 1.987 Å, while the two other fluorine atoms are apically situated in one half of the complexes in the crystal and equatorially in the

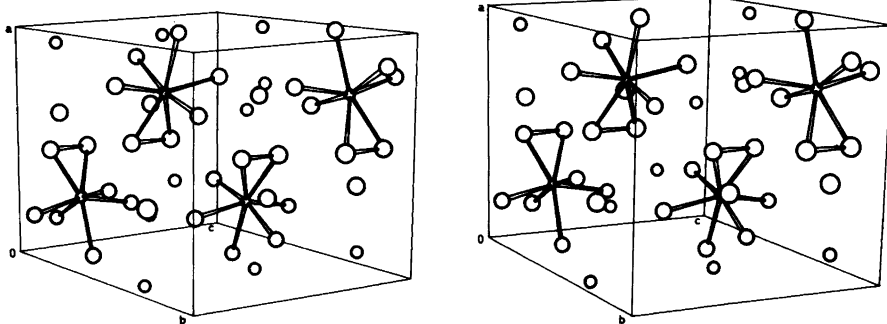
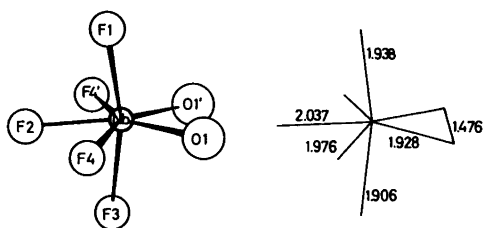


Fig. 1. Stereoscopic drawing of the unit cell of $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$.

Table 3. Bond distances (Å) and angles (°) in $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$. Values within brackets refer to film data.

Nb—O1	1.928(4)	[1.93(2)]	O1—Nb—O1'	45.0(2)	[43.0(7)]
F1	1.938(4)	[1.94(2)]	F1	95.0(2)	[93.8(5)]
F2	2.037(4)	[2.08(2)]	F2	157.3(1)	[158.0(3)]
F3	1.906(4)	[1.93(2)]	F3	98.5(2)	[99.4(6)]
F4	1.976(3)	[1.98(1)]	F4	79.5(2)	[80.4(5)]
O1—O1'	1.476(7)	[1.42(3)]	F4'	124.5(2)	[123.4(5)]
			F1—Nb—F2	81.2(2)	[81.0(6)]
			F3	165.4(2)	[165.8(6)]
			F4	89.0(1)	[89.6(3)]
			F2—Nb—F3	84.2(2)	[84.7(6)]
			F4	78.1(1)	[78.2(3)]
			F3—Nb—F4	88.0(1)	[87.5(3)]
			F4—Nb—F4'	156.1(1)	[156.3(6)]

Fig. 2. The ion $[\text{NbF}_5(\text{O}_2)]^{2-}$.

other half. The observed Nb—F distances, 1.936 and 1.938 Å, respectively, are therefore only average values. The structure of still another compound containing the $[\text{NbF}_5(\text{O}_2)]^{2-}$ ion, namely $[\text{C}_9\text{H}_8\text{NO}]_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$, has been solved by Ružič-Toroš *et al.* using film data.¹¹ A reinvestigation by Stomberg based on diffractometer data has shown that it, too, contains disorderly oriented anions.⁵ Further observed Nb—F distances can be found in Ref. 1. Obviously the

Table 4. Coordination distances to the sodium ions.

	Distance/Å
Na1—F1 (1+x, y, z)	2.602(2)
F2 (1+x, y, z)	2.371(2)
F4 (1+x, y, z)	2.460(4)
O2	2.305(9)
Na2—F1	2.680(6)
F2 (\bar{x} , $\frac{1}{2} + y$, z)	2.368(5)
F3	2.438(6)
F4 (x, $\frac{1}{2} - y$, \bar{z})	2.270(3)
O1 (1-x, $\frac{1}{2} + y$, $\frac{1}{2} - z$)	2.531(5)

equatorial fluorine atoms are more remote from the niobium atom than the apical ones. In $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5\text{O}] \cdot 3\text{H}_2\text{O}$, the crystals of which contain two crystallographically different anions, all bond distances between niobium and the octahedrally coordinated fluorine atoms are almost the same, having values between 1.909 and 1.943 Å.⁵ The difference between the Nb—F_{equatorial} and Nb—F_{apical} bond length may simply depend on different packing conditions, the five equatorial atoms exerting larger repulsive effects on each other than on the four atoms in the plane perpendicular to the pentagonal plane.

The Nb—O bond distance, 1.928 Å, is normal for an Nb—O single bond, observed distances in $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$, $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ and $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ being 1.924–1.940, 1.933–1.962 and 1.89–2.00 Å, respectively.⁵

The distance between the oxygen atoms in the peroxo group, 1.476 Å, compares well with other observations (see Table 7 in Ref. 9). In $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$ the O—O distance is 1.481(4) Å and in $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ the average O—O distance is 1.46 Å.

The two sodium ions are situated on a twofold symmetry axis and in a mirror plane, respectively. Na1 is surrounded by eight and Na2 by seven nearest neighbours. The sum of the ionic radii for the sodium and fluoride ions is 2.31 Å (0.95 Å + 1.36 Å). This is to be compared with the observed packing distances between these ions, ranging from 2.270 to 2.680 Å.

The shortest sodium to water oxygen distance is 2.305 Å which is a normal value (see, *e.g.*, Refs. 12 and 13). The next shortest distance between the water oxygen and a neighbouring atom, a peroxo

oxygen atom, is 2.818 Å, indicating hydrogen bonding. These reasonable values together with the observed rather large hole for the water molecule (the distance between the two statistically half-filled water positions is 0.785 Å) support the statistical interpretation of the water oxygen position.

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