

The Crystal Structure of $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$ at 290 K and a Refinement of the Crystal Structure of the Isomorphous $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$ at 250 and 290 K

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The crystal structure of (tri)ammonium fluoride tetrafluorooxoperoxotungstate (VI), $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$, has been determined by single-crystal X-ray methods. The compound crystallizes, as colourless needles, in space group *Pbca* with $a = 16.668(5)$, $b = 15.883(5)$, $c = 6.824(2)$ Å, $V = 1807(1)$ Å³ and $Z = 8$. Full-matrix least-squares refinement yielded a final R value of 0.043 for 1878 observed [$I > 3\sigma(I)$] reflections. The structure is isomorphous with that of the corresponding molybdenum compound, determined earlier. The latter structure was refined to $R = 0.043$ for 1832 observed reflections at 250 K and to $R = 0.043$ for 1649 observed reflections at 290 K.

The complex anions have pentagonal-bipyramidal configuration with the peroxo group in the equatorial plane. The tungsten atom is displaced 0.217(6) Å out of the equatorial plane towards the double-bonded oxygen atom. The corresponding value for molybdenum is 0.238(2) Å.

Bond distances: $\text{W}-\text{O}_{\text{peroxo}}$ 1.905(12)–1.937(12) Å, $\text{W}=\text{O}_{\text{apical}}$ 1.716(15) Å, $\text{W}-\text{F}_{\text{equatorial}}$ 1.936(12)–1.986(9) Å, $\text{W}-\text{F}_{\text{apical}}$ 2.036(9) Å and $\text{O}-\text{O}_{\text{peroxo}}$ 1.435(20) Å.

$\text{Mo}-\text{O}_{\text{peroxo}}$ 1.903(5)–1.917(5) Å, $\text{Mo}=\text{O}_{\text{apical}}$ 1.670(5) Å, $\text{Mo}-\text{F}_{\text{equatorial}}$ 1.943(5)–1.990(4) Å, $\text{Mo}-\text{F}_{\text{apical}}$ 2.070(4) Å and $\text{O}-\text{O}_{\text{peroxo}}$ 1.434(8) Å.

A number of different fluoroperoxometallates are known for the group 5 elements, structurally investigated compounds being $(\text{NH}_4)_2[\text{VFO}(\text{O}_2)_2]$,¹ $(\text{NH}_4)_3[\text{VF}_2\text{O}(\text{O}_2)_2]$,² $\text{K}_2[\text{VFO}(\text{O}_2)_2]$,³ $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$,⁴ $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot \text{H}_2\text{O}$,⁵ $\text{Na}_2[\text{NbF}_5(\text{O}_2)] \cdot 2\text{H}_2\text{O}$,⁶ $\text{Na}_3[\text{HF}_2][\text{NbF}_5(\text{O}_2)]$,⁷ $(\text{C}_9\text{H}_8\text{NO})_2[\text{NbF}_5(\text{O}_2)] \cdot 3\text{H}_2\text{O}$,^{8,9} $(\text{C}_{12}\text{H}_{10}\text{N}_2)[\text{NbF}_5(\text{O}_2)]$,¹⁰ $\text{K}_3[\text{HF}_2][\text{TaF}_5(\text{O}_2)]$ ^{11,12} and $\text{K}_6[\text{TaF}_5(\text{O}_2)][\text{O}\{\text{TaF}_4(\text{O}_2)\}_2] \cdot \text{H}_2\text{O}$.¹³ With few exceptions they are mononuclear. In some of these systems different phases are formed due to minor differences in concentrations and pH. Thus, three crystalline phases separated out successively in the $\text{Na}^+ - \text{Nb}_2\text{O}_5 - \text{HF} - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ system in the same crystallization vessel.^{5–7} This may also happen among compounds of the group 6 elements, as observed in the systems $\text{NH}_4^+ - \text{MO}_4^{2-} - \text{HF} - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ ($\text{M} = \text{Mo}, \text{W}$).

In these, the dominant crystalline phase seems to be $(\text{NH}_4)_3\text{F}[\text{MF}_4\text{O}(\text{O}_2)]$, which separates from fluoride-rich solutions at low pH. In $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$ the rather short $(\text{O}-\text{O})_{\text{peroxo}}$ bond distance of 1.36(3) Å was found from film data.¹⁴ Moreover, the hydrogen atoms were not located. In view of this and the general need for more precise structural parameters, a redetermination of the structure $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$ was performed using diffractometer data. The space group and the unit cell dimensions of $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$ indicate isomorphism with the molybdenum counterpart. $\text{K}_2[\text{O}\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2] \cdot 2\text{H}_2\text{O}$ and $\text{K}_2[\text{O}\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2] \cdot 2\text{H}_2\text{O}$, e.g., are, however, not isomorphous though they both crystallize in $P\bar{1}$ and have similar cell dimensions.^{41,42} Furthermore, the change of central atom might effect the $(\text{O}-\text{O})_{\text{peroxo}}$

bond distance. The structure analysis of $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$ was, therefore, also performed and is described in the present paper.

As for the group 5 elements, the crystalline phases obtained in the systems $\text{NH}_4^+ - \text{MO}_4^{2-} - \text{HF} - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ ($\text{M} = \text{Mo}, \text{W}$) are also mostly mononuclear. This is in contrast to the compounds formed in the fluoride-free systems $\text{M}^+ - \text{MoO}_4^{2-} - \text{H}_2\text{O}_2 - \text{H}^+ - \text{H}_2\text{O}$ ($\text{M}^+ = \text{NH}_4^+, \text{K}^+$). A comprehensive investigation of these systems has shown the existence of both oxoperoxo mono-, di-, tri-, tetra-, penta-, hepta-, octa- and decamolybdates (a preliminary report is given in Ref. 15; see also Ref. 16).

It deserves mentioning that among the most fluoride-rich complexes there is a difference in stoichiometry between the group 5 and 6 ele-

ments. Thus, while niobium and tantalum form $[\text{MF}_5(\text{O}_2)]^{2-}$ ions, molybdenum and tungsten form $[\text{MF}_4\text{O}(\text{O}_2)]^{2-}$ ions.

Experimental

Preparation of $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$. 1 g of ammonium tungstate(VI) was dissolved in 25 ml of 1 M hydrogen fluoride, and ammonia was added to adjust the pH to 3–4. 0.5 ml of 30% hydrogen peroxide was added and the solution was kept in a refrigerator at 2°C. Isothermal evaporation yielded colourless crystals in the form of prismatic needles after a couple of days. One of these was removed from the mother liquor and cut to a suitable size.

Table 1. Crystal and experimental data for $(\text{NH}_4)_3\text{F}[\text{MF}_4\text{O}(\text{O}_2)]$ ($\text{M} = \text{Mo}, \text{W}$).

	$(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$	$(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$
T/K	250	290
M_r	293.05	380.96
Crystal system	Orthorhombic	Orthorhombic
Space group ^a	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)
Unit cell dimensions/Å	<i>a</i> = 16.556(7) <i>b</i> = 15.957(6) <i>c</i> = 6.774(3) <i>V</i> = 1790(1)	<i>a</i> = 16.668(5) <i>b</i> = 15.883(5) <i>c</i> = 6.824(2) <i>V</i> = 1807(1)
<i>Z</i>	8	8
$D_x/\text{g cm}^{-3}$	2.175	2.801
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	1.52	13.6
Crystal size/mm	0.12 × 0.13 × 0.35	0.17 × 0.19 × 0.23
No. of reflections for cell determination (θ range/°)	15(2.6 < θ < 11.8)	6(12.9 < θ < 15.4)
Scan mode	ω -2 θ	ω -2 θ
2 θ range/°	3.5 < 2 θ < 60.0	3.5 < 2 θ < 60.0
2 θ scan speed/° min ⁻¹	3.0–10.0	5.0–29.3
Total No. of reflections measured	3026	3054
No. of observed independent reflections [$I > 3\sigma(I)$]	1832	1878
Test reflection (standard deviation/%)	400(±1.7) 020(±1.0) 002(±1.3)	041(±4.2) 230(±10.6)
Correction for absorption	Empirical ^b	Empirical ^b
No. of parameters refined	157	145
Weights calculated according to $w = (a + F_o + c F_o ^2 + d F_o ^3)^{-1c}$	<i>a</i> = 15.0 <i>c</i> = 0.006 <i>d</i> = 0	<i>a</i> = 40.0 <i>c</i> = 0.0001 <i>d</i> = 0
<i>R</i> (R_w)	0.043 (0.051)	0.043 (0.054)
Maximum residual electron density/e Å ⁻³	0.71	1.06

^aRef. 17a. ^bRef. 18. ^cRef. 19.

Preparation of (NH₄)₃F[MoF₄O(O₂)]. 7 g of ammonium fluoride and 10 g of ammonium molybdate were dissolved in a solution of 5 ml of conc. hydrogen fluoride and 35 ml of 5% hydrogen peroxide in a platinum dish. A clear solution was obtained after gentle heating. The solution was allowed to evaporate at room temperature. Yellow prismatic needles were obtained and were cut to a size suitable for the diffraction experiment.

Structure determination. Crystal data and conditions for the data collection are given in Table 1. Several crystals were used of both compounds. Intensity data were recorded with a Syntex P2₁ X-ray diffractometer (graphite-monochromated MoK α radiation) for both compounds. Integrated intensity values were obtained by the Lehmann-Larsen profile analysis method.²⁰ The intensities were corrected for Lorentz, polarization and absorption effects. The unit cell dimensions were determined from a

least-squares fit of refined diffractometer setting angles.

The cell dimensions and space group strongly indicated isomorphism between (NH₄)₃F[WF₄O(O₂)] and the molybdenum analogue.¹⁴ The structure of the tungsten compound could be successively refined using the atomic parameters of (NH₄)₃F[MoF₄O(O₂)] as a starting point. Least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms gave $R = 0.091$. With anisotropic thermal parameters R became 0.070. Correction for absorption reduced R to 0.045. Correction of the intensities for the observed disintegration of the crystal affected the R value only in the initial cycles of the refinement; with isotropic thermal parameters R became 0.062, and with anisotropic thermal parameters R was reduced to 0.045, i.e. the same value with data not corrected for disintegration. Clearly, the anisotropic thermal pa-

Table 2. Atomic coordinates and B_{eq} (B_{iso} for H) for (NH₄)₃F[MF₄O(O₂)] (M = Mo, W). All atoms occupy the general eight-fold site 8c of space group $Pbca$. $B_{\text{eq}} = \frac{1}{3} \sum \beta_{ij} \cdot a_i \cdot a_j$.

Atom	(NH ₄) ₃ F[MoF ₄ O(O ₂)] ($T = 250$ K)				(NH ₄) ₃ F[WF ₄ O(O ₂)] ($T = 290$ K)			
	x	y	z	B_{eq}	x	y	z	B_{eq} Å
M	0.12858(2)	0.08357(2)	0.19589(6)	2.272(9)	0.12687(3)	0.08370(3)	0.20878(6)	2.14(1)
F1	0.0707(2)	0.0732(2)	0.4656(5)	4.26(9)	0.0698(6)	0.0734(5)	0.471(1)	4.3(2)
F1	0.1431(2)	0.1989(2)	0.3017(6)	5.3(1)	0.1366(5)	0.2011(6)	0.306(2)	4.4(3)
F3	0.2264(3)	0.0790(3)	0.3539(9)	7.6(2)	0.2228(6)	0.0749(8)	0.368(2)	6.9(4)
F4	0.0244(2)	0.1360(2)	0.1221(5)	3.60(7)	0.0242(5)	0.1328(5)	0.128(1)	3.7(2)
F5	0.3688(2)	0.2973(2)	0.4832(5)	4.07(8)	0.3699(5)	0.2922(6)	0.502(1)	3.8(2)
O1	0.1721(3)	0.1043(3)	-0.0211(8)	5.7(1)	0.1760(9)	0.1062(7)	-0.006(2)	6.2(4)
O2	0.1465(4)	-0.0340(3)	0.2149(8)	5.4(1)	0.1425(9)	-0.0350(7)	0.220(2)	5.7(4)
O3	0.0700(3)	-0.0157(3)	0.1255(8)	5.2(1)	0.0675(7)	-0.0151(7)	0.127(2)	4.5(3)
N1	0.2672(3)	0.3042(3)	0.1630(8)	3.4(1)	0.2633(7)	0.3057(8)	0.176(2)	2.8(2)
N2	0.3850(3)	0.0612(3)	0.1913(8)	3.4(1)	0.3798(8)	0.061(1)	0.203(2)	3.5(3)
N3	0.0053(3)	0.3148(3)	0.2157(8)	3.3(1)	-0.0017(8)	0.3139(7)	0.229(1)	2.6(2)
H1(N1)	0.301(5)	0.313(5)	0.25(1)	4(2)	0.28(1)	0.33(1)	0.30(3)	4.00
H2(N1)	0.221(4)	0.277(4)	0.20(1)	2(1)	0.22(1)	0.26(1)	0.21(3)	4.00
H3(N1)	0.308(4)	0.265(4)	0.09(1)	2(1)	0.32(1)	0.26(1)	0.12(3)	4.00
H4(N1)	0.253(4)	0.348(4)	0.08(1)	2(2)	0.25(1)	0.34(1)	0.09(3)	4.00
H1(N2)	0.335(6)	0.048(5)	0.25(1)	4(2)	0.31(1)	0.07(1)	0.27(3)	4.00
H2(N2)	0.419(5)	0.071(4)	0.29(1)	2(2)	0.41(2)	0.05(2)	0.28(3)	4.00
H3(N2)	0.377(3)	0.099(3)	0.130(8)	-1(1)	0.37(1)	0.13(1)	0.10(3)	4.00
H4(N2)	0.403(4)	0.019(4)	0.11(1)	2(1)	0.39(2)	0.05(2)	0.13(4)	4.00
H1(N3)	-0.005(4)	0.337(4)	0.306(9)	1(1)	0.00(1)	0.37(1)	0.34(3)	4.00
H2(N3)	0.036(5)	0.273(5)	0.23(1)	3(2)	0.03(1)	0.27(1)	0.22(3)	4.00
H3(N3)	0.034(3)	0.346(3)	0.132(8)	0(1)	0.03(1)	0.36(1)	0.12(3)	4.00
H4(N3)	-0.045(5)	0.303(5)	0.15(1)	3(2)	-0.07(1)	0.32(1)	0.14(3)	4.00

rameters have a compensating effect. Plausible hydrogen atom positions were derived from an electron density difference map. The introduction of these with fixed $B_{\text{iso}}(\text{H}) = 4.0$ gave a final R value of 0.043.

The structure of $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$ was refined using data collected at room temperature as well as at 250 K (different crystals) in the same way as for the tungsten compound. The variation of the three test reflections was somewhat larger at 290 K. The hydrogen atom positions were derived from an electron density difference map (the hydrogen atoms were not located in the original structure analysis). Full-matrix least-squares refinement of positional parameters, anisotropic thermal parameters for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms yielded a final R value of 0.043.

Further details concerning the refinement of the structures are summarized in Table 1. Atomic scattering factors were taken from Ref. 17b. Calculations were carried out on an IBM 3081 computer with programs in use at this department.

Results

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2 (only those at 250 K are given for the molybdenum compound), and bond distances and bond angles in Table 3. Fig. 1 shows a stereoscopic view of the unit cell, and Fig. 2 the complex and the atomic labelling.

The structure analysis has shown that $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$ is isomorphous with $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$. Both contain pentagonal bipyramidal anions. Furthermore, the bond distances obtained in the original structure analysis of the latter compound, based on film data (with e.s.d.'s in the range 0.01–0.03 Å),¹⁴ do not deviate by more than 2σ from those obtained in the present refinement. The original description and discussion of the structure is, therefore, valid, but some further remarks may be added.

In a number of investigations of transition metal peroxo complexes using film data, often collected with CuK radiation with a new crystal mounted for each layer line, rather short $(\text{O}-\text{O})_{\text{peroxo}}$ bond distances were observed, e.g. 1.36(3) Å in $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$.¹⁴ In view of more recent structure determinations, based on data sets collected by a diffractometer, these

short bond distances can be understood in terms of partial decomposition of the peroxo group to an oxo group. If due account is taken of partial occupancy of the peroxo group normal peroxo bond distances are obtained (see e.g., Refs. 16 and 21). In the present investigation the observed average $(\text{O}-\text{O})_{\text{peroxo}}$ bond distance is 1.428(8) Å (r.m.s. deviation is given in parentheses), in close agreement with the weighted average value of 1.436(17) Å calculated from data for six other oxomonoperoxomolybdates,^{22–27} and is thus significantly shorter than $(\text{O}-\text{O})_{\text{peroxo}}$ bond distances in oxodiperoxomolybdates (weighted average value 1.471(11) Å, calculated from 23 observations).^{22,28–36}

The $\text{Mo}-\text{O}_{\text{peroxo}}$ bond distances do not differ significantly from each other, but are shorter than those observed in oxodiperoxomolybdates.^{22,28–36} In, e.g., the fluorooxodiperoxomolybdate $(\text{NH}_4)_2[\text{MoF}_2\text{O}(\text{O}_2)_2]$ the $\text{Mo}-\text{O}_{\text{peroxo}}$ bond distances are 1.931(2) and 1.976(2) Å.³⁵ Corresponding observations were made for $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$. Furthermore, in diperoxometallates the distances from the metal atom to the two oxygen atoms of a peroxo group are different (see, e.g., Ref. 37 and references therein). The $M = \text{O}$ bond lengths also agree well with other observations.^{22–38}

In both $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$ and $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$ the $M-\text{F}_{\text{apical}}$ bond is somewhat longer than the $M-\text{F}_{\text{equatorial}}$ bonds. The difference is, however, not so pronounced as in oxodiperoxometallates, in which the $M-\text{L}_{\text{apical}}$ bond lengths often are about 2.2 Å or more; in some cases the apical position *trans* to $M = \text{O}$ is even unoccupied.^{3,39,40} The $M-\text{F}_{\text{equatorial}}$ bond lengths are not very different, but $M-\text{F}(2)$ (*trans* to the peroxo group) might be somewhat longer than the other $M-\text{F}_{\text{equatorial}}$ bonds.

The deviations of the ligand atoms from their respective pentagonal equatorial plane, which they define, are all less than 0.028(4) Å in $(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$, and less than 0.010(9) Å in $(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$. The molybdenum atom is displaced 0.238(2) Å from the equatorial plane towards the double-bonded oxygen atom, which is close to displacements observed in other oxomonoperoxomolybdates.^{22–27} The corresponding displacement in the tungsten complex is 0.217(6) Å. This type of displacement is more pronounced in oxodiperoxomolybdates and oxodiperoxotungstates, values of about 0.35 Å being observed.^{28–38}

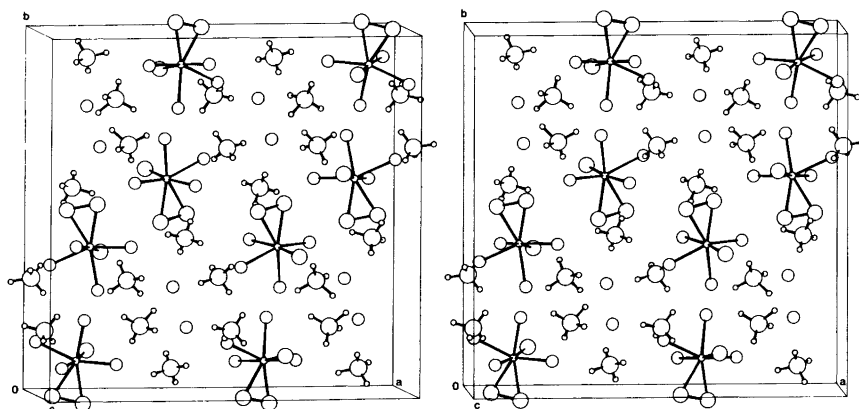
Table 3. Distances (Å) and angles(°) in (NH₄)₃F[MF₄O(O₂)] (M = Mo, W).

	(NH ₄) ₃ F[MoF ₄ O(O ₂)]		(NH ₄) ₃ F[WF ₄ O(O ₂)]
	250 K	290 K	290 K
Distance			
M—O1	1.670(5)	1.687(6)	1.716(15)
M—O2	1.903(5)	1.905(6)	1.905(12)
M—O3	1.917(5)	1.914(6)	1.937(12)
M—F1	2.070(4)	2.069(4)	2.036(9)
M—F2	1.990(4)	1.999(4)	1.986(9)
M—F3	1.943(5)	1.948(6)	1.936(12)
M—F4	1.981(3)	1.986(4)	1.959(12)
O2—O3	1.434(8)	1.417(11)	1.435(20)
F1...F2	2.588(5)	2.589(6)	2.573(13)
F1...F3	2.688(5)	2.686(7)	2.647(15)
F1...F4	2.647(5)	2.656(5)	2.636(13)
F1...O2	2.717(6)	2.735(8)	2.716(17)
F1...O3	2.705(6)	2.715(8)	2.738(15)
O1...F2	2.700(7)	2.713(8)	2.691(18)
O1...F3	2.725(8)	2.744(9)	2.711(21)
O1...F4	2.678(6)	2.692(8)	2.724(17)
O1...O2	2.757(7)	2.761(9)	2.779(19)
O1...O3	2.740(7)	2.746(9)	2.794(18)
F2...F3	2.386(7)	2.444(7)	2.502(15)
F2...F4	2.520(5)	2.531(6)	2.481(13)
F3...O2	2.425(7)	2.422(9)	2.419(18)
F4...O3	2.536(6)	2.513(7)	2.458(14)
Angle			
F1—M—F2	79.2(2)	79.1(2)	79.5(4)
F1—M—F3	84.1(2)	83.9(2)	83.5(5)
F1—M—F4	81.6(1)	81.8(2)	82.6(4)
F1—M—O1	173.0(2)	172.8(2)	172.5(5)
F1—M—O2	86.2(2)	86.9(3)	87.1(5)
F1—M—O3	85.4(2)	85.8(2)	87.1(5)
F2—M—F3	74.7(2)	76.5(2)	79.2(5)
F2—M—F4	78.8(2)	78.8(2)	78.0(4)
F2—M—O1	94.7(2)	94.4(2)	93.0(5)
F3—M—O1	97.6(2)	97.8(3)	95.7(6)
F3—M—O2	78.2(2)	77.9(3)	78.1(6)
F4—M—O1	94.0(2)	93.9(3)	95.4(6)
F4—M—O3	81.2(2)	80.2(2)	78.2(4)
O1—M—O2	100.8(2)	100.3(3)	100.1(6)
O1—M—O3	99.4(2)	99.2(3)	99.6(6)
O2—M—O3	44.1(2)	43.6(3)	43.9(6)
Hydrogen bonds			
N1...F2	2.814(7)	2.834(8)	2.831(15)
H2(N1)...F2	1.90(7)	1.79(9)	1.81(23)
N1—H2(N1)...F2	166(6)	159(7)	168(20)
N1...F3'	2.883(8)	2.908(9)	2.912(18)
H4(N1)...F3'	1.96(7)	2.33(10)	2.02(23)
N1—H4(N1)...F3'	167(6)	141(9)	170(20)

contd.

Table 3 (contd)

	$(\text{NH}_4)_3\text{F}[\text{MoF}_4\text{O}(\text{O}_2)]$		$(\text{NH}_4)_3\text{F}[\text{WF}_4\text{O}(\text{O}_2)]$
	250 K	290 K	290 K
N1...F5	2.748(6)	2.779(8)	2.854(14)
H1(N1)...F5	1.96(10)	1.88(10)	2.14(22)
N1-H1(N1)...F5	161(8)	174(8)	133(18)
N1...F5'	2.634(6)	2.645(8)	2.643(15)
H3(N1)...F5'	1.60(7)	1.73(9)	1.47(21)
N1-H3(N1)...F5'	178(6)	173(9)	162(18)
N2...F1'	2.734(6)	2.755(8)	2.781(18)
H4(N2)...F1'	1.83(7)	1.88(10)	2.34(30)
N2-H4(N2)...F1'	173(6)	176(9)	139(37)
N2...F3	2.862(7)	2.883(8)	2.858(17)
H1(N2)...F3	2.00(9)	1.90(10)	1.54(22)
N2-H1(N2)...F3	152(8)	168(8)	173(17)
N2...F4'	2.889(6)	2.896(7)	2.905(16)
H2(N2)...F4'	2.11(7)	2.35(10)	2.36(25)
N2-H2(N2)...F4'	146(7)	135(8)	127(22)
N2...F5'	2.675(6)	2.691(8)	2.716(19)
H3(N2)...F5'	1.93(5)	1.80(10)	1.39(23)
N2-H3(N2)...F5'	172(5)	169(9)	179(20)
N3...F1'	2.689(6)	2.721(7)	2.778(14)
H3(N3)...F1'	1.82(5)	1.68(9)	1.68(22)
N3-H3(N3)...F1'	166(5)	166(8)	174(19)
N3...F2	2.994(7)	2.995(8)	2.965(15)
H2(N3)...F2	2.18(8)	2.27(10)	2.11(22)
N3-H2(N3)...F2	161(7)	163(9)	154(19)
N3...F4'	2.880(6)	2.893(7)	2.883(13)
H1(N3)...F4'	2.24(6)	1.92(10)	2.06(22)
N3-H1(N3)...F4'	147(6)	165(8)	127(15)
N3...F5'	2.646(6)	2.667(8)	2.682(14)
H4(N3)...F5'	1.69(8)	1.86(10)	1.50(21)
N3-H4(N3)...F5'	171(7)	174(9)	159(18)

Fig. 1. Stereoscopic view of the unit cell of $(\text{NH}_4)_3\text{F}[\text{MF}_4\text{O}(\text{O}_2)]$ ($M = \text{Mo}, \text{W}$).

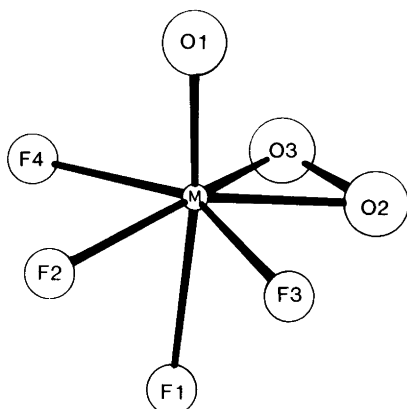


Fig. 2. The complex ion $[MF_4O(O_2)]^{2-}$ ($M = Mo, W$) showing the atomic numbering.

In the present structure analysis of $(NH_4)_3F[WF_4O(O_2)]$ and in the refinement of $(NH_4)_3F[MoF_4O(O_2)]$ the hydrogen atoms have been located, though not very accurately for the tungsten compound. From Table 3 it is evident that, besides ionic bonding, the structures are further stabilized by extensive hydrogen bonding; almost all hydrogen atoms are involved. The strongest hydrogen bond is between N1 and F5', with a hydrogen bond distance of about 2.64 Å.

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