

# The Crystal Structure of Trisodium Pentafluoroperoxoniobate(V) Hydrogendifluoride, $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$

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Crystals of  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$  are orthorhombic, space group  $Pbcn$  (No. 60), with  $a=6.703(2)$  Å,  $b=14.982(4)$  Å,  $c=14.092(5)$  Å,  $V=1415.1(7)$  Å<sup>3</sup> and  $Z=8$ . In all 2422 independent reflexions were registered with a SYNTEX automatic single crystal X-ray diffractometer using  $\text{MoK}\alpha$  radiation. 1694 reflexions were considered observed and used in the structure determination. Least-squares refinement of positional and thermal parameters yielded a final  $R$ -value of 0.022.

In the pentafluoroperoxoniobate(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 displaced 0.039 Å from the pentagonal plane. The symmetry of the anion is almost  $C_{2v}$ . Average bond distances are: Nb–O 1.93 Å, O–O 1.481 Å, Nb–F<sub>equatorial</sub> 1.99 Å, Nb–F<sub>apical</sub> 1.92 Å and H $\cdots$ F 1.14 Å.

On synthesizing the sodium fluoroperoxoniobate mentioned by Balke and Smith<sup>1</sup> in connection with work on transition metal peroxy complexes, the author was able to isolate three crystallographically different compounds,<sup>2</sup> none of which had the stoichiometry given by Balke and Smith. According to crystal structure studies, they have the formulae  $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot\text{H}_2\text{O}$ ,<sup>2</sup>  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$ , and  $\text{Na}_2[\text{NbF}_5(\text{O}_2)]\cdot 2\text{H}_2\text{O}$ ,<sup>3</sup> of which the second compound is described in this paper.

## EXPERIMENTAL

**Preparation and analysis.** 0.12 mol sodium fluoride and 0.02 mol niobium(V) oxide were dissolved in 20 ml of boiling 38 % hydrofluoric acid. Hydrogen peroxide was added and the solution was left to

evaporate at room temperature. Well-developed, yellow prismatic crystals were formed. Usually, sodium hydrogendifluoride crystals separated out first.

The sodium content was determined by means of atomic absorption spectroscopy using a Perkin Elmer 403 spectrometer. The peroxide content was determined by titration with a standardized permanganate solution. (Found: Na 21.1;  $\text{O}_2^{2-}$  9.6. Calc. for  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$ : Na 21.03;  $\text{O}_2^{2-}$  9.76.) The compound was investigated thermodynamically up to 550 °C using the universal microthermometer Mettler TA1. The DTA curve indicated an endothermic reaction starting at 180 °C and an exothermic one starting at 280 °C. The endothermic reaction was taken to be due to loss of hydrogen fluoride and the exothermic one to loss of oxygen. (Mass loss found: HF 6.0;  $\text{O}_2$  4.9. Calc. for  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$ : HF 6.10;  $\text{O}_2$  4.88.)

**X-Ray methods.** X-Ray powder photographs were obtained by the Guinier-Hägg method ( $\text{CuK}\alpha_1$ -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  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$  are given in Table 1.

Intensity data were recorded at room temperature with a SYNTEX P2<sub>1</sub> automatic four-circle single-crystal X-ray diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation and a crystal with dimensions 0.27 × 0.22 × 0.27 mm. To diminish the deterioration of the crystal, it was coated with a thin layer of epoxy resin. The  $\omega$ – $2\theta$  scan method was used and the  $2\theta$  scan speed was allowed to vary between 1.5 and 6°/min, depending on the intensity of the measured reflexion. Data were collected for  $2\theta \leq 60^\circ$ . A profile analysis based on the Lehmann-Larsen method<sup>4</sup> was applied to the 96-step profile collected for each reflexion. A reflexion measured after each twenty-fifth reflexion showed no significant difference in intensity during the collection of the data.

Table 1. Observed lines in the powder photograph of  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$  at room temperature registered with  $\text{CuK}\alpha_1$  radiation, using lead nitrate ( $a=7.8566 \text{ \AA}$ ) as internal standard.

$d_o$	$d_c$	$hkl$	$I_o$	$d_o$	$d_c$	$hkl$	$I_o$
7.046	7.028	0 0 2	w	1.7965	1.7967	1 6 5	w
6.600	6.602	0 2 1	m	1.7738	1.7738	3 5 1	vvw
4.848	4.846	1 0 2	m		1.7444	{ 2 7 2	
4.702	4.700	1 2 1	s	1.7444	{ 1.7442	{ 1 8 2	vw
4.069	4.067	1 2 2	vvw	1.7364	1.7356	3 1 5	vvw
3.975	3.971	0 2 3	s	1.7002	1.6996	1 0 8	w
3.740	3.739	0 4 0	w	1.6826	1.6819	3 4 4	vvw
3.416	3.415	1 2 3	w	1.6784	1.6780	2 2 7	vvw
3.348	3.346	2 0 0	m	1.6727	1.6729	4 0 0	m
3.303	3.301	0 4 2	vw	1.6502	1.6504	0 8 4	m
3.182	3.179	1 4 1	vvw	1.6320	1.6320	2 8 0	w
3.115	3.111	1 0 4	w	1.6300	1.6290	2 6 5	w
3.023	3.021	2 0 2	w	1.6221	1.6217	4 2 1	vw
2.9876	2.9847	2 2 1	m		1.5898	{ 1.5902	{ 4 2 2
2.9638	2.9605	1 4 2	s	1.5898	{ 1.5898	{ 2 8 2	vvw
2.6834	2.6807	1 5 1	vvw	1.5636	1.5638	0 6 7	w
2.5628	2.5608	0 4 4	m		1.5478	{ 1.5472	{ 1 4 8
2.4950	2.4933	2 4 0	vvw	1.5478	{ 1.5470	{ 4 3 2	vw
2.4534	2.4491	1 2 5	vw	1.5417	1.5417	4 2 3	w
2.4244	2.4234	2 0 4	vvw	1.4906	1.4906	1 2 9	m
2.3932	2.3916	1 4 4	vw	1.4802	1.4802	2 8 4	w
2.3516	2.3498	2 4 2	vw	1.4515	1.4517	1 10 1	vw
2.2496	2.2471	0 4 5	vvw		1.4365	{ 1.4363	{ 2 4 8
2.2381	2.2359	0 2 6	vvw	1.4365	{ 1.4361	{ 0 6 8	vvw
2.2027	2.2007	0 6 3	m	1.4305	1.4296	3 3 7	w
2.1805	2.1796	3 1 1	vw	1.4247	1.4247	0 10 3	vvw
2.1283	2.1261	3 0 2	m	1.4167	1.4167	2 6 7	vvw
2.1153	2.1132	3 2 1	m	1.4039	1.4039	3 8 2	vw
2.0909	2.0905	1 6 3	vw	1.4005	1.4005	4 4 4	vvw
2.0694	2.0685	2 2 5	vw	1.3319	1.3317	4 6 3	vw
2.0344	2.0335	2 4 4	w	1.3158	1.3158	0 4 10	vvw
2.0142	2.0143	1 7 1	vvw	1.2985	1.2983	1 6 9	vvw
1.9860	1.9854	0 4 6	m	1.2955	1.2949	3 4 8	vw
1.9800	1.9790	2 6 1	vw	1.2919	1.2919	4 6 4	vvw
1.9402	1.9395	0 2 7	m	1.2794	1.2792	4 4 6	vw
1.9041	1.9033	1 4 6	m		1.2668	{ 1.2668	{ 4 2 7
1.8836	1.8833	3 0 4	vw	1.2668	{ 1.2664	{ 2 8 7	w
1.8695	1.8695	0 8 0	w	1.2612	1.2610	3 2 9	w
1.8488	1.8483	3 4 2	m	1.2579	1.2574	1 8 8	vw
1.8388	1.8386	2 6 3	vw				

A total of 2422 independent reflexions were measured. Of these, 1694 having  $I_o \geq 3\sigma(I_o)$  were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz, polarization, absorption and extinction effects. For the absorption correction the crystal was divided into a  $6 \times 6 \times 6$  grid. The transmission factor varied between 0.67 and 0.73.

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

## CRYSTAL DATA



Unit cell	Orthorhombic with $a = 6.703(1) \text{ \AA} [6.692(2)]$ $b = 14.982(4) \text{ \AA} [14.956(5)]$ $c = 14.092(5) \text{ \AA} [14.058(5)]$ $V = 1415.1(7) \text{ \AA}^3 [1407(2)]$ $Z = 8$
Formula weight	$M_r = 327.87$
Density	$D_c = 3.078 \text{ g cm}^{-3}$
Systematic absences	$hk0$ for $h+k=2n+1$ $h0l$ for $l=2n+1$ $0kl$ for $k=2n+1$
Space group	$Pbcn$ (No. 60)
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 19.6 \text{ cm}^{-1}$

Values in brackets refer to powder diffraction data. The errors given are  $\sigma$ . Lists of structure factors and temperature parameters are available from the author upon request.

## STRUCTURE DETERMINATION

The positions of all atoms were found from a Patterson map and subsequent electron density calculations (DRF).<sup>5</sup> Least-squares refinement of an overall scale factor and positional and isotropic temperature parameters for all the non-hydrogen atoms yielded an  $R$ -value of 0.054 (BLOCK)<sup>5</sup> ( $R = \Sigma \|F_o\| - |F_c| / \Sigma |F_o|$ ). When the hydrogen atoms, anisotropic thermal parameters for all the non-hydrogen atoms and an isotropic extinction coefficient were introduced, the  $R$ -value became 0.022 ( $R_w = 0.042$ ) (LINUS).<sup>5</sup> The weighting scheme used was that of Cruickshank:<sup>6</sup>  $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$  with  $a = 20.0$ ,  $c = 0.050$  and  $d = 0.0$ . The scattering factors for Nb, Na<sup>+</sup>, F, O and H were taken from the *International Tables for X-Ray Crystallography, Vol. III*, as was the dispersion correction applied to Nb.

A difference synthesis calculated after the final cycle of refinement showed no peak higher than  $0.64 \text{ e/\AA}^3$ .

Table 2. Atomic coordinates, expressed as fractions of the cell edges, for Na<sub>3</sub>[HF<sub>2</sub>][NbF<sub>5</sub>(O<sub>2</sub>)]. Space group  $Pbcn$ ,  $Z = 8$ . Standard deviations are given in parentheses. The extinction coefficient is  $0.33(4) \times 10^4$ . For the hydrogen atoms H1 and H2 the isotropic temperature parameters  $B$  9(4) and 4(2)  $\text{\AA}^2$ , respectively, were used.

Atom	Position	$x$	$y$	$z$	$U_{eq}/\text{\AA}^2$ <sup>a</sup>
Nb	8d	0.25206(4)	0.13146(2)	0.10392(2)	0.0089
Na1	8d	0.1976(2)	0.2652(1)	0.3426(1)	0.020
Na2	8d	0.2624(2)	0.3728(1)	0.0665(1)	0.028
Na3	8d	0.2800(2)	0.5020(1)	0.3611(1)	0.021
F1	8d	0.1756(3)	0.2352(1)	0.1840(1)	0.023
F2	8d	0.2107(3)	0.0271(1)	0.0205(1)	0.023
F3	8d	0.2109(3)	0.0536(2)	0.2090(1)	0.027
F4	8d	0.2399(3)	0.2161(1)	0.0003(1)	0.024
F5	8d	-0.0478(3)	0.1316(1)	0.0901(2)	0.020
F6	8d	0.4683(4)	0.3770(1)	0.3296(1)	0.023
F7	8d	0.0239(3)	0.4015(1)	0.3305(1)	0.026
O1	8d	0.5253(4)	0.0993(2)	0.0739(2)	0.023
O2	8d	0.5105(4)	0.1730(2)	0.1437(2)	0.024
H1	4c	1/2	0.380(8)	1/4	
H2	4c	0	0.401(7)	1/4	

<sup>a</sup> $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ .

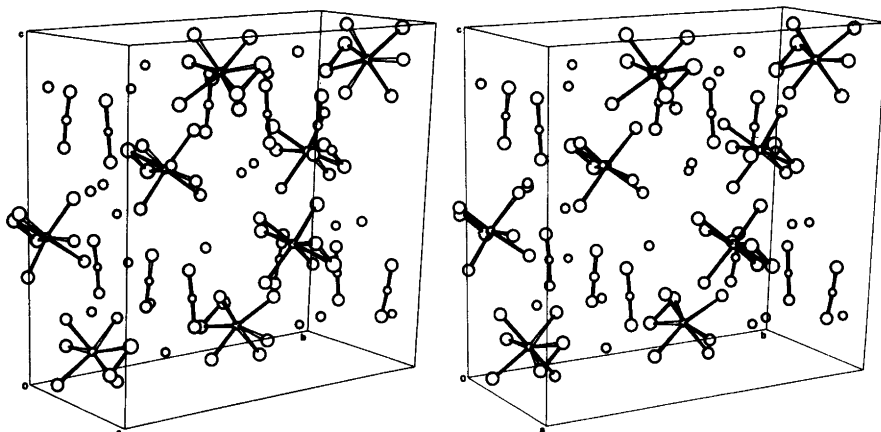


Fig. 1. Stereoscopic drawing of the unit cell of  $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$ .

## RESULTS AND DISCUSSION

The positional parameters obtained in the last refinement cycle are given in Table 2. 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 and hydrogen bond distances in Table 4.

The crystals of trisodium pentafluoroperoxonioate(V) hydrogendifluoride consist of sodium ions, pentafluoroperoxonioate(V) ions and hydrogendifluoride ions.

$[\text{NbF}_5(\text{O}_2)]^{2-}$  has a pentagonal bipyramidal arrangement of ligands (Fig. 2), a configuration observed in several transition metal peroxo complexes (see, *e.g.*, Refs. 2, 7–9). The distances from the least-squares plane through F1, F2, F5, O1 and O2 to these atoms and to Nb, F3 and F4 are in order  $-0.014$ ,  $-0.060$ ,  $0.042$ ,  $0.075$ ,  $-0.043$ ,  $-0.039$ ,  $-1.933$  and  $1.887$  Å, respectively. The distances from the least-squares plane through F3, F4, F5

and the midpoint between O1 and O2 to these atoms and to Nb, F1 and F2 are in order  $-0.030$ ,  $-0.032$ ,  $0.032$ ,  $0.770$ ,  $-0.710$ ,  $0.025$ ,  $-1.918$  and  $1.960$ , respectively. The angle between these planes is  $87.7^\circ$ . Hence, the point symmetry of  $[\text{NbF}_5(\text{O}_2)]^{2-}$  is almost  $C_{2v}$ .

The niobium atom is displaced  $0.039$  Å from the equatorial plane. Such a small displacement is usually observed for transition metal peroxo compounds, when, as in this case, the apical positions are occupied by identical ligands. When the apical atoms are different, or are differently coordinated, the central atom is in most cases displaced by  $0.2$ – $0.5$  Å (see Table 6 in Ref. 8).

The Nb–F<sub>equatorial</sub> bond distances,  $1.975$ – $2.019$  Å, are somewhat longer than the Nb–F<sub>apical</sub> bond distances,  $1.906$ – $1.936$  Å. This compares well with the corresponding distances in  $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$ ,<sup>2</sup> in which they are  $1.976$ – $2.037$  Å and  $1.906$ – $1.938$  Å, respectively. A possible

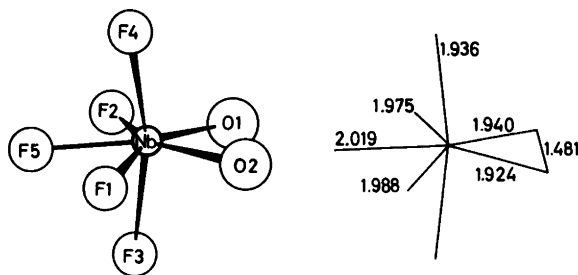


Fig. 2. The anion  $[\text{NbF}_5(\text{O}_2)]^{2-}$ .

Table 3. Bond distances and angles in Na<sub>3</sub>[HF<sub>2</sub>][NbF<sub>5</sub>(O<sub>2</sub>)].

Distance/Å		Angle/°	
Nb—F1	1.988 (2)	F1—Nb—F2	156.98 (9)
F2	1.975 (2)	F3	90.02 (9)
F3	1.906 (2)	F4	84.53 (9)
F4	1.936 (2)	F5	78.31 (8)
F5	2.019 (2)	O1	124.12 (10)
O1	1.940 (2)	O2	79.27 (10)
O2	1.924 (2)	F2—Nb—F3	87.59 (9)
O1—O2	1.481 (4)	F4	93.66 (9)
H1—F6	1.142 (4)	F5	78.68 (8)
H2—F7	1.146 (2)	O1	78.84 (10)
		O2	123.75 (10)
		F3—Nb—F4	168.92 (9)
		F5	86.06 (9)
		O1	98.89 (10)
		O2	95.86 (10)
		F4—Nb—F5	83.40 (9)
		O1	92.15 (10)
		O2	92.60 (10)
		F5—Nb—O1	156.74 (10)
		O2	157.50 (10)
		O1—Nb—O2	45.08 (11)
		F6—H1—F6'	176 (12)
		F7—H2—F7'	179 (10)

Table 4. Cation environment and hydrogen bond distances in Na<sub>3</sub>[HF<sub>2</sub>][NbF<sub>5</sub>(O<sub>2</sub>)].

	Distance/Å
Na1...F4 (1/2 - x, 1/2 - y, 1/2 + z)	2.279 (2)
F1	2.284 (2)
F7	2.357 (3)
O2 (1 - x, y, 1/2 - z)	2.403 (3)
F5 (x̄, y, 1/2 - z)	2.432 (2)
F6	2.476 (3)
F1 (x̄, y, 1/2 - z)	2.569 (3)
Na2...F6 (1 - x, y, 1/2 - z)	2.325 (3)
F2 (1/2 - x, 1/2 + y, z)	2.408 (3)
F7 (x̄, y, 1/2 - z)	2.444 (3)
F4	2.530 (3)
F5 (1/2 + x, 1/2 - y, z̄)	2.549 (3)
O1 (-1/2 + x, 1/2 - y, z̄)	2.572 (3)
F1	2.706 (3)
Na3...F3 (1/2 - x, 1/2 + y, z)	2.279 (2)
F2 (1/2 - x, 1/2 - y, 1/2 + z)	2.289 (2)
F6	2.301 (3)
F7	2.324 (3)
F5 (1/2 + x, 1/2 + y, 1/2 - z)	2.361 (2)
O1 (-1/2 + x, 1/2 + y, 1/2 - z)	2.425 (3)
F6...F6 (1 - x, y, 1/2 - z)	2.283 (4)
F7...F7 (x̄, y, 1/2 - z)	2.292 (4)

explanation to these differences is given in Ref. 2. It should also be noted that the fluorine atom involved in the shortest Nb—F distance is coordinated to only one sodium ion, while the fluorine atom involved in the longest Nb—F distance is coordinated to three sodium ions.

The Nb—O distances, 1.924 and 1.940 Å, are normal Nb—O single bond values, the observed distances in Na<sub>2</sub>[NbF<sub>5</sub>(O<sub>2</sub>)]·H<sub>2</sub>O and (C<sub>9</sub>H<sub>8</sub>NO)<sub>2</sub>·[NbF<sub>5</sub>(O<sub>2</sub>)]·3H<sub>2</sub>O being 1.928 Å and 1.91–1.95 Å, respectively.<sup>2,10</sup> Additional Nb—F and Nb—O distances can be found in Ref. 11 and references therein.

The distance between the oxygen atoms in the peroxy group, 1.481 Å, compares well with other observations (see Table 7 in Ref. 8). In Na<sub>2</sub>·[NbF<sub>5</sub>(O<sub>2</sub>)]·H<sub>2</sub>O the O—O distance is 1.476(7) Å.<sup>2</sup>

The observed coordination distances between the sodium and fluoride ions range from 2.279 to 2.706 Å, most of them being less than 2.5 Å. This is to be compared with the radii sum 2.31 Å.

The F...H...F distances 2.283 and 2.292 Å agree well with the corresponding distance 2.294 Å observed in potassium hydrogenfluoride by the neutron diffraction method.<sup>12,13</sup> Within the limitations of experimental error the F...H...F bond is linear with the hydrogen atom at the midpoint.

Na<sub>3</sub>[HF<sub>2</sub>][NbF<sub>5</sub>(O<sub>2</sub>)] is not isomorphous with the corresponding potassium pentafluoroperoxotantalate(V), K<sub>3</sub>[HF<sub>2</sub>][TaF<sub>5</sub>(O<sub>2</sub>)].<sup>14</sup> Since the reported structure of the latter is of limited accuracy and since a reinvestigation using diffractometer data<sup>15</sup> has shown that a more suitable space group can be chosen, no comparison of the two structures is made here.

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