

The Disordered Structure of Bis(8-hydroxyquinolinium) Pentafluoroperoxoniobate(V) Trihydrate, $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$. A Redetermination at 170 and 275 K

ROLF STOMBERG

Department of Inorganic Chemistry CTH/GU, Chalmers Tekniska Högskola, S-412 96 Göteborg, Sweden

The crystal structure of $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$, originally solved using the film method, has been reinvestigated. The structure determination is based on reflexion intensities collected by an automatic four-circle single-crystal X-ray diffractometer using MoK α radiation. Crystals of $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$ are monoclinic, space group $P2_1/c$ (No. 14), with $a=6.717(1)$, $b=24.683(8)$, $c=13.703(3)$ Å, $\beta=103.35(1)^\circ$, $V=2210.6(9)$ Å³ at 170 K and $a=6.761(2)$, $b=24.707(15)$, $c=13.737(8)$ Å, $\beta=103.35(4)^\circ$, $V=2233(2)$ Å³ at 275 K. $Z=4$. Least-squares refinement of structural and thermal parameters yielded a final R -value of 0.061 for 3315 observed independent reflexions at 170 K and of 0.067 for 2079 reflexions at 275 K.

The investigation indicates a disordered orientation of the pentagonal bipyramidal $[NbF_5(O_2)]^{2-}$ ion, also met with in some other pentafluoroperoxoniobates, at both 170 and 275 K. Two different, mutually overlapping orientations seem to predominate. Because of the disorder, the interatomic distances obtained are considerably less accurate than those usually obtained using diffractometer data. The ranges of interatomic distances at 170 K, being the more accurate ones, are: Nb–O 1.87–2.02 Å, Nb–F 1.89–2.01 Å, O–O 1.45–1.47 Å, C–O 1.34–1.36 Å, C–N 1.32–1.38 Å, and C–C 1.36–1.42 Å. Disregarding the structure of the anion and its orientation, the possible disorder of one water molecule, and the conclusions drawn about the peroxo group, the structural results previously obtained have been confirmed.

The $[NbF_5(O_2)]^{2-}$ ion in $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$ has a very distorted geometry according to a crystal structure analysis by Ružić-Toroš *et al.* (R–T).¹ On the other hand, in $Na_2[NbF_5(O_2)] \cdot H_2O$,^{2,4} $Na_3[HF_2][NbF_5(O_2)]$,^{2,5} $Na_2[NbF_5(O_2)] \cdot 2H_2O$,⁶ and $(C_{12}H_{10}N_2)[NbF_5(O_2)]$,⁷ the $[NbF_5(O_2)]^{2-}$ ion is quite symmetrical (approximately C_{2v}). Moreover, the reported (R–T) occupation numbers, 1.0 and 0.3, for the peroxo oxygen atoms O1 and O2 are unreasonable from a chemical point of view, despite the well-known fact that peroxo complexes are unstable. A more natural model would have been a peroxo group with the occupation number 0.3 and an oxide oxygen atom with the occupation number 0.7 (the IR spectrum of the fresh sample does not, however, show an absorption typical for Nb=O), but this does not explain the distortion of the ion. It is the author's experience that a number of pentafluoroperoxocomplexes,^{6–8} as well as pentafluorooxononiobates, *e.g.* $(C_9H_8NO)[NbF_5O] \cdot 2H_2O$,⁹ are disordered. It was therefore thought worthwhile to undertake a reinvestigation.

EXPERIMENTAL

Preparation and thermogravimetrical analysis. 5.3 g (0.02 mol) niobium(V) oxide was dissolved in 20 ml hot 40 % hydrogen fluoride in a platinum crucible and 11.6 g (0.08 mol) 8-hydroxyquinoline was added. $(C_9H_8NO)_2$

$[\text{NbF}_5\text{O}] \cdot 2\text{H}_2\text{O}$ was obtained as a crystalline mass. Part of this was dissolved in water and to the solution, which had been filtered to remove small amounts of remaining undissolved niobium(V) oxide, an excess of hydrogen peroxide was added. Crystals suitable for the X-ray work were obtained by slow evaporation of the solvent. They were formed as thin plates with the crystallographic *b*-axis perpendicular to the plate plane. Many of the crystals were twins; these were twice as thick as the single crystals.

The niobium content was determined by carefully heating a weighed sample in a platinum crucible to red heat. (Found: Nb 16.37. Calc. for $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$: 16.41). A thermogravimetric analysis was carried out on the substance between 20 and 680 °C with a universal thermobalance (Mettler TA1). Water is lost between 50 and 110 °C (Found: 9.1 Calc.: 9.5). At 140 °C a general disintegration begins, which becomes rapid above 450 °C. Just below 600 °C a constant weight is obtained [niobium(V) oxide].

X-ray methods. The collection of intensity data was performed by a SYNTEX $P2_1$ automatic single-crystal X-ray diffractometer at 170 and 275 K. For the two data sets different crystals, with the dimensions $0.14 \times 0.32 \times 0.44$ mm (at 170 K) and $0.04 \times 0.14 \times 0.33$ mm (at 275 K), were used. The X-ray intensities were measured by the ω scan technique at 170 K ($2\theta \leq 58^\circ$) and by the $\theta - 2\theta$ scan technique at 275 K ($2\theta \leq 50^\circ$) using graphite-monochromatized $\text{MoK}\alpha$ radiation. Two test reflexions measured after each fiftieth reflexion showed no decrease in intensity at 170 K and only a minor one at 275 K during the collection of the data. The ω scan speed was varied between 3 and $30^\circ/\text{min}$ and the 2θ scan speed between 2 and $8^\circ/\text{min}$ depending on the intensity of the measured reflexion. A 19-step and a 96-step profile at 170 and 275 K, respectively, were recorded for each reflexion. A profile analysis based on the Lehmann-Larsen method was then applied to each reflexion.¹⁰ A total of 6030 independent reflexions at 170 K and 4068 at 275 K were measured. Of these, 3315 and 2079 reflexions at 170 and 275 K, respectively, for which $I_o \geq 3\sigma(I_o)$, were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz, polarisation and absorption effects.

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

CRYSTAL DATA

Bis(8-hydroxyquinolinium) pentafluoroperoxoniate(V) trihydrate,

$(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$. F.W. = 566.28. Space group $P2_1/c$ (No. 14).

	At 170 K	At 275 K	At 298 K (Ref. 1)
<i>a</i> (Å)	6.717(1)	6.761(2)	6.771(2)
<i>b</i> (Å)	24.683(8)	24.707(15)	24.785(5)
<i>c</i> (Å)	13.703(3)	13.737(8)	13.768(3)
β (°)	103.35(1)	103.35(4)	103.3(3)
<i>V</i> (Å ³)	2210.6(9)	2232.7(20)	2248.6
<i>D_c</i> (g cm ⁻³)	1.702	1.685	1.666

$Z=4$, $\mu(\text{MoK}\alpha)=0.611 \text{ mm}^{-1}$,

$\lambda(\text{MoK}\alpha)=0.71069 \text{ Å}$.

STRUCTURE REFINEMENT

Three cycles of block-diagonal least-squares refinement of positional and isotropic thermal parameters using the 275 K data set and the parameters reported by R-T¹ led to an *R*-value of 0.119 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). A few atoms showed unreasonably high *B*-values ($B(\text{O}1)=10$, $B(\text{O}2)=21$, $B(\text{O}w3)=12 \text{ Å}^2$), some quite large ($B(\text{F}2)-B(\text{F}4) 9-10 \text{ Å}^2$), while all other 27 non-hydrogen atoms had normal *B*-values ($3-6 \text{ Å}^2$), and the peroxo bond distance appeared unacceptably short, 1.00 Å. Thus, the model proposed by R-T could not be completely correct. R-T put forward the opinion that oxygen is lost by disintegration of the peroxo group, and introduced unequal occupation numbers, 0.3 and 1.0, for the peroxo oxygen atoms. If oxygen is lost the corresponding amount of peroxide is replaced by oxide. Thus, such a model was tested with, at the start, equal occupation numbers, 0.5, for the oxo and peroxo oxygen atoms. This led to more reasonable *B*-values and a peroxo bond distance of 1.33 Å ($R=0.072$ with anisotropic thermal parameters). The Nb-“O”_{oxo} bond distance of 1.91 Å obtained at this stage indicates a normal single bond and thus supports the observation made from IR-data that an Nb=O bond does not seem to exist. The idea of a complex with part of the peroxide being replaced by oxide was therefore abandoned for the moment.

It was observed by the author that the anion in $(\text{C}_{12}\text{H}_{10}\text{N}_2)[\text{NbF}_5(\text{O}_2)]$ as well as in

$(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5\text{O}] \cdot 2\text{H}_2\text{O}$ is disorderly orientated.^{7,9} The same situation might prevail also in this case. Inspection of the difference electron density map, the signs of the F's being determined by all but the coordinated atoms ($R=0.22$), and refinement of occupation numbers, led to a model with the complex orientated in mainly two ways. One orientation, comprising the atoms denoted Nb, F1–F5, O1 and O2, is very close to the one observed by R–T and the other, comprising the atoms denoted Nb, F1–F3, F5, F6, O3 and O4, has the centre of the peroxo group approximately at F4, both orientations

having occupation numbers 0.5. Nb, F1–F3, and F5 are thus common to both orientations; the corresponding peaks could not be resolved into two parts. Further least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms as well as an overall scale factor reduced the R -value to 0.067. A difference synthesis calculated after the final cycle of refinement showed no peak higher than $1.0 \text{ e } \text{\AA}^{-3}$.

The structure was further studied at low temperature (170 K) in order to explore whether the disorder still existed and to obtain more reliable interatomic distances. It was soon found

Table 1. Atomic coordinates for $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ at 170 K and 275 K. All atoms occupy the general four-fold site of space group $P2_1/c$. The occupation number is 0.5 for F4, F6, O1, O2, O3 and O4; 0.6 for Ow3; 0.4 for Ow4; and 1.0 for all other atoms. $U_{\text{eq}} = \frac{1}{3} \sum_i U_{ij} a_i^* a_j a_j \cos \alpha_{ij}$

170 K					275 K				
Atom	x	y	z	U_{eq}	x	y	z	U_{eq}	
Nb	0.4212(1)	0.11575(2)	0.25000(4)	0.0281(1)	0.4164(2)	0.11715(4)	0.24858(7)	0.0441(2)	
F1	0.2848(7)	0.1686(2)	0.1472(3)	0.044(1)	0.2818(11)	0.1691(3)	0.1458(5)	0.069(2)	
F2	0.2113(10)	0.0678(2)	0.1830(5)	0.076(2)	0.2146(15)	0.0686(4)	0.1821(8)	0.125(3)	
F3	0.2327(8)	0.1410(3)	0.3282(4)	0.082(2)	0.2374(14)	0.1441(5)	0.3271(7)	0.134(4)	
F4	0.5498(18)	0.0726(4)	0.3608(7)	0.064(3)	0.5570(26)	0.0773(7)	0.3625(13)	0.094(5)	
F5	0.5834(9)	0.1815(2)	0.3067(4)	0.059(1)	0.5843(13)	0.1808(3)	0.3025(6)	0.087(2)	
F6	0.6074(13)	0.1002(4)	0.1684(7)	0.047(2)	0.5837(23)	0.1077(7)	0.1573(11)	0.089(5)	
O1	0.5228(21)	0.0740(5)	0.1493(11)	0.064(4)	0.5359(37)	0.0783(9)	0.1585(19)	0.112(7)	
O2	0.6668(18)	0.1153(5)	0.1963(11)	0.092(4)	0.6775(23)	0.1124(9)	0.2048(14)	0.085(5)	
O3	0.6285(17)	0.0940(4)	0.3750(7)	0.037(2)	0.6261(33)	0.0932(8)	0.3672(16)	0.090(6)	
O4	0.4770(31)	0.0531(5)	0.3285(11)	0.097(5)	0.4675(56)	0.0598(10)	0.3347(23)	0.173(10)	
Ow1	0.8678(10)	0.1786(2)	0.0990(4)	0.049(1)	0.8665(15)	0.1763(4)	0.0983(7)	0.080(3)	
Ow2	0.9676(9)	0.1731(3)	0.4323(4)	0.069(2)	0.9668(13)	0.1717(5)	0.4293(6)	0.084(3)	
Ow3	−0.0125(17)	0.0349(4)	0.3812(8)	0.058(3)	−0.0172(40)	0.0314(9)	0.3873(16)	0.109(6)	
Ow4	−0.0885(29)	0.0078(5)	0.4263(9)	0.065(4)	−0.0981(69)	0.0132(16)	0.4158(27)	0.144(11)	
Ox1	0.6639(8)	0.2977(2)	0.4151(3)	0.034(1)	0.6689(12)	0.2986(3)	0.4143(6)	0.055(2)	
Ox2	0.0070(9)	0.3932(2)	0.0842(3)	0.046(1)	0.0102(13)	0.3929(3)	0.0825(6)	0.062(2)	
N1	0.5661(8)	0.2799(2)	0.2163(4)	0.031(1)	0.5699(12)	0.2802(3)	0.2160(6)	0.044(2)	
N2	0.0956(9)	0.4533(2)	0.2521(5)	0.036(1)	0.0991(13)	0.4521(3)	0.2507(7)	0.049(2)	
C1	0.5227(11)	0.2675(3)	0.1184(5)	0.038(2)	0.5243(18)	0.2675(5)	0.1196(9)	0.056(3)	
C2	0.4953(12)	0.3100(4)	0.0470(5)	0.048(2)	0.4985(17)	0.3092(5)	0.0475(8)	0.058(3)	
C3	0.5107(11)	0.3622(4)	0.0784(6)	0.044(2)	0.5167(17)	0.3625(5)	0.0802(9)	0.058(3)	
C4	0.5538(10)	0.3759(3)	0.1813(5)	0.034(1)	0.5583(16)	0.3757(4)	0.1804(10)	0.055(3)	
C5	0.5850(10)	0.3325(2)	0.2511(5)	0.029(1)	0.5875(15)	0.3319(4)	0.2497(8)	0.040(2)	
C6	0.5748(11)	0.4292(3)	0.2180(7)	0.045(2)	0.5788(18)	0.4292(5)	0.2192(11)	0.066(4)	
C7	0.6235(11)	0.4388(3)	0.3208(6)	0.041(2)	0.6218(19)	0.4378(5)	0.3184(11)	0.070(4)	
C8	0.6521(10)	0.3950(3)	0.3888(5)	0.036(2)	0.6577(17)	0.3950(5)	0.3867(9)	0.058(3)	
C9	0.6361(10)	0.3420(3)	0.3552(5)	0.028(1)	0.6420(15)	0.3428(5)	0.3539(8)	0.048(3)	
C10	0.1354(12)	0.4850(3)	0.3316(8)	0.057(2)	0.1379(18)	0.4841(5)	0.3312(11)	0.070(4)	
C11	0.1786(15)	0.4629(4)	0.4292(7)	0.067(2)	0.1804(21)	0.4616(6)	0.4266(10)	0.076(4)	
C12	0.1769(13)	0.4082(4)	0.4390(6)	0.051(2)	0.1825(19)	0.4085(6)	0.4355(9)	0.067(4)	
C13	0.1393(9)	0.3740(3)	0.3558(5)	0.033(1)	0.1379(15)	0.3730(5)	0.3540(8)	0.052(3)	
C14	0.0926(9)	0.3977(2)	0.2590(5)	0.026(1)	0.0951(15)	0.3978(4)	0.2586(8)	0.039(2)	
C15	0.1361(11)	0.3164(3)	0.3619(6)	0.041(2)	0.1420(17)	0.3151(5)	0.3587(9)	0.057(3)	
C16	0.0979(12)	0.2862(3)	0.2770(7)	0.045(2)	0.0982(18)	0.2863(5)	0.2740(10)	0.062(3)	
C17	0.0522(10)	0.3101(3)	0.1807(6)	0.037(2)	0.0547(16)	0.3099(4)	0.1792(9)	0.051(3)	
C18	0.0477(10)	0.3659(3)	0.1707(5)	0.031(1)	0.0523(16)	0.3663(4)	0.1688(8)	0.046(3)	

that the situation is the same as at 275 K. The electron density peaks about niobium were more fully examined in a series of difference electron density maps, calculated by omitting the ligand atoms one at a time in determining the *F*-signs. The omitted atoms showed up at the same positions as those found at 275 K. Thus, the same model is applicable both at 170 and 275 K. Furthermore, in both cases the water oxygen Ow3 was found statistically to occupy two positions, denoted Ow3 and Ow4, with the occupation numbers 0.6 and 0.4, respectively. Introduction of the hydrogen atoms belonging to the ring systems with calculated positions and $B=5 \text{ \AA}^2$ and least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms as well as a common scale factor, gave a final *R*-value of 0.061. In this case the highest peak in an electron density difference map was less than 1.2 e \AA^{-3} .

The weighting scheme used was that of Cruickshank:¹¹ $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$ with $a=20.0$, $c=0.005$, and $d=0$ at 275 K and $a=30.0$, $c=0.008$, and $d=0$ at 170 K. The atomic scattering factors were taken from Ref. 12 as were the dispersion corrections.

Calculations were carried out on an IBM 3033 computer using a set of crystallographic programs in use at this department.¹³ Lists of structure factors and anisotropic thermal parameters are available from the author upon request.

RESULTS AND DISCUSSION

The positional parameters as well as U_{eq} 's obtained in the last refinement cycles are given in Table 1. Within the limits of experimental error the structures at 170 and 275 K are the same. All distances and angles quoted in this discussion refer to the 170 K data set, since this is the more accurate one. With the exception of the orientations of the anion and the positions of one water molecule, Fig. 3 in Ref. 1, showing the unit cell content, is applicable. The relative orientations of the anion are shown in Fig. 1. Bond distances and angles are given in Table 2 and hydrogen bond distances in Table 3.

The crystals of bis(8-hydroxyquinolinium) pentafluoroperoxoniobate(V) trihydrate, $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$, consist of 8-hydroxyquinolinium and pentafluoroperoxoniobate(V) ions and water of crystallization, held

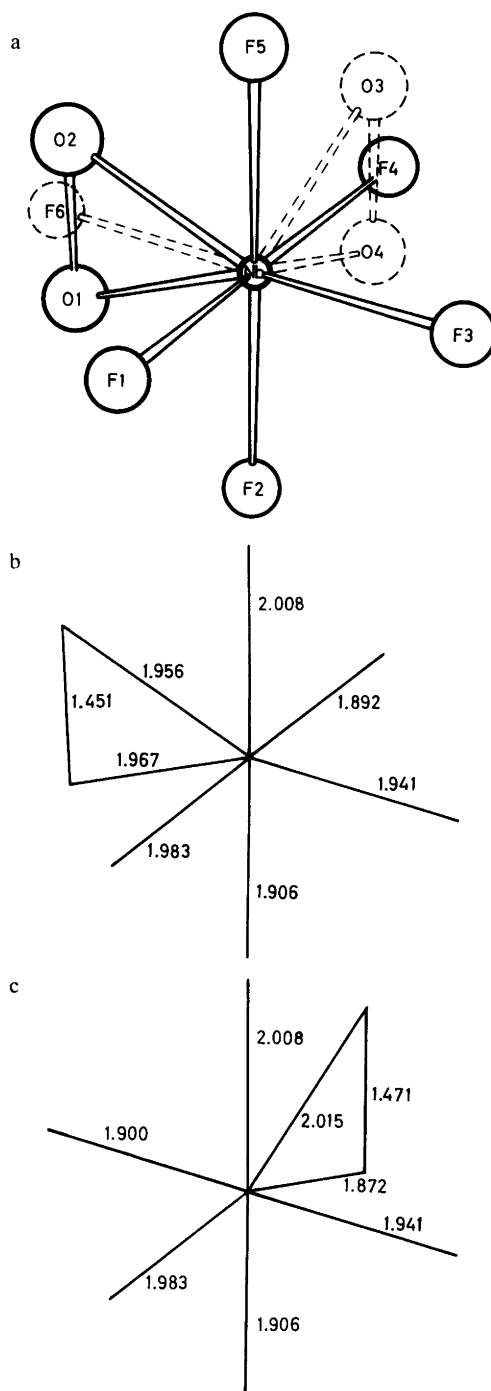


Fig. 1. (a) The two orientations A and B of the disordered anion. Orientation A comprises the atoms Nb, F1-F5, O1 and O2 and B the atoms Nb, F1-F3, F5, F6, O3 and O4. (b) Bond distances in A at 170 K. (c) Bond distances in B at 170 K.

Table 2. Bond distances at 170 and 275 K and angles at 170 K in $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$. Nb, F1, F2, F3, F4, F5, O1 and O2 comprise one anionic complex, Nb, F1, F2, F3, F5, F6, O3 and O4 the other.

	170 K	275 K				
Distance/Å			Angle (°)			
Nb-F1	1.983(4)	1.97(1)	F1-Nb-F2	84.1(2)	C1-N1-C5	123.0(6)
Nb-F2	1.906(6)	1.89(1)	F1-Nb-F3	85.9(2)	N1-C1-C2	118.8(7)
Nb-F3	1.941(6)	1.92(1)	F1-Nb-F4	172.3(3)	C1-C2-C3	119.8(7)
Nb-F4	1.892(10)	1.91(2)	F1-Nb-F5	82.2(2)	C2-C3-C4	121.8(7)
Nb-F5	2.008(5)	1.98(1)	F1-Nb-F6	88.5(3)	C3-C4-C5	117.2(7)
Nb-F6	1.900(9)	1.89(2)	F1-Nb-O1	91.4(4)	C3-C4-C6	124.1(7)
Nb-O1	1.967(14)	1.89(2)	F1-Nb-O2	91.6(4)	C5-C4-C6	118.7(7)
Nb-O2	1.956(13)	2.00(2)	F1-Nb-O3	153.5(3)	N1-C5-C4	119.4(6)
Nb-O3	2.015(10)	1.99(2)	F1-Nb-O4	161.9(6)	N1-C5-C9	119.3(6)
Nb-O4	1.872(14)	1.83(3)	F2-Nb-F3	87.7(3)	C4-C5-C9	121.4(6)
O1-O2	1.451(19)	1.32(3)	F2-Nb-F4	100.8(4)	C4-C6-C7	120.1(7)
O3-O4	1.471(19)	1.35(4)	F2-Nb-F5	164.3(2)	C6-C7-C8	120.2(7)
N1-C1	1.342(9)	1.33(1)	F2-Nb-F6	96.1(3)	C7-C8-C9	121.1(7)
C1-C2	1.420(12)	1.41(2)	F2-Nb-O1	71.0(4)	C5-C9-Ox1	116.5(6)
C2-C3	1.355(13)	1.39(2)	F2-Nb-O2	114.2(5)	C8-C9-Ox1	124.9(6)
C3-C4	1.413(11)	1.38(2)	F2-Nb-O3	122.2(3)	C5-C9-C8	118.6(6)
C4-C5	1.419(10)	1.42(2)	F2-Nb-O4	78.0(6)	C10-N2-C14	122.6(7)
C5-N1	1.378(8)	1.36(1)	F3-Nb-F4	88.4(4)	N2-C10-C11	120.7(7)
C4-C6	1.406(11)	1.42(2)	F3-Nb-F5	83.8(3)	C10-C11-C12	118.3(8)
C6-C7	1.391(12)	1.34(2)	F3-Nb-F6	172.9(3)	C11-C12-C13	121.7(8)
C7-C8	1.411(11)	1.40(2)	F3-Nb-O1	158.8(4)	C12-C13-C14	118.4(7)
C8-C9	1.383(10)	1.36(2)	F3-Nb-O2	157.6(5)	C12-C13-C15	123.9(7)
C9-C5	1.407(9)	1.42(2)	F3-Nb-O3	91.5(3)	C14-C13-C15	117.6(6)
C9-Ox1	1.355(8)	1.36(1)	F3-Nb-O4	91.0(6)	N2-C14-C13	118.2(6)
N2-C10	1.317(12)	1.34(2)	F4-Nb-F5	92.2(4)	N2-C14-C18	119.8(6)
C10-C11	1.413(14)	1.39(2)	F4-Nb-O1	95.8(5)	C13-C14-C18	122.0(6)
C11-C12	1.357(14)	1.32(2)	F4-Nb-O2	91.8(6)	C13-C15-C16	120.2(7)
C12-C13	1.394(11)	1.40(2)	F5-Nb-F6	91.1(3)	C15-C16-C17	121.8(7)
C13-C14	1.416(9)	1.42(2)	F5-Nb-O1	116.7(4)	C16-C17-C18	120.2(7)
C14-N2	1.377(8)	1.35(1)	F5-Nb-O2	73.8(4)	C14-C18-Ox2	116.1(6)
C13-C15	1.424(11)	1.43(2)	F5-Nb-O3	71.3(3)	C17-C18-Ox2	125.8(6)
C15-C16	1.356(11)	1.34(2)	F5-Nb-O4	115.3(5)	C14-C18-C17	118.2(6)
C16-C17	1.413(12)	1.40(2)	F6-Nb-O3	91.6(4)		
C17-C18	1.384(10)	1.40(2)	F6-Nb-O4	95.7(6)		
C18-C14	1.415(9)	1.43(2)	O1-Nb-O2	43.4(6)		
C18-Ox2	1.335(8)	1.33(1)	O3-Nb-O4	44.3(6)		

together by ionic and hydrogen bond forces. The anion and one water molecule show disorder at 275 K as well as at 170 K. The anion has two equally occupied orientations with a common centre and one water molecule occupies two positions with the occupation numbers 0.6 and 0.4, respectively.

The two 8-hydroxyquinolinium ions are planar within the experimental errors. These planes form an angle of 0.6° to each other. The corresponding bond distances in the two non-equivalent 8-hydroxyquinolinium ions are equal; the largest difference is less than 3σ . The three carbon-carbon distances C2-C3, C6-C7 and C8-C9, and the corresponding ones in the other

cation, are significantly shorter than the other carbon-carbon distances; the average ones * are 1.371(15) and 1.413(7) Å, respectively. They compare well with the corresponding values of 1.364(6) and 1.410(10), 1.365(12) and 1.404(13), and 1.369(12) and 1.415(10) for $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5\text{O}] \cdot 2\text{H}_2\text{O}$,⁹ $(\text{C}_9\text{H}_8\text{NO})[\text{Mo}(\text{C}_9\text{H}_6\text{NO})\text{Cl}_3\text{O}]$,¹⁴ and $[\text{V}(\text{C}_9\text{H}_6\text{NO})_2(\text{i-OC}_3\text{H}_7)\text{O}]$,¹⁵ respectively. One C-N distance is shorter than the other in both cations; the mean distance is 1.330(13) Å for the shorter and 1.378(1) Å for the larger one. The same observations were made

* R.m.s. deviations from the mean are given in parentheses.

Table 3. Hydrogen bond distances (Å) in $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$.

	170 K	275 K
Ow1...F1 ⁱ	2.737(8)	2.74(1)
Ow1...F6	2.912(11)	2.81(2)
Ow1...O2	2.621(15)	2.67(2)
Ow1...Ox1 ⁱⁱ	2.641(7)	2.65(1)
Ow2...F3 ⁱ	2.647(8)	2.64(1)
Ow2...F5	2.759(8)	2.77(1)
Ow2...O3	2.964(12)	2.98(2)
Ow2...Ox2 ⁱⁱⁱ	2.612(9)	2.60(1)
Ow3...Ow4 ^{iv}	2.776(16)	2.86(5)
Ow3 ⁱ ...O3	2.803(15)	2.81(3)
Ow3...N2 ^v	2.690(12)	2.69(3)
Ow4 ⁱ ...F4	2.875(20)	2.77(5)
Ow4 ⁱ ...O3	2.832(18)	2.69(5)
Ow4...Ox2 ^v	2.892(15)	3.03(5)
Ow4...N2 ^v	2.781(14)	2.74(4)
N1...F5	2.717(7)	2.72(1)

Symmetry codes

- i $1+x, y, z$
- ii $x, 1/2-y, -1/2+z$
- iii $1+x, 1/2-y, 1/2+z$
- iv $\bar{x}, \bar{y}, 1-z$
- v $\bar{x}, -1/2+y, 1/2-z$

for the other three compounds mentioned above; the corresponding distances are 1.326(5) and 1.373(6) Å,⁹ 1.321(3) and 1.367(3) Å,¹⁴ and 1.329(5) and 1.362(1) Å,¹⁵ respectively. All bond distances and angles in the 8-hydroxyquinolinium ion agree well with other observations for this ion and the 8-hydroxyquinolinato ligand.^{9,14-18}

The pentafluoroperoxoniobate(V) anions are disorderly orientated in the crystal; this was not realised by R-T. Two main orientations, denoted A and B, both with occupancies 0.5, were observed (Fig. 1). The possibility of the existence of still other orientations with small occupation numbers cannot, however, be ruled out. It should be noted that the situation is the same at 275 and 170 K; one of the orientations might have been stabilized at the lower temperature. The disorder may be compared to the ones observed in $(C_{12}H_{10}N_2)[NbF_5(O_2)]^7$ and $Na_2[NbF_5(O_2)] \cdot 2H_2O$,⁶ where two main orientations of the anions also were observed. Though having a common central atom position in all three cases, the relative orientations of the anions are, however, quite different. In $(C_{12}H_{10}N_2)[NbF_5(O_2)]$ the equatorial planes of the two disorderly orientated pentagonal bipyramidal anions almost coincide, forming an angle of 3° with

one another, and the pentagons are mutually twisted 61°. In $Na_2[NbF_5(O_2)] \cdot 2H_2O$, turning the complex 90° about a line through niobium and the midpoint of the peroxo group gives the other orientation of the anion. Finally, the present investigation has shown that in $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$, orientation B is reached from orientation A by rotating the anion 87° about a line through niobium, parallel to the O-O bond in the peroxo group (Fig. 1). The disorder in, e.g., $(NH_4)_3[TiF_5(O_2)]$ is completely different, the complex assuming random orientations.^{8,19}

The geometry of the anion $[NbF_5(O_2)]^{2-}$ is pentagonally bipyramidal as was found in $Na_2[NbF_5(O_2)] \cdot H_2O$,⁴ $Na_3[HF_2][NbF_5(O_2)]$,⁵ $Na_2[NbF_5(O_2)] \cdot 2H_2O$ ⁶ and $(C_{12}H_{10}N_2)[NbF_5(O_2)]$.⁷ The consistency of this geometry for the pentafluoromonoperoxometallates is evident from Table 5 in Ref. 6, listing interatomic distances in some compounds of this type, and is further supported by the values obtained for $(C_{12}H_{10}N_2)[NbF_5(O_2)]$,⁷ $K_3[HF_2][TaF_5(O_2)]$,²⁰ and in the present investigation (see Table 5). Table 4 shows that the equatorial atoms are significantly displaced from the respective pentagonal planes; this has been found for other pentafluoroniobates, also.⁴⁻⁷ The pentagonally bipyramidal configuration has been observed for all seven coordinated transition metal peroxo complexes hitherto investigated (see, e.g., Refs. 4-8, 20-25). Since there are three, energetically about equally favourable, geometries for seven coordination, the pentagonal bipyramid, the monocapped octahedron and the monocapped trigonal prism, the bidentate ligand O_2^{2-} obviously stabilizes the pentagonal bipyramidal arrangement.

The Nb-F and Nb-O bond distances, ranging from 1.892 to 2.008 Å and from 1.872 to 2.015 Å, respectively, are considered to be metal-ligand single-bond distances, comparable to other observations.^{4-7,9,25} The anion orientation A comprises the positions denoted Nb, F1-F5, O1 and O2 and B those denoted Nb, F1-F3, F5, F6, O3 and O4. Nb, F1-F3, and F5 thus belong to both orientations. Each of these experimentally observed positions is probably split into two unresolvable ones. As a consequence of this, the interatomic distances involving these atoms are considered to be more uncertain than can be judged from the e.s.d.'s.

Table 4. Displacements (\AA) of the atoms from certain least-squares planes in $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$. Defining atoms, given equal weights, are: Plane I F2, F3, F5, O2 and O1
Plane II F5, F1, F2, O4 and O3

Plane I			Plane II		
Atom	170 K	275 K	Atom	170 K	275 K
F2	0.102(6)	0.10(1)	F5	0.063(5)	0.06(1)
F3	-0.110(6)	-0.13(1)	F1	-0.055(4)	-0.02(1)
F5	0.108(5)	0.15(1)	F2	0.038(6)	-0.03(1)
O2	-0.065(13)	-0.12(2)	O4	0.008(14)	0.12(3)
O1	-0.036(14)	0.00(2)	O3	-0.054(10)	-0.14(2)
Nb	-0.120(1)	-0.07(1)	Nb	-0.081(1)	-0.06(0)
F1	1.858(4)	1.88(1)	F3	1.856(6)	1.85(1)
F4	-2.006(10)	-1.96(2)	F6	-1.977(9)	-1.92(2)

Table 5. The length of the edges of the pentagonal bipyramidal coordination polyhedron in $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ at 170 K. The designation of the edges conforms to Fig. 3 in Ref. 6. Compare with Table 5 in Refs. 6 and 7 and with Table 4 in Ref. 20.

Edge	Distance/ \AA		Distance/ \AA	
a	F2...F3	2.666(9)	F5...F1	2.622(7)
b	F3...F5	2.638(8)	F1...F2	2.605(8)
c	F5...O2	2.379(15)	F2...O4	2.377(19)
d	O2...O1	1.451(19)	O4...O3	1.471(19)
e	O1...F2	2.250(15)	O3...F5	2.344(10)
f	F1...F2	2.605(8)	F3...F5	2.638(8)
g	F1...F3	2.673(7)	F3...F1	2.673(7)
h	F1...F5	2.622(7)	F3...F2	2.666(9)
i	F1...O2	2.823(14)	F3...O4	2.720(17)
j	F1...O1	2.827(14)	F3...O3	2.834(12)
k	F4...F2	2.926(13)	F6...F5	2.790(10)
l	F4...F3	2.672(13)	F6...F1	2.709(10)
m	F4...F5	2.810(11)	F6...F2	2.829(10)
n	F4...O2	2.763(18)	F6...O4	2.797(18)
o	F4...O1	2.862(17)	F6...O3	2.807(13)

The peroxo oxygen bond distances, 1.471(19) and 1.451(19) \AA , compare well with other observations. In the pentafluoroperoxonioates hitherto investigated, the following distances were observed: 1.476(7) \AA in $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$,⁴ 1.481(4) \AA in $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$,⁵ 1.506(26) and 1.411(31) \AA in $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ (disordered),⁶ and 1.483(8) and 1.440(16) \AA in $(\text{C}_{12}\text{H}_{10}\text{N}_2)[\text{NbF}_5(\text{O}_2)]$ (disordered).⁷ Comparable values have been found in other transition metal peroxo complexes (see Tables of O—O bond distances in, *e.g.*, Refs. 21–23). The distances obtained at 275 K in the present investigation are rather short, though, owing to their large standard deviations, it is doubtful whether they are significantly different

from other observations. There is, in fact, evidence for O—O bond distances determined at room temperature to appear a bit short, not only those obtained using film data but also diffractometer data, a recent example being 1.419(6) \AA , observed in $[\text{Ti}(\text{O}_2)(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{OPN}_3\text{C}_6\text{H}_{18})]$.²⁴ Possible reasons for this effect may be thermal motion and partial decomposition of the compound during the data collection, both these factors being less pronounced at low temperatures.

Substantial hydrogen bonding stabilizes the structure; the shortest hydrogen bond is 2.612(9) \AA . One of the water molecules (w3 according to R–T) was observed to be disordered; this molecule occupies two positions, denoted w3 and w4,

with the occupancies 0.6 and 0.4, respectively. This together with the existence of two orientations of the anion (four new atomic positions were introduced), leads to a modification of the hydrogen bonding scheme put forward by R-T, and is evident from Table 3.

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