

The Crystal Structure of 1,10-Phenanthrolineium Pentafluoroperoxoniobate(V), $(C_{12}H_{10}N_2)[NbF_5(O_2)]$

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Crystals of $(C_{12}H_{10}N_2)[NbF_5(O_2)]$ are triclinic, space group $P\bar{1}$ (No. 2), with $a=9.467(1)$ Å, $b=10.374(2)$ Å, $c=7.594(1)$ Å, $\alpha=102.38(1)^\circ$, $\beta=113.11(1)^\circ$, $\gamma=92.92(1)^\circ$, $V=662.4(2)$ Å³ and $Z=2$. With an automatic single crystal X-ray diffractometer using MoK α radiation 5142 independent reflexions were registered. Least-squares refinement of structural and thermal parameters yielded a final R -value of 0.029.

The crystals are composed of 1,10-phenanthrolineium and pentafluoroperoxoniobate(V) ions, held together by ionic and hydrogen bond forces, the shortest hydrogen bond distance, $N-H\cdots F$, being 2.566(7) Å. The anion has a pentagonal bipyramidal arrangement of ligands, the peroxo group and three fluorine atoms forming the pentagonal plane, while the other two fluorine atoms occupy the apical positions of the bipyramid. The symmetry of the anion is almost C_{2v} .

The anions are disordered in the crystal and have two main orientations, with occupation numbers 0.60 and 0.40, respectively. The differently orientated anions have the same niobium and apical fluorine atom positions within the limits of experimental errors, while the approximately coplanar pentagonal planes are mutually twisted 61°.

Weighted average bond distances within the anions are: Nb–O 1.89 Å, O–O 1.47 Å, Nb–F_{equatorial} 2.00 Å and Nb–F_{apical} 1.92 Å.

In their study of 8-hydroxyquinolinium pentafluoroperoxoniobate(V) trihydrate, $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$, Ružić-Toroš *et al.* claim to have observed a rather short peroxo oxygen bond distance, 1.17(9) Å, and a population parameter of only 0.3 for one of the peroxo oxygen atoms.¹ It is the author's experience that O–O distances in transition metal peroxo compounds as short as at least 0.1 Å less the normal value of 1.49 Å may be

observed, especially when dealing with rather unstable compounds (see *e.g.* Refs. 2–5 and references therein). Different occupation numbers for the two oxygen atoms of a peroxo group have, however, not been observed. A reinvestigation of the structure of $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$, using single crystal diffractometer data was therefore undertaken.⁶ Preliminary results indicate disorder but not significant decomposition during the data collection. For comparison, it was thought worthwhile to determine the structure of the corresponding 1,10-phenanthrolineium complex, which turned out to be $(C_{12}H_{10}N_2)[NbF_5(O_2)]$.

EXPERIMENTAL

Preparation. Niobium(V) oxide was dissolved in an excess of boiling 38 % hydrofluoric acid. The stoichiometric amount of 1,10-phenanthroline and an excess of hydrogen peroxide were added. By evaporation of the solvent at room temperature, well-developed, pale yellow transparent crystals were obtained.

Data collection. Intensities were recorded at room temperature with a SYNTeX P2₁ automatic four-circle single crystal X-ray diffractometer using graphite-monochromatized MoK α radiation. The crystal, having the dimensions 0.35 × 0.39 × 0.49 mm, was coated with a thin layer of epoxy resin. The ω -2 θ scan method was used, and the 2 θ scan speed was allowed to vary between 2–8°/min, depending on the intensity of the measured reflexion. Data were collected for $2\theta \leq 65^\circ$. Three test reflexions, measured after each fiftieth reflexion, showed no significant difference in intensity during the data collection. A profile analysis based on the Lehmann-Larsen method⁷ was applied to the 96-step profile collected for each reflexion.

A total of 5142 independent reflexions were measured. Of these, 4648 having $I_o \geq 2\sigma(I_o)$ were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz and polarization effects but not for absorption.

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

CRYSTAL DATA

1,10-Phenanthroline pentafluoroperoxoniobate (V) ($C_{12}H_{10}N_2[NbF_5(O_2)]$; F.W. = 402.12
Space group $P\bar{1}$ (No. 2)
 $a = 9.467(1)$ Å, $b = 10.374(2)$ Å, $c = 7.594(1)$ Å,
 $\alpha = 102.38(1)^\circ$, $\beta = 113.11(1)^\circ$, $\gamma = 92.92(1)^\circ$,
 $V = 662.4(2)$ Å³, $Z = 2$, $D_c = 2.016$ g cm⁻³,
 $\mu(\text{MoK}\alpha) = 9.4$ cm⁻¹, $\lambda(\text{MoK}\alpha) = 0.71069$ Å.

List of structure factors and thermal parameters are available from the author upon request.

STRUCTURE DETERMINATION

The Patterson function showed a large peak at (0.521, 0.545, 0.177) taken to be an Nb–Nb vector.

If $P\bar{1}$ is assumed to be the correct space group, Nb thus occupies the general position $2i$ with the approximate coordinates (0.261, 0.273, 0.089). With F_o -signs based on the niobium coordinates, a Fourier summation was undertaken. In the resulting Fourier map, the 22 non-hydrogen atoms were located, giving a plausible structure with a pentagonally bipyramidal coordination about niobium. Successive full-matrix least-squares and Fourier calculations reduced the R -value to 0.045. All coordination distances to niobium and bond distances within the 1,10-phenanthroline ion had normal values at this stage. The obtained peroxo oxygen bond distance of 1.9 Å as well as too short an $F(1) \cdots F(1)$ packing distance showed, however, that the proposed model was not completely correct, despite the low R -value.

At an early stage of the structure determination, it was observed that the pentagonal ring atoms O(1), O(2), F(1), F(2) and F(3) had higher B -values ($B = 6-9$ Å⁻²) than the apically situated atoms F(4) and F(5) ($B = 4$ Å⁻²) as well as the other atoms ($B = 2.6-4.1$ Å⁻²). Furthermore, a difference synthesis, excluding the ring atoms of the anion, showed broad peaks extending in the equatorial plane in a direction perpendicular to the niobium-ligand atom direction (see Fig. 1). This had been

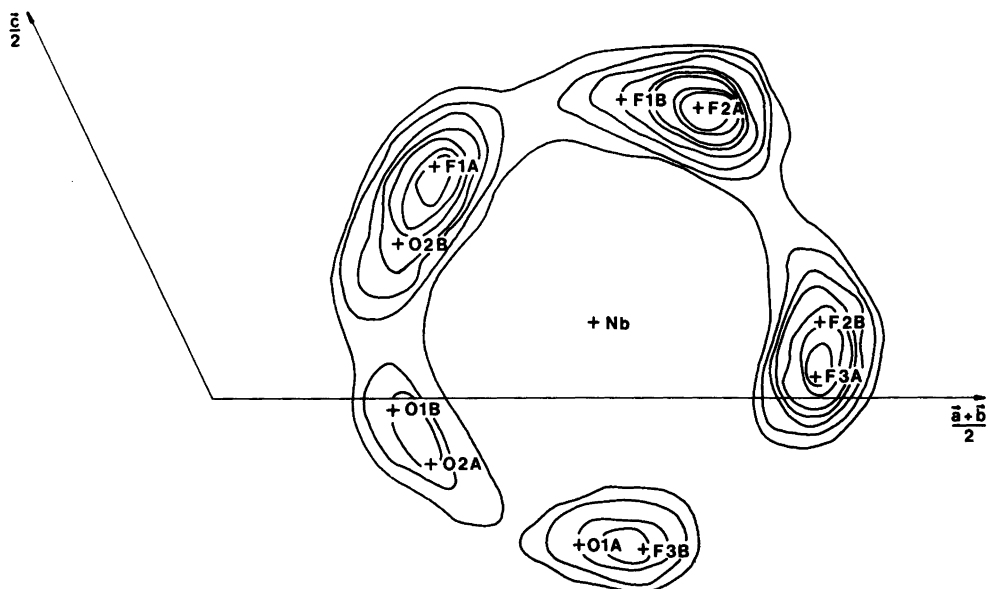


Fig. 1. Section of the electron density difference map. The equatorial atoms F(1), F(2), F(3), O(1) and O(2) were not included in the F_c 's ($R = 0.22$). Contours at integral multiples of $1 \text{ e } \text{\AA}^{-3}$, beginning at $1 \text{ e } \text{\AA}^{-3}$. Contours about Nb have been omitted. The final atomic positions are indicated by crosses.

taken to be due to anisotropy. Despite large thermal vibrations, the average atomic positions should, however, have led to acceptable interatomic distances among the five ring atoms. Since this was not the case, several models were tried, using space group $P\bar{1}$ as well as $P1$, consistent with the observed peak extension in the equatorial plane of the anion. One model, which had two orientations of the anion with refined occupation numbers of 0.6 and 0.4, respectively, could be successfully refined. The

atoms in the pentagonal planes of the two overlapping anions, A and B, could be separated by the least-squares method, while the corresponding niobium and apical fluorine atoms, being too close, could not. A difference map revealed all hydrogen atoms. Refinement of all positional parameters as well as isotropic thermal parameters for the hydrogen atoms and anisotropic ones for all others gave a final R -value of 0.029 ($R = \Sigma \|F_o| - |F_c|| / \Sigma |F_o|$). A difference synthesis calculated after

Table 1. Atomic coordinates, expressed as fraction of the cell edges, for (C₁₂H₁₀N₂)[NbF₅(O₂)]. All atoms occupy the general position $2i$ of space group $P\bar{1}$. A and B denote different anions. $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$. Occupation numbers are 0.6 and 0.4 for atoms marked with A and B, respectively.

Atom	x	y	z	$U_{eq}/\text{\AA}^2$ ($U_{iso}/\text{\AA}^2$ for H)
Nb	0.26168(2)	0.27460(2)	0.09021(3)	0.039
F(1A)	0.2125(5)	0.2139(4)	0.2900(6)	0.087
F(1B)	0.3662(8)	0.3589(7)	0.3767(8)	0.092
F(2A)	0.4102(3)	0.4101(3)	0.3640(5)	0.055
F(2B)	0.4050(7)	0.4190(5)	0.0923(13)	0.110
F(3A)	0.3814(5)	0.4043(4)	0.0245(6)	0.086
F(3B)	0.2198(8)	0.2385(6)	-0.1909(9)	0.085
F(4)	0.4307(2)	0.1739(2)	0.1375(3)	0.068
F(5)	0.1325(2)	0.4117(2)	0.1000(3)	0.059
O(1A)	0.1641(7)	0.2158(6)	-0.1881(7)	0.082
O(1B)	0.1034(12)	0.1206(9)	-0.0161(19)	0.121
O(2A)	0.0954(7)	0.1418(5)	-0.0868(9)	0.094
O(2B)	0.1619(9)	0.1710(7)	0.1955(13)	0.097
N(1)	0.2602(2)	0.5478(2)	0.5436(3)	0.041
N(2)	0.3720(2)	0.6656(2)	0.3022(3)	0.040
C(1)	0.2095(3)	0.4907(3)	0.6541(4)	0.049
C(2)	0.1337(3)	0.5614(4)	0.7603(4)	0.056
C(3)	0.1144(3)	0.6906(3)	0.7507(4)	0.053
C(4)	0.1692(3)	0.7506(3)	0.6338(4)	0.046
C(5)	0.2431(2)	0.6748(2)	0.5280(3)	0.037
C(6)	0.1543(4)	0.8869(3)	0.6264(5)	0.058
C(7)	0.2078(4)	0.9417(3)	0.5146(5)	0.058
C(8)	0.2815(3)	0.8669(2)	0.4030(4)	0.046
C(9)	0.2993(3)	0.7337(2)	0.4089(3)	0.037
C(10)	0.3397(4)	0.9240(3)	0.2878(5)	0.057
C(11)	0.4147(4)	0.8516(3)	0.1860(5)	0.057
C(12)	0.4286(3)	0.7203(3)	0.1948(4)	0.048
H(N1)	0.288(5)	0.476(5)	0.457(8)	0.121(18)
H(N2)	0.384(3)	0.582(3)	0.294(4)	0.027(7)
H(C1)	0.218(4)	0.395(3)	0.633(5)	0.035(8)
H(C2)	0.096(4)	0.524(4)	0.843(5)	0.053(10)
H(C3)	0.073(4)	0.747(3)	0.841(5)	0.036(8)
H(C6)	0.110(3)	0.934(3)	0.719(5)	0.033(8)
H(C7)	0.193(4)	1.033(3)	0.498(5)	0.037(9)
H(C10)	0.302(5)	1.011(5)	0.252(7)	0.090(15)
H(C11)	0.450(4)	0.903(3)	0.117(5)	0.040(9)
H(C12)	0.468(5)	0.690(4)	0.136(7)	0.089(16)

Table 2. Bond distances and angles in $(C_{12}H_{10}N_2)[NbF_5(O_2)]$. A and B denote different anions.

Distance/Å			
Nb—F(1A)	1.962(4)	C(4)—C(6)	1.439(4)
Nb—F(1B)	1.971(6)	C(5)—C(9)	1.433(3)
Nb—F(2A)	2.127(3)	C(6)—C(7)	1.347(5)
Nb—F(2B)	1.963(6)	C(8)—C(7)	1.430(4)
Nb—F(3A)	1.980(4)	C(8)—C(9)	1.409(3)
Nb—F(3B)	1.958(6)	C(8)—C(10)	1.410(4)
Nb—F(4)	1.913(2)	C(11)—C(10)	1.378(4)
Nb—F(5)	1.931(2)	C(11)—C(12)	1.388(4)
Nb—O(1A)	1.884(5)	N(2)—C(9)	1.368(3)
Nb—O(1B)	1.924(10)	N(2)—C(12)	1.337(5)
Nb—O(2A)	1.872(6)	N(1)—H(N1)	1.00(5)
Nb—O(2B)	1.883(8)	N(2)—H(N2)	0.87(3)
O(1A)—O(2A)	1.483(8)	C(1)—H(C1)	0.98(3)
O(1B)—O(2B)	1.440(16)	C(2)—H(C2)	0.97(4)
N(1)—C(1)	1.337(3)	C(3)—H(C3)	1.02(3)
N(1)—C(5)	1.360(3)	C(6)—H(C6)	1.00(3)
C(2)—C(1)	1.400(4)	C(7)—H(C7)	0.99(3)
C(2)—C(3)	1.375(5)	C(10)—H(C10)	1.04(4)
C(4)—C(3)	1.417(4)	C(11)—H(C11)	0.96(3)
C(4)—C(5)	1.408(3)	C(12)—H(C12)	0.72(5)
Angle/°			
F(1A)—Nb—F(2A)	75.3(2)	N(1)—C(1)—C(2)	120.2(3)
F(1A)—Nb—F(3A)	149.1(2)	C(1)—C(2)—C(3)	118.8(3)
F(1A)—Nb—F(4)	90.2(1)	C(2)—C(3)—C(4)	120.6(3)
F(1A)—Nb—F(5)	89.0(1)	C(3)—C(4)—C(5)	118.5(2)
F(1A)—Nb—O(1A)	129.7(2)	C(3)—C(4)—C(6)	121.4(3)
F(1A)—Nb—O(2A)	83.2(2)	C(4)—C(5)—N(1)	118.7(2)
F(2A)—Nb—F(3A)	73.8(2)	N(1)—C(5)—C(9)	122.0(2)
F(2A)—Nb—F(4)	85.2(1)	C(5)—C(4)—C(6)	120.1(2)
F(2A)—Nb—F(5)	79.9(1)	C(4)—C(6)—C(7)	120.2(3)
F(2A)—Nb—O(1A)	154.3(2)	C(6)—C(7)—C(8)	121.1(3)
F(2A)—Nb—O(2A)	157.8(2)	C(7)—C(8)—C(9)	120.0(2)
F(3A)—Nb—F(4)	88.2(1)	C(7)—C(8)—C(10)	121.5(2)
F(3A)—Nb—F(5)	84.7(1)	C(5)—C(9)—C(8)	119.2(2)
F(3A)—Nb—O(1A)	80.9(2)	C(5)—C(9)—N(2)	122.3(2)
F(3A)—Nb—O(2A)	127.4(2)	C(4)—C(5)—C(9)	119.3(2)
F(4)—Nb—F(5)	164.8(1)	C(9)—C(8)—C(10)	118.5(2)
F(4)—Nb—O(1A)	99.1(2)	C(8)—C(10)—C(11)	120.7(2)
F(4)—Nb—O(2A)	100.6(2)	F(3B)—Nb—F(4)	90.8(2)
F(5)—Nb—O(1A)	93.1(2)	F(3B)—Nb—F(5)	98.5(2)
F(5)—Nb—O(2A)	94.4(2)	F(3B)—Nb—O(1B)	79.6(4)
O(1A)—Nb—O(2A)	46.5(3)	F(3B)—Nb—O(2B)	124.1(3)
F(1B)—Nb—F(2B)	79.8(3)	F(4)—Nb—O(1B)	94.8(3)
F(1B)—Nb—F(3B)	158.3(3)	F(4)—Nb—O(2B)	92.7(2)
F(1B)—Nb—F(4)	84.7(2)	F(5)—Nb—O(1B)	98.7(3)
F(1B)—Nb—F(5)	82.2(2)	F(5)—Nb—O(2B)	92.0(2)
F(1B)—Nb—O(1B)	121.8(4)	O(1B)—Nb—O(2B)	44.4(5)
F(1B)—Nb—O(2B)	77.4(3)	C(1)—N(1)—C(5)	123.2(2)
F(2B)—Nb—F(3B)	78.7(3)	C(10)—C(11)—C(12)	118.9(3)
F(2B)—Nb—F(4)	86.2(2)	C(11)—C(12)—N(2)	120.5(2)
F(2B)—Nb—F(5)	83.8(2)	C(9)—N(2)—C(12)	122.9(2)
F(2B)—Nb—O(1B)	158.4(5)	C(8)—C(9)—N(2)	118.5(2)
F(2B)—Nb—O(2B)	157.2(4)		

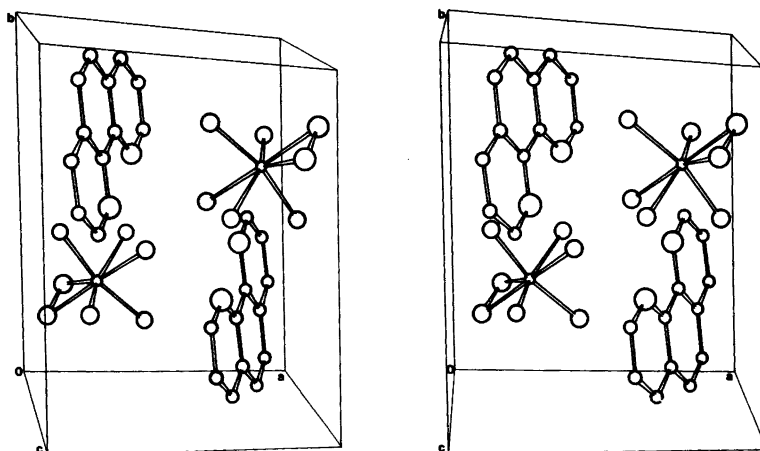


Fig. 2. Stereoscopic drawing of the unit cell of $(C_{12}H_{10}N_2)[NbF_5(O_2)]$. Only the orientation A of the anion is shown.

the final cycle of refinement showed no peak higher than $0.53 \text{ e}/\text{\AA}^3$.

The weighting scheme used was that of Cruickshank:⁸ $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$ with $a=20$, $c=0.02$ and $d=0.0004$. The atomic scattering factors for Nb, F, O and H were taken from the *International Tables for X-Ray Crystallography*, Vol. III, as was the dispersion correction applied to Nb, while those for N and C are from Cromer *et al.*⁹

Calculations were carried out on an IBM 360/65 computer using the crystallographic programmes described by Lindgren.¹⁰

RESULTS AND DISCUSSION

The positional parameters as well as U_{eq} (or U_{iso}) are given in Table 1. A stereoscopic view of the unit cell content is shown in Fig. 2. Bond distances and angles are given in Table 2 and Figs. 3 and 4 and interionic distances in Table 3.

The crystals of 1,10-phenanthroline pentafluoroperoxoniobate(V), $(C_{12}H_{10}N_2)[NbF_5(O_2)]$, consist of 1,10-phenanthroline and pentafluoroperoxoniobate(V) ions held together by ionic and hydrogen bond forces.

The 1,10-phenanthroline ion is planar. The distances from the non-hydrogen atoms defining

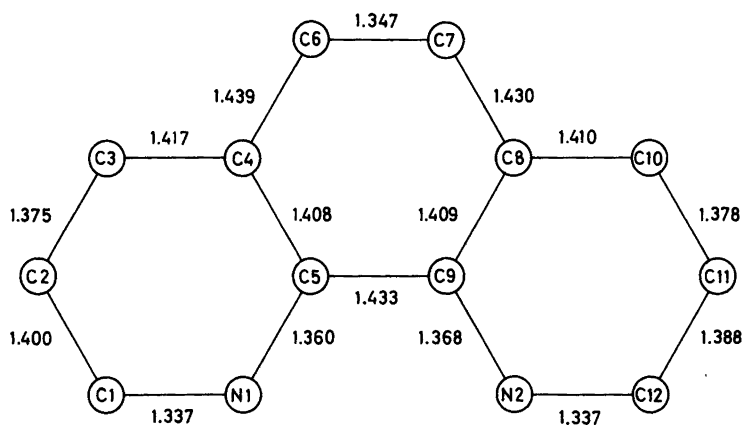


Fig. 3. The ion $C_{12}H_{10}N_2^{2+}$.

this plane to the plane are given in Table 4. Corresponding bond distances in the two hetero rings are equal, the largest difference of 0.012 Å being 3σ . One C—N distance is shorter than the other in both hetero rings, the mean distance* being 1.337(0) Å for the shorter and 1.364(4) Å for the longer one. One C—C distance, C(6)—C(7), is shorter than the other C—C distances, which can be divided into four groups with mean distances of 1.434(4) Å, 1.411(4) Å, 1.394(6) Å and 1.376(2) Å. All bond distances and angles in the 1,10-phenanthroline ion agree well with other observations for this ion and 1,10-phenanthroline.^{11–14}

The pentafluoroperoxoniobate(V) anions are disorderly orientated in the crystal. Two main orientations, denoted A and B, with occupancies 0.6 and 0.4, respectively, were observed. The two anions $[\text{NbF}_5(\text{O}_2)]^{2-}$ have a pentagonal bipyramidal arrangement of ligands (Fig. 4), a configuration observed in several transition metal peroxo complexes (see, e.g., Refs. 4, 5, 15–18). The consistency of this geometry for the pentafluoromonoperoxometallates is evident from Table 5 in Ref. 17, listing interatomic distances in some compounds of this type, and is further supported by the values obtained in the present investigation (see Table 5). The distances

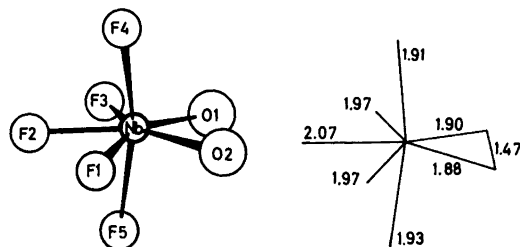


Fig. 4. The ion $[\text{NbF}_5(\text{O}_2)]^{2-}$. Average distances (weighted mean) are given.

from the equatorial plane, defined by F(1), F(2), F(3), O(1) and O(2), to these atoms and to Nb, F(4) and F(5) are given in Table 4. F(2), F(4), F(5), Nb and the midpoint between O(1) and O(2) form a plane too. The angle between these planes is 90.5° in the A anion and 87.3° in the B anion. Hence, the point symmetry of $[\text{NbF}_5(\text{O}_2)]^{2-}$ is almost C_{2v} .

The disorder of the anions A and B can be described in the following way. Neither the central atom positions nor those of the apical atoms in A could be distinguished from the corresponding ones in B.* The equatorial pentagonal planes form an

* R.m.s. deviation from the mean is given in parenthesis.

Table 3. Interionic distances in $(\text{C}_{12}\text{H}_{10}\text{N}_2)[\text{NbF}_5(\text{O}_2)]$. A and B denote different anions. Distances of less than 3.2 Å have been included.

Distance/Å			
F(1B)···N(1)	2.566(7)	F(3A)···C(12 ⁱⁱ)	3.057(5)
F(1B)···N(2 ⁱ)	2.782(7)	F(3A)···N(2)	3.086(5)
F(1B)···F(2A ⁱ)	2.879(8)	F(3A)···F(3A ⁱⁱ)	3.105(9)
F(1B)···C(1)	3.151(7)	F(3A)···C(12)	3.194(5)
F(2A)···F(2A ⁱ)	2.430(6)	F(3B)···C(1 ⁱⁱⁱ)	3.081(7)
F(2A)···N(1)	2.609(4)	F(4)···C(5 ⁱ)	3.177(3)
F(2A)···N(2)	2.806(3)	F(5)···N(2)	3.059(3)
F(2A)···N(2 ⁱ)	2.865(4)	F(5)···N(1)	3.065(3)
F(2A)···N(1 ⁱ)	2.903(3)	F(5)···C(2 ^{iv})	3.098(3)
F(2B)···N(2)	2.811(7)	F(5)···C(3 ^{iv})	3.197(3)
F(2B)···C(12)	3.029(6)	O(2B)···C(3 ^{iv})	3.169(8)
F(2B)···F(3A ⁱⁱ)	3.156(8)	O(2B)···C(10 ^v)	3.190(8)
F(3A)···C(1 ⁱⁱⁱ)	3.000(5)		

Symmetry codes

- ⁱ (1 - x, 1 - y, 1 - z)
- ⁱⁱ (1 - x, 1 - y, z)
- ⁱⁱⁱ (x, y, z - 1)
- ^{iv} (x, 1 - y, 1 - z)
- ^v (x, y - 1, z)

Table 4. Displacements (Å) of the atoms from certain least-squares planes in $(C_{12}H_{10}N_2)[NbF_5(O_2)]$. Defining atoms are

Plane I F(1A), F(2A), F(3A), O(1A) and O(2A)

Plane II F(1B), F(2B), F(3B), O(1B) and O(2B)

Plane III N1, N2, C1–C12

Atom	Plane I	Atom	Plane II	Atom	Plane III
F(1A)	–0.034	F(1B)	–0.032	N(1)	–0.008
F(2A)	0.036	F(2B)	0.035	C(1)	–0.022
F(3A)	–0.028	F(3B)	–0.029	C(2)	–0.006
O(1A)	0.004	O(1B)	0.008	C(3)	0.006
O(2A)	0.022	O(2B)	0.018	C(4)	0.015
Nb	–0.076	Nb	0.019	C(5)	0.013
F(4)	–1.971	F(4)	–1.887	C(6)	–0.012
F(5)	1.839	F(5)	1.919	N(2)	0.024
				C(12)	–0.004
				C(11)	–0.028
				C(10)	–0.003
				C(8)	0.011
				C(9)	0.022
				C(7)	–0.007

angle of 3.3° with one another, and the pentagons are mutually twisted 61° . This disorder differs from that observed for $Na_2[NbF_5(O_2)] \cdot 2H_2O$,¹⁷ $(NH_4)_3[TiF_5(O_2)]$ ^{19,20} and $(C_9H_8NO)_2[NbF_5(O_2)] \cdot 3H_2O$.⁶

The Nb–F_{equatorial} bond distances, 1.958–2.127 Å, are somewhat longer than the Nb–F_{apical} bond distances, 1.913–1.931 Å. This compares well with the corresponding distances in $Na_2[NbF_5(O_2)] \cdot H_2O$ ¹⁵ and $Na_3[HF_2][NbF_5(O_2)]$.¹⁶ A

possible explanation to these differences is given in Ref. 15.

The Nb–O distances, 1.872–1.924 Å, are normal Nb–O single bond distances, observed ones in $Na_2[NbF_5(O_2)] \cdot H_2O$,¹⁵ $Na_3[HF_2][NbF_5(O_2)]$ ¹⁶ and $Na_2[NbF_5(O_2)] \cdot 2H_2O$ ¹⁷ being 1.928, 1.924–1.940 and 1.933–1.962 Å, respectively. Additional Nb–F and Nb–O distances can be found in Ref. 21 and references therein.

The peroxo oxygen bond distances, 1.483 and

Table 5. The lengths of the edges (Å) of the pentagonal bipyramidal coordination polyhedra. The designation of the edges conforms to Fig. 3 in Ref. 17. Compare with Table 5 in Ref. 17.

Edge	Distance/Å	Distance/Å
a	F(1A)···F(2A)	2.501(5)
b	F(2A)···F(3A)	2.471(5)
c	F(3A)···O(1A)	2.508(7)
d	O(1A)···O(2A)	1.483(8)
e	O(2A)···F(1A)	2.546(8)
f	F(4)···F(1A)	2.745(5)
g	F(4)···F(2A)	2.739(4)
h	F(4)···F(3A)	2.710(5)
i	F(4)···O(1A)	2.889(6)
j	F(4)···O(2A)	2.914(7)
k	F(5)···F(1A)	2.727(4)
l	F(5)···F(2A)	2.610(3)
m	F(5)···F(3A)	2.636(5)
n	F(5)···O(1A)	2.770(5)
o	F(5)···O(2A)	2.790(6)
	F(1B)···F(2B)	2.523(10)
	F(2B)···F(3B)	2.487(9)
	F(3B)···O(1B)	2.485(13)
	O(1B)···O(2B)	1.440(16)
	O(2B)···F(1B)	2.411(10)
	F(4)···F(1B)	2.618(7)
	F(4)···F(2B)	2.649(6)
	F(4)···F(3B)	2.757(7)
	F(4)···O(1B)	2.824(11)
	F(4)···O(2B)	2.747(8)
	F(5)···F(1B)	2.565(7)
	F(5)···F(2B)	2.601(7)
	F(5)···F(3B)	2.945(6)
	F(5)···O(1B)	2.925(10)
	F(5)···O(2B)	2.744(8)

1.440 Å, compare well with other observations (see Table 7 in Ref. 4 and Table 5 in Ref. 17).

The niobium atom is displaced 0.076 and 0.019 Å from the equatorial planes. Such small displacements have been observed for the $[\text{NbF}_5(\text{O}_2)]^{2-}$ ion in other compounds¹⁵⁻¹⁷ and for other 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. 4).

The short distances between F(1B) and N(1) and between F(2A) and N(1) indicate rather strong hydrogen bonding. The small distance of 2.430 Å between F(2A) and F(2Aⁱ) is energetically not a plausible distance and therefore not judged to really exist. It is supposed to be a consequence of the disorder, which might be more complicated though not observed in the final electron density difference map. It should also be noted that the fluorine atoms involved in the shortest Nb–F_{equatorial} and Nb–F_{apical} distances, respectively, have only one intermolecular neighbouring atom, while those involved in the longest ones have three or four such neighbouring atoms.

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