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# The Crystal Structure of 8-Hydroxyquinolinium Pentafluorooxoniobate(V) Dihydrate, $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$

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Crystals of $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$ are triclinic, space group $P\bar{1}$, with $a=10.752(3)$ Å, $b=13.313(4)$ Å, $c=7.662(2)$ Å, $\alpha=109.41(2)$ °, $\beta=95.84(2)$ °, $\gamma=96.00(2)$ °, $V=1017.8(5)$ Å$^3$ and $Z=2$. A total of 3608 independent reflexions were collected with a SYNTEX automatic single-crystal X-ray diffractometer, using Mo$K\alpha$ radiation. Of these 2490 were considered observed and used in the structure determination. Least-squares refinement of structural and thermal parameters yielded a final $R$-value of 0.046.

The crystals consist of 8-hydroxyquinolinium ions, pentafluorooxoniobate(V) ions and water of crystallization, held together by ionic and hydrogen bond forces, the shortest hydrogen bond being 2.494(6) Å. It was not possible to distinguish between the oxygen atom and the fluorine atoms within the anion. The observed symmetry is nearly $O_h$ instead of $C_{4v}$, as expected. This indicates a disordered anion. The bond distances of 1.909–1.943 Å between the niobium and the ligand atoms are, therefore, average ones.

Niobium forms a number of pentavalent fluoro and oxofluoro complexes, many of which can be isolated from aqueous solutions or from melts.[1] Addition of hydrogen peroxide to water solutions of fluorooxoniobates(V) yields fluoroperoxoniobates.[1–6] In connection with a study of the disorder in the 8-hydroxyquinolinium pentafluoroperoxoniobate(V) trihydrate, $(C_9H_8NO)_2[NbF_5(O_2)]\cdot 3H_2O$, the structure of which has been reported by Ružić-Toroš *et al.*,[7] it was thought worthwhile to elucidate the structure of the corresponding oxo complex.

## EXPERIMENTAL

*Preparation.* Niobium(V) oxide was dissolved in an excess of boiling 38% hydrofluoric acid. The stoichiometric amount of 8-hydroxyquinoline was added, yielding a crystalline mass, which was dissolved in hot water. By evaporation of the solvent at room temperature, well-developed prismatic crystals were obtained.

The compound was investigated thermogravimetrically up to 800 °C using the universal microthermobalance Mettler TA1. The DTA curve indicated an endothermic reaction at 60–110 °C, which was assumed to be due to loss of water, an endothermic one at 110–180 °C and exothermic ones at 400–550 °C. The maximum mass loss, due to combustion, was observed at 450–500 °C. Above 550 °C the mass of the product, assumed to be niobium(V) oxide, was constant. (Found: $H_2O$ 6.7; $Nb_2O_5$ 24.5. Calc. for $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$: $H_2O$ 6.77; $Nb_2O_5$ 24.97).

The IR-spectrum was recorded with a Beckman IR9 instrument. A strong absorption at 945 cm$^{-1}$, lacking in $(C_9H_8NO)_2[NbF_5(O_2)]\cdot 3H_2O$,[7,8] was assigned to the Nb=O stretching mode.

*Data collection.* Intensities were recorded at 2 °C with a SYNTEX $P2_1$ automatic four-circle single crystal X-ray diffractometer using graphite-monochromatized Mo$K\alpha$ radiation and a prismatic crystal with the dimensions $0.10\times 0.10\times 0.15$ mm. To reduce 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 1.3 and 8.4 °/min depending on the intensity of the measured reflexion. Data were collected for $2\theta\leq 50°$. Three test reflexions, measured after each forty-seventh reflexion, showed no significant difference in intensity during the data collection. A profile analysis based on the Lehmann-Larsen method[9] was applied to the 96-step profile collected for each reflexion.

A total of 3608 independent reflexions were measured. Of these, 2490 having $I_o\geq 2\sigma(I_o)$ were regarded as being observed and were used in the subsequent calculations. The intensities were

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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 11 reflexions.

## CRYSTAL DATA

8-Hydroxyquinolinium pentafluorooxoniobate-(V) dihydrate
$(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$ $F.W.=532.27$
Space group $P\bar{1}$ (No. 2)
$a=10.752(3)$ Å, $b=13.313(4)$ Å, $c=7.662(2)$ Å,
$\alpha=109.41(2)°$, $\beta=95.84(2)°$, $\gamma=96.00(2)°$,
$V=1017.8(5)$ Å$^3$, $Z=2$, $D_c=1.737$ g cm$^{-3}$,
$\mu(MoK\alpha)=6.6$ cm$^{-1}$, $\lambda=0.71069$ Å.

Lists of structure factors and thermal parameters are available from R.S. upon request.

## STRUCTURE DETERMINATION

The Patterson function showed a large peak at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, assumed to be an Nb–Nb vector. The anion $[NbF_5O]^{2-}$ cannot be centrosymmetrical. Hence, the positions (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ of space group $P\bar{1}$ were ruled out as possible sites for the niobium atoms. Instead, niobium was presumed to occupy the general position 2*i* of space group $P\bar{1}$ with $x\approx\frac{1}{4}$, $y\approx\frac{1}{4}$ and $z\approx\frac{1}{4}$. Successive Fourier summations and least-squares refinement cycles soon revealed that the two anions were not centrosymmetrically related. It was necessary, therefore, to continue the structure determination assuming $P1$ to be the correct space group. Nb1 was fixed at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, thus specifying the origin of the cell. From a Fourier summation all non-hydrogen atoms were found. Three cycles of least-squares refinement of these 62 atomic positions and isotropic temperature factors gave an *R*-value of 0.108. The cations in pairs as well as the ligand atoms within each of the complex anions then seemed to be centrosymmetrically situated. At this stage niobium–ligand atom distances were found to be within $1.91\pm0.05$ Å. Thus, no Nb=O distance with an expected value of about 1.7 Å could be identified. Passing on to space group $P\bar{1}$ by averaging "symmetry-related" coordinates, that is, coordinated fluorine and oxygen atoms were not distinguished, and shifting the origin $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, gave a corresponding *R*-value of 0.105. Further block-diagonal least-squares refinement of an overall scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms as well as the introduction of the hydrogen atoms belonging to the ring systems (the corresponding parameters were not refined) gave a final *R*-value of 0.046 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). The weighting scheme used was that of Cruickshank: $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$ with $a=30$, $c=0.005$ and $d=0.0001$.[10] The atomic scattering factors for Nb, F, O and H were taken from the *International*

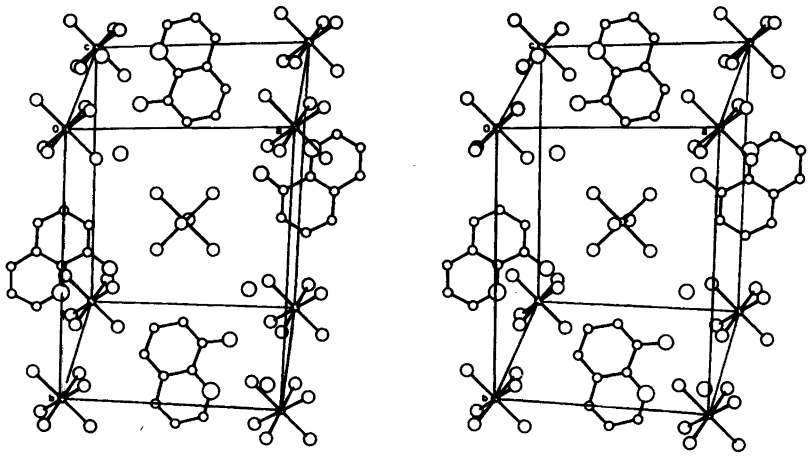

*Fig. 1.* Stereoscopic drawing of the unit cell of $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$.

*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.*[11]

A difference synthesis calculated after the final cycle of refinement showed no spurious peaks.

Calculations were carried out on an IBM 360/65 computer using the crystallographic programmes described in Ref. 12.

## RESULTS AND DISCUSSION

The positional parameters obtained in the last refinement cycle, as well as $U_{eq}$, are given in Table 1. The content of the unit cell is shown in Fig. 1. Bond distances and angles are given in Table 2 and hydrogen bond distances in Table 3.

The crystals of 8-hydroxyquinolinium pentafluorooxoniobate(V) dihydrate, $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$, consist of 8-hydroxyquinolinium ions, pentafluorooxoniobate(V) ions and water of crystallization, held together by ionic and hydrogen bond forces.

The two 8-hydroxyquinolinium ions are planar. The distances from the non-hydrogen atoms defining these planes to the respective plane are given in Table 4. The planes form an angle of 7.1° to each other. The corresponding bond distances in the

*Table 1.* Atomic coordinates, expressed as fractions of the cell edges, for $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$. Space group $P\bar{1}$. Coordinated fluorine and oxygen atoms could not be distinguished; they are all denoted F as shorthand notation for (F,O). $U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j\cos\alpha_{ij}$.

| Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Nb1 | 0 | 0 | 0 | 0.044 |
| Nb2 | ½ | ½ | ½ | 0.048 |
| F1 | 0.1304(4) | 0.1234(3) | 0.0563(5) | 0.063 |
| F2 | −0.1182(4) | 0.0950(3) | 0.0973(6) | 0.071 |
| F3 | 0.0470(4) | −0.0021(3) | 0.2474(5) | 0.070 |
| F4 | 0.6364(4) | 0.6062(3) | 0.5059(9) | 0.106 |
| F5 | 0.6193(4) | 0.4182(4) | 0.5700(9) | 0.107 |
| F6 | 0.4929(5) | 0.5805(4) | 0.7557(7) | 0.096 |
| O1 | 0.2630(4) | 0.0933(3) | 0.5916(6) | 0.056 |
| O2 | 0.1688(4) | 0.6301(3) | 0.3553(6) | 0.053 |
| O3 | 0.1954(4) | 0.2284(3) | 0.4365(6) | 0.054 |
| O4 | 0.0906(4) | −0.1214(3) | 0.4661(6) | 0.050 |
| N1 | 0.3370(4) | −0.0751(4) | 0.6686(7) | 0.045 |
| N2 | −0.0476(4) | 0.6784(3) | 0.2217(7) | 0.044 |
| C1 | 0.3659(6) | −0.1614(5) | 0.7033(8) | 0.051 |
| C2 | 0.4896(6) | −0.1631(5) | 0.7785(9) | 0.061 |
| C3 | 0.5804(6) | −0.0764(5) | 0.8139(8) | 0.052 |
| C4 | 0.5507(5) | 0.0157(5) | 0.7738(7) | 0.045 |
| C5 | 0.6402(6) | 0.1072(6) | 0.8028(9) | 0.057 |
| C6 | 0.6024(6) | 0.1924(5) | 0.7595(9) | 0.054 |
| C7 | 0.4749(6) | 0.1914(5) | 0.6899(8) | 0.049 |
| C8 | 0.3858(5) | 0.1034(4) | 0.6590(8) | 0.040 |
| C9 | 0.4243(5) | 0.0151(4) | 0.7022(8) | 0.041 |
| C10 | −0.1492(6) | 0.7064(5) | 0.1456(9) | 0.058 |
| C11 | −0.2570(6) | 0.6316(6) | 0.0665(9) | 0.061 |
| C12 | −0.2609(6) | 0.5311(6) | 0.0743(9) | 0.057 |
| C13 | −0.1542(6) | 0.4992(5) | 0.1519(8) | 0.048 |
| C14 | −0.1494(6) | 0.3950(5) | 0.1608(9) | 0.056 |
| C15 | −0.0386(7) | 0.3712(5) | 0.2306(10) | 0.060 |
| C16 | 0.0717(6) | 0.4481(5) | 0.2980(9) | 0.051 |
| C17 | 0.0694(5) | 0.5495(4) | 0.2962(8) | 0.043 |
| C18 | −0.0448(5) | 0.5762(4) | 0.2232(7) | 0.040 |

*Table 2.* Bond distances and angles in $(C_9H_8NO)_2[NbF_5O]\cdot 2H_2O$. The Nb–F distances recorded are average Nb–(F,O) distances due to disordered anions. The same applies to F–Nb–F angles.

| | | | |
|---|---|---|---|
| Distance/Å | | | |
| Nb1–F1 | 1.943(4) | Nb2–F4 | 1.913(4) |
| Nb1–F2 | 1.916(4) | Nb2–F5 | 1.913(4) |
| Nb1–F3 | 1.921(4) | Nb2–F6 | 1.909(5) |
| N1–C1 | 1.321(7) | N2–C10 | 1.331(8) |
| N1–C9 | 1.379(7) | N2–C18 | 1.367(7) |
| C2–C1 | 1.401(9) | C11–C10 | 1.385(9) |
| C2–C3 | 1.364(9) | C11–C12 | 1.356(10) |
| C4–C3 | 1.419(9) | C13–C12 | 1.407(9) |
| C4–C5 | 1.411(9) | C13–C14 | 1.418(9) |
| C4–C9 | 1.411(8) | C13–C18 | 1.406(8) |
| C6–C5 | 1.371(9) | C15–C14 | 1.367(10) |
| C6–C7 | 1.417(9) | C15–C16 | 1.411(9) |
| C8–C7 | 1.372(8) | C17–C16 | 1.357(8) |
| C8–C9 | 1.412(7) | C17–C18 | 1.425(8) |
| C8–O1 | 1.344(7) | C17–O2 | 1.356(7) |
| Angle/° | | | |
| F1–Nb1–F2 | 89.8(2) | F4–Nb2–F5 | 89.7(2) |
| F1–Nb1–F3 | 88.9(2) | F4–Nb2–F6 | 88.2(2) |
| F2–Nb1–F3 | 88.7(2) | F5–Nb2–F6 | 91.6(2) |
| C1–N1–C9 | 122.9(5) | C10–N2–C18 | 122.0(5) |
| N1–C1–C2 | 119.8(6) | N2–C10–C11 | 120.2(6) |
| C1–C2–C3 | 120.1(6) | C10–C11–C12 | 119.8(6) |
| C2–C3–C4 | 120.4(6) | C11–C12–C13 | 121.0(6) |
| C3–C4–C9 | 117.7(5) | C12–C13–C18 | 117.4(6) |
| C4–C9–N1 | 119.1(5) | C13–C18–N2 | 119.5(5) |
| C3–C4–C5 | 123.6(5) | C12–C13–C14 | 124.5(6) |
| C9–C4–C5 | 118.8(5) | C18–C13–C14 | 118.2(5) |
| C4–C5–C6 | 119.3(6) | C13–C14–C15 | 119.5(6) |
| C5–C6–C7 | 121.4(6) | C14–C15–C16 | 122.0(6) |
| C6–C7–C8 | 120.7(5) | C15–C16–C17 | 119.9(6) |
| C7–C8–C9 | 118.1(5) | C16–C17–C18 | 119.1(5) |
| C7–C8–O1 | 125.7(5) | C16–C17–O2 | 125.6(5) |
| O1–C8–C9 | 116.1(5) | O2–C17–C18 | 115.2(5) |
| C8–C9–C4 | 121.7(5) | C17–C18–C13 | 121.2(5) |
| C8–C9–N1 | 119.2(5) | C17–C18–N2 | 119.3(5) |

two non-equivalent 8-hydroxyquinolinium ions are equal, the largest difference of 0.016 Å being less than $2\sigma$. The three carbon–carbon distances C2–C3, C5–C6 and C7–C8, and the corresponding ones in the other cation, are significantly shorter than the other carbon–carbon distances, the average ones* being 1.364(6) and 1.410(10) Å, respectively. They compare well with the corresponding values of 1.365(12) and 1.404(13), respectively, for $(C_9H_8NO)[Mo(C_9H_6NO)Cl_3O]$.[13]

One C–N distance is shorter than the other in both cations, the mean distance being 1.326(5) Å for the shorter and 1.373(6) Å for the longer one. The same observation was made for $(C_9H_8NO)[Mo(C_9H_6NO)Cl_3O]$, the corresponding distances being 1.321(3) and 1.367(3) Å, respectively. All bond distances and angles in the 8-hydroxyquinolinium ion agree well with other observations for this ion and the 8-hydroxyquinolinato ligand[13–17] as well as with the theoretical parameters obtained for 8-hydroxyquinoline by the LCAO–MO method.[18] The agreement supports the choice of space group $P\bar{1}$ in the present investigation.

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

*Table 3.* Hydrogen bond distances (Å). O3 and O4 are water oxygen atoms. X···F distances are average X···(F,O) distances.

| | | |
|---|---|---|
| O1···O3 | (*x*, *y*, *z*) | 2.588(6) |
| O2···F5 | (1−*x*, 1−*y*, 1−*z*) | 2.494(6) |
| O3···F4 | (1−*x*, 1−*y*, 1−*z*) | 2.583(6) |
| O3···F1 | (*x*, *y*, *z*) | 2.757(6) |
| O4···F3 | (*x*, *y*, *z*) | 2.705(6) |
| O4···N1 | (*x*, *y*, *z*) | 2.827(6) |
| O4···N2 | (*x*, *y*−1, *z*) | 2.848(6) |
| O4···F3 | ($\bar{x}$, $\bar{y}$, 1−*z*) | 2.912(6) |

*Table 4.* Displacements of the atoms in the 8-hydroxyquinolinium ions from the mean planes.

| Atom | Plane I | Atom | Plane II |
|---|---|---|---|
| N1 | 0.013 Å | N2 | −0.057 |
| C1 | 0.022 | C10 | −0.008 |
| C2 | −0.002 | C11 | 0.060 |
| C3 | −0.022 | C12 | 0.015 |
| C4 | −0.007 | C13 | −0.019 |
| C5 | 0.005 | C14 | −0.031 |
| C6 | 0.021 | C15 | 0.005 |
| C7 | −0.002 | C16 | 0.028 |
| C8 | −0.005 | C17 | 0.002 |
| C9 | −0.013 | C18 | −0.027 |
| O1 | −0.011 | O2 | 0.031 |

As is apparent from the structure determination part, it has not been possible to distinguish the oxygen atoms coordinated to the niobium atoms from the fluorine atoms. This has been assumed to be due to disorder, in which the coordination polyhedron is orientated in six equally frequent directions. Disorderly orientated fluorooxometallate ions are not uncommon; in fact, there are numerous examples in which the ions in question are either completely randomly orientated about a fixed point or in which the oxygen and fluorine atoms cannot otherwise be distinguished (see, *e.g.*, Refs. 19−21). The observed distances between the ligand atoms and niobium, 1.909−1.943 Å (average 1.919(11)), are, therefore, only mean Nb−(F,O) distances. These may be compared with the observed bond distances in $(N_2H_6)[NbF_5O]\cdot H_2O$, Nb=O 1.75 Å, Nb−$F_{trans}$ 2.21 Å and Nb−$F_{equatorial}$ 1.93 and 1.96 Å, respectively, giving an average Nb−(F,O) distance of 1.96 Å.[22] The corresponding values for $K_2[NbF_5O]$ are Nb=O 1.68 Å, Nb−$F_{trans}$ 2.06 and Nb−$F_{equatorial}$ 1.84 Å, the mean Nb−(F,O) distance being 1.85 Å.[23] In $Li_2NbF_5O$ the Nb−(F,O) distance was found to be 1.95 Å.[21] Further Nb−F and Nb−O distances are given in Refs. 1 and 24.

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