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Studies on peroxomolybdates XVIII. Crystal structure of ammonium μ-fluoro-μ-oxo-bis[oxodiperoxomolybdate(VI)]-water(2/1), $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$, a dibridged peroxodimolybdate

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Abstract

The crystal structure of ammonium μ-fluoro-μ-oxo-bis[oxodiperoxomolybdate(VI)]-water(2/1), $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$, has been determined from single-crystal X-ray diffraction data. The yellow compound crystallizes as multiple-twins in the monoclinic space group $P2_1/c$ with $a = 13.803(3)$ Å, $b = 11.230(2)$ Å, $c = 15.975(3)$ Å, $\beta = 109.46(2)°$ and $Z = 8$. Full-matrix least-squares refinement of 316 structural parameters gave $R = 0.057$ for 3265 observed $[I > 3\sigma(I)]$, independent reflections. The $[FO\{MoO(O_2)_2\}_2]^{3-}$ anions, of which there are two crystallographically different ones in the asymmetric unit, have approximately C_{2v} symmetry and are composed of two edge-sharing pentagonal bipyramids, the molybdenum atoms thus being seven-coordinated. The molybdenum atoms are displaced 0.312–0.365 Å from the equatorial planes towards the respective double-bonded apical oxygen atom. Bond distances are as follows: $Mo\text{–}O_{peroxo}$ 1.884(10)–1.975(8) Å, $Mo = O_{apical}$ 1.670(8)–1.682(8) Å, $Mo\text{–}F_{bridge}$ 2.246(6)–2.313(6) Å, $Mo\text{–}O_{bridge}$ 1.925(7)–1.941(7) Å and $(O\text{–}O)_{peroxo}$ 1.436(15)–1.465(12) Å. $Mo\cdots Mo$ is 3.369(1)–3.379(1) Å, Mo–O–Mo 120.5(4)–122.6(4)° and Mo–F–Mo 94.0(2)–95.5(2)°. The powder photograph of the title compound was recorded at room temperature and was indexed.

Keywords: Fluoroperoxomolybdate; X-ray structure

1. Introduction

Addition of hydrogen peroxide to water solutions containing ammonium fluoride, hydrogen fluoride and ammonium heptamolybdate results in the formation of ammonium fluorooxoperoxomolybdates. The crystalline phase formed depends on the ratio between the concentrations of the components and on pH. Hitherto, seven different crystalline phases have been observed in the system $NH_4^+\text{–}MoO_4^{2-}\text{–}H_2O_2\text{–}HF\text{–}H_2O$. Of these, five have been subjected to structure analysis, namely $(NH_4)_3F[MoF_4O(O_2)]$ [1,2], $(NH_4)_2[MoF_2O(O_2)_2]$ [3], $(NH_4)_3[F\{MoFO(O_2)_2\}_2]$ [4], $(NH_4)_3F[MoF_2O(O_2)_2]$ [5] and $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$. The structure of the last-mentioned compound is described in this paper.

2. Experimental details

2.1. Preparation of $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$

Ammonium fluoride (1 g) and ammonium heptamolybdate (2 g) were dissolved in 6% hydrogen peroxide (30 ml) and the pH was adjusted to 6. The solution was left to evaporate at room temperature. After a few hours large six-pointed star-shaped, multiple-twinned, yellow crystals were formed. The peroxide content was determined by iodometric titration (found: O_2^{2-}, 28.1%; calculated for $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$, 28.44%).

2.2. X-ray methods

The positions of the diffraction peaks obtained from a powdered specimen were determined by the Guinier–Hägg film technique with Cu $K\alpha_1$ radiation (from a sealed X-ray tube) which was monochromatized with a bent quartz crystal. A small amount of silicon was added to the specimen as an internal standard. The photographic film was scanned by an optical line scanner using the evaluation programme SCANPI [6]. Observed lines in the powder photograph are given in Table 1; they were indexed after the structure determination. Cell parameters derived from

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Table 1
Observed lines in the powder photograph of $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$ at room temperature registered with a Guinier–Hägg camera, using Cu $K\alpha_1$ radiation (λ = 1.54060 Å) and silicon (NBS standard) as internal standard

hkl	$2\theta_{obs}$ (°)	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$\|F_{obs}\|$
1 0 −2	11.40	7.756	7.734	2.0	143
2 1 0	15.66	5.654	5.637	100	693
0 2 0			5.618		771
1 1 2	17.32	5.116	5.117	1.3	126
1 2 −2	19.52	4.545	4.545	1.6	147
3 1 −2	21.43	4.143	4.146	1.4	138
1 0 −4	22.25	3.992	3.992	15.9	596
3 1 −4	26.84	3.319	3.321	14.9	503
4 0 0	27.41	3.251	3.259	42.9	467
1 2 −4			3.254		528
2 3 0			3.247		488
1 1 4	27.88	3.197	3.198	10.2	452
4 2 0	31.73	2.818	2.819	1.2	193
3 3 −4	35.23	2.546	2.548	1.8	207
3 2 3	≈35.54	≈2.538	2.542		243
5 1 0			2.539		199
1 3 4	36.13	2.484	2.491	1.2	226
1 4 −3			2.484		226
5 2 −3	36.80	2.440	2.442	1.4	244
4 2 −5			2.438		148
5 2 −4	38.33	2.346	2.347	1.3	263
1 4 −4	39.17	2.298	2.297	1.8	327
4 4 0	42.45	2.128	2.128	3.2	228
2 5 0			2.124		217
2 4 −6	47.02	1.931	1.931	1.2	316
6 3 0	48.40	1.879	1.879	3.4	382
1 6 −4	54.06	1.695	1.695	1.2	273

A total of 42 lines were registered and indexed; of these, 23 lines with I_{obs} < 1.2 have been omitted from the table.

the powder photograph are given in Table 2 (within square brackets).

For the single crystal work one point of a star-shaped crystal was cleaved in three mutually perpendicular directions. This yielded a single crystal probably with, as was shown, a small (about 4%) residual

Table 2
Crystal and experimental data for $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$

M_r	449.99
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions (Å or °)	a = 13.803(3) [13.822(2)] b = 11.230(2) [11.235(2)] c = 15.975(3) [15.983(4)] β = 109.46(2) [109.43(2)] V = 2334.7(9) [2340.7(8)]
Z	8
D_c (g cm^{-3})	2.560
μ(Mo $K\alpha$) (mm^{-1})	2.19
Crystal size (mm)	0.10 × 0.16 × 0.27
No. of reflections for cell determination (θ range/°)	15 ($3.6 < \theta < 14.4$)
Scan mode	ω–2θ
2θ range (°)	$3.5 < 2\theta < 56.0$
2θ scan speed (° min^{-1})	3.9–19.5
Total No. of reflections measured	6181
No. of observed independent reflections [$I > 3\sigma(I)$]	3265
Test reflections (standard deviation/%)	002 (2.1); 060 (1.4); 800 (2.7)
No. of parameters refined	316
Weights calculated according to	$w = (30 + \|F_0\| + 0.002\|F_0\|^2)^{-1}$
R (R_w)	0.057 (0.066)
Maximum residual electron density (eÅ^{-3})	2.6

twin fragment. Crystal data and conditions for the data collection are given in Table 2. Intensity data were recorded with a Syntex $P2_1$ X-ray diffractometer (graphite-monochromatized Mo Kα radiation). 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 for 15 reflections. Data were collected at room temperature. Three test reflections, monitored each fiftieth reflection, showed no sign of crystal deterioration during the data collection.

3. Structure determination

The heavy atom positions were obtained by direct methods (MITHRIL [7]) and the remaining non-hydrogen atoms from electron density difference maps. The structure was refined by full-matrix least-squares calculations to $R = 0.070$ with isotropic thermal parameters and to 0.057 with anisotropic thermal parameters. The subsequent electron density difference map showed several rather large residual peaks (< 2.6 e Å^{-3}) located on each side of the molybdenum atoms in the c direction and at about 1.2 Å from the respective molybdenum atom. They seem to be somewhat larger than what is found as a consequence of normal series termination errors. Contributing causes for their largness might be the presence of residual twin fragments, affecting the observed reflection intensities, or partial disorder in the c direction. The hydrogen atom positions could not be determined unequivocally.

Calculations were carried out on an IBM 3081 computer with programs in use at this department [8–10]. Atomic scattering factors were taken from Ref. [11]. Further details concerning the refinement are summarized in Table 2. Lists of structure factors and anisotropic thermal parameters can be obtained from the author on request.

4. Results and discussion

Fractional atomic coordinates and equivalent isotropic thermal parameters are given in Table 3, and bond distances, bond angles and hydrogen bond distances in Table 4. Fig. 1 shows a stereoscopic view of the unit cell and Fig. 2 the complex ions.

The crystals of $(NH_4)_3[FO\{MoO(O_2)_2\}_2] \cdot \frac{1}{2}H_2O$ consist of ammonium ions, μ-fluoro-μ-oxo-bis[oxodiperoxomolybdate(VI)] ions and water of crystallization (the amount of water was estimated from the structure analysis). Besides ionic bonding the crystals are held together by extensive hydrogen bonding. There are two crystallographically different anions in the asymmetric unit. The molybdenum atoms Mo1, Mo2 $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, Mo3 and Mo4 $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ are coplanar within 5σ. The plane defined by these atoms is perpendicular to the bc-plane within the experimental errors.

The two anions are very similar, as is evident from Tables 3 and 4 and Fig. 2. Mo1 and Mo2 belong to one anion and Mo3 and Mo4 to the other, O1–O10 correspond to O11–O20, F1 to F2 and O21 to O22. Each dinuclear anion can be described as two edge-sharing pentagonal bipyramids. The molybdenum atoms are seven-coordinated and each molybdenum atom is coordinated to two peroxo groups and one bridging oxygen atom, forming the equatorial pentagonal plane, and to a double-bonded oxygen atom and to a bridging fluorine atom at the apices. The two pentagonal bipyramids have very similar dimensions (Table 4). The planes defined by the two molybdenum atoms and the bridging atoms in each complex are approximately mirror planes as are the planes perpen-

Table 3
Atomic fractional coordinates and equivalent isotropic thermal parameters B_{eq} for $(NH_4)_3[FO\{MoO(O_2)_2\}_2] \cdot \frac{1}{2}H_2O$: $T = 290$ K; $B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$; the occupation number is 0.5 for Ow

Atom	x	y	z	B_{eq}
Mo1	0.39509(6)	0.23696(8)	0.11561(5)	2.47(2)
Mo2	0.40086(6)	0.23939(7)	0.32876(5)	2.35(2)
Mo3	0.87902(7)	0.27182(8)	0.25554(6)	2.55(2)
Mo4	0.87732(7)	0.26675(8)	0.46591(5)	2.47(2)
O1	0.4534(7)	0.3981(7)	0.1416(6)	4.5(3)
O2	0.3708(8)	0.3884(9)	0.0560(6)	5.2(3)
O3	0.2661(7)	0.189(1)	0.0306(6)	5.3(3)
O4	0.3000(6)	0.1039(7)	0.1025(6)	4.1(3)
O5	0.4810(6)	0.1746(7)	0.0762(5)	3.8(2)
O6	0.3015(6)	0.1070(7)	0.2915(5)	3.7(2)
O7	0.2725(7)	0.1978(8)	0.3436(6)	4.4(3)
O8	0.3841(8)	0.3953(8)	0.3719(6)	5.0(3)
O9	0.4654(7)	0.3962(7)	0.3324(6)	4.4(3)
O10	0.4879(6)	0.1746(7)	0.4167(5)	3.6(2)
O11	1.0258(7)	0.239(1)	0.3119(7)	5.7(3)
O12	0.9741(8)	0.1624(9)	0.2384(7)	5.2(3)
O13	0.7698(8)	0.1806(9)	0.1761(6)	5.3(3)
O14	0.7291(7)	0.2618(9)	0.2254(6)	5.1(3)
O15	0.8872(6)	0.3892(7)	0.1928(5)	4.0(3)
O16	0.7279(6)	0.2551(7)	0.4122(5)	3.6(2)
O17	0.7703(7)	0.1728(9)	0.4866(6)	4.8(3)
O18	0.9734(7)	0.1596(8)	0.5455(5)	4.4(3)
O19	1.0259(5)	0.2340(7)	0.4990(5)	3.4(2)
O20	0.8842(7)	0.3848(8)	0.5319(5)	4.4(3)
O21	0.4588(5)	0.1955(6)	0.2388(4)	2.8(2)
O22	0.8827(6)	0.3549(7)	0.3631(5)	3.3(2)
F1	0.2952(4)	0.3125(5)	0.1943(4)	3.0(2)
F2	0.8701(5)	0.1335(5)	0.3592(4)	3.5(2)
N1	0.1156(7)	0.1020(8)	0.1452(6)	3.2(2)
N2	0.1256(8)	0.4105(8)	0.2151(7)	3.8(3)
N3	0.1454(9)	0.076(1)	0.4425(7)	4.8(4)
N4	0.6423(6)	0.0719(8)	0.2875(6)	3.1(3)
N5	0.6368(7)	0.0763(8)	−0.0013(6)	3.4(3)
N6	0.6271(7)	0.4210(8)	0.0856(6)	3.5(3)
Ow	0.165(2)	0.066(2)	0.885(1)	9.0(3)

Table 4
Distances (Å) and angles (°) in $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$; corresponding distances in the four crystallografically different pentagonal bipyramids are given on the same line

Intraionic bond distances							
Mo1–O1	1.967(8)	Mo2–O6	1.975(8)	Mo3–O11	1.959(10)	Mo4–O16	1.956(8)
Mo1–O2	1.923(10)	Mo2–O7	1.922(9)	Mo3–O12	1.884(10)	Mo4–O17	1.932(9)
Mo1–O3	1.920(9)	Mo2–O8	1.924(9)	Mo3–O13	1.912(10)	Mo4–O18	1.924(9)
Mo1–O4	1.953(8)	Mo2–O9	1.966(8)	Mo3–O14	1.965(9)	Mo4–O19	1.974(7)
Mo1–O5	1.670(8)	Mo2–O10	1.680(7)	Mo3–O15	1.682(8)	Mo4–O20	1.677(9)
Mo1–O21	1.925(7)	Mo2–O21	1.927(7)	Mo3–O22	1.941(7)	Mo4–O22	1.941(7)
Mo1–F1	2.313(6)	Mo2–F1	2.308(6)	Mo3–F2	2.304(6)	Mo4–F2	2.246(6)
O1–O2	1.463(13)	O6–O7	1.455(12)	O11–O12	1.436(15)	O16–O17	1.465(12)
O3–O4	1.449(13)	O8–O9	1.459(14)	O13–O14	1.436(14)	O18–O19	1.460(11)
Other intraionic distances							
Mo1···Mo2	3.379(1)			Mo3···Mo4	3.369(1)		
Intraionic angles							
Mo1–O21–Mo2	122.6(4)	Mo1–F1–Mo2	94.0(2)	Mo3–O22–Mo4	120.5(4)	Mo3–F2–Mo4	95.5(2)
O1–Mo1–O2	44.2(4)	O6–Mo2–O7	43.8(4)	O11–Mo3–O12	43.8(4)	O16–Mo4–O17	44.3(4)
O1–Mo1–O21	89.5(3)	O6–Mo2–O21	90.1(3)	O11–Mo3–O22	88.1(4)	O16–Mo4–O22	89.7(3)
O2–Mo1–O3	85.9(4)	O7–Mo2–O8	87.2(4)	O12–Mo3–O13	89.3(4)	O17–Mo4–O18	86.8(4)
O3–Mo1–O4	43.9(4)	O8–Mo2–O9	44.1(4)	O13–Mo3–O14	43.5(4)	O18–Mo4–O19	44.0(3)
O4–Mo1–O21	89.2(3)	O9–Mo2–O21	87.4(3)	O14–Mo3–O22	87.7(4)	O19–Mo4–O22	89.6(3)
O5–Mo1–O1	100.0(4)	O10–Mo2–O6	99.0(4)	O15–Mo3–O11	9.1(4)	O20–Mo4–O16	99.2(4)
O5–Mo1–O2	102.3(4)	O10–Mo2–O7	102.9(4)	O15–Mo3–O12	103.7(4)	O20–Mo4–O17	102.2(4)
O5–Mo1–O3	102.9(4)	O10–Mo2–O8	103.4(4)	O15–Mo3–O13	102.7(4)	O20–Mo4–O18	101.4(4)
O5–Mo1–O4	100.1(4)	O10–Mo2–O9	99.9(4)	O15–Mo3–O14	100.0(4)	O20–Mo4–O19	98.2(4)
O5–Mo1–O21	98.3(3)	O10–Mo2–O21	98.9(3)	O15–Mo3–O22	99.4(4)	O20–Mo4–O22	96.8(4)
F1–Mo1–O1	79.9(3)	F1–Mo2–O6	80.1(3)	F2–Mo3–O11	80.6(4)	F2–Mo4–O16	81.3(3)
F1–Mo1–O2	84.7(3)	F1–Mo2–O7	83.1(3)	F2–Mo3–O12	82.6(3)	F2–Mo4–O17	85.6(3)
F1–Mo1–O3	84.6(3)	F1–Mo2–O8	84.0(3)	F2–Mo3–O13	84.1(3)	F2–Mo4–O18	86.1(3)
F1–Mo1–O4	80.7(3)	F2–Mo2–O9	81.3(3)	F2–Mo3–O14	80.4(3)	F2–Mo4–O19	81.8(3)
F1–Mo1–O21	71.7(3)	F1–Mo2–O21	71.8(3)	F2–Mo3–O22	71.3(3)	F2–Mo4–O22	72.6(3)
Interionic distances (<3 Å)							
N1···O4	2.846(12)	N2····F2^{iv}	2.780(11)	N4···O14	2.785(13)	N6···O1	2.837(13)
N1···O6	2.838(12)	N2···Ow^{v}	2.605(22)	N4···O16	2.835(12)	N6···O6^{iv}	2.811(12)
N1···O12^{i}	2.903(13)	N3···O11^{i}	2.851(15)	N4···O21	2.764(11)	N6···O10^{v}	2.944(12)
N1···O19^{ii}	2.908(12)	N3···O15^{vi}	2.937(14)	N5···O4^{vii}	2.901(12)	N6···O14	2.842(13)
N1···O22^{iii}	2.778(12)	N3···O19^{i}	2.771(13)	N5···O8^{vi}	2.981(13)	Ow···O3^{viii}	2.666(24)
N2···O18^{ii}	2.929(13)	N4···O1^{vi}	2.799(12)	N5···O9^{v}	2.925(13)	Ow···O11^{ix}	2.895(28)
N2····F1	2.706(11)	N4···O9^{vi}	2.806(12)	N5···O16	2.869(12)	Ow···O20^{x}	2.630(26)
Distances between ammonium ions (<4 Å)							
N1····N2	3.629(13)	N2····N4^{iv}	3.692(13)	N3····N6^{vi}	3.745(15)		

Symmetry codes:

i	$-1+x, y, z$	iv	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	vii	$1-x, -y, -z$	ix	$-1+x, \frac{1}{2}-y, \frac{1}{2}+z$
ii	$-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$	v	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	viii	$x, y, 1+z$	x	$1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$
iii	$-1+x, -\frac{1}{2}+y, \frac{1}{2}-z$	vi	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$				

dicular to *c*, bisecting the bridging atoms; these two plane types are approximately mutually perpendicular in the two complexes. The symmetry of the anions is, therefore, near C_{2v}. As is evident from Table 5, the equatorial atoms in each bipyramid are almost coplanar. The molybdenum atoms are displaced 0.312(4)–0.365(5) Å from the respective equatorial plane towards the double-bonded oxygen atom. In the three other fluorooxodiperoxomolybdates studied, the observed displacements range between 0.285(2) and 0.324(1) Å [3–5]; similar displacements have been observed in a series of other diperoxomolybdates (see Table 4 in Ref. [3], which lists important distances in about 30 oxoperoxomolybdates). As a consequence of these displacements the apical atoms are about equally remote from the respective equatorial plane; the distances from the respective equatorial plane to the double-bonded oxygen atoms are 1.987(10)–2.047(10) Å and to the fluorine atoms 1.913(8)–1.941(7) Å.

As in other pentagonal-bipyramidal oxoperoxometallates the $M{-}L_{apical}$ bond *trans* to the $M=O_{apical}$ bond is longer than the $M{-}L_{equatorial}$ bonds. In the

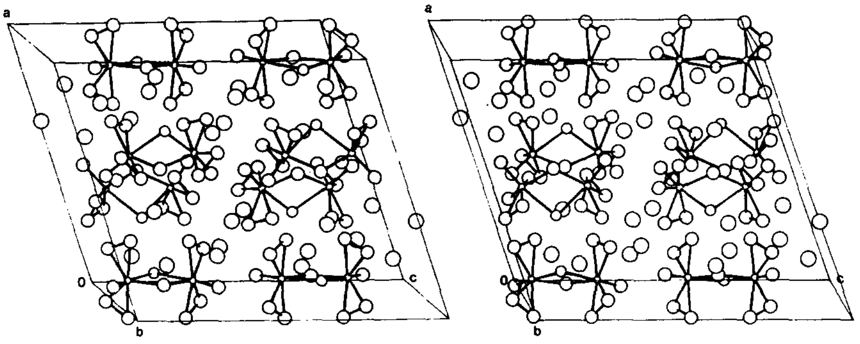

Fig. 1. Stereoscopic view of the unit cell of $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$.

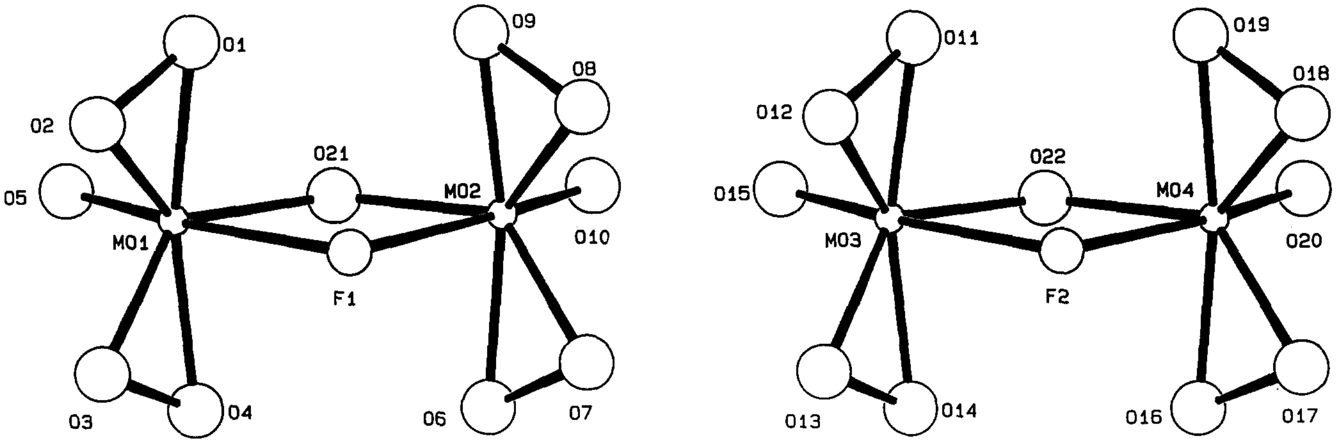

Fig. 2. The atomic numbering in the two anions $[FO\{MoO(O_2)_2\}_2]^{3-}$.

Table 5
Distances from certain atoms to least-squares planes in $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$

Defining atoms:

Plane I	O1–O4, O21	Plane IV	O11–O14, O22
Plane II	O6–O9, O21	Plane V	O16–O19, O22
Plane III	Mo1, Mo2, O21, F1	Plane VI	Mo3, Mo4, O22, F2

Atom	Plane I	Plane II	Plane III	Atom	Plane IV	Plane V	Plane VI
Mo1	−0.351(4)		0.000(0)	Mo3	0.365(5)		0.000(0)
Mo2		0.358(4)	0.000(0)	Mo4		0.312(4)	0.000(0)
O1	−0.009(7)		1.934(10)	O11	0.054(8)		1.932(11)
O2	0.002(7)		1.294(11)	O12	−0.037(7)		1.314(12)
O3	0.019(8)		−1.325(12)	O13	−0.008(8)		−1.353(12)
O4	−0.015(6)		−1.926(9)	O14	0.025(7)		−1.938(10)
O5	−2.021(10)		0.013(10)	O15	2.047(10)		0.012(10)
O6		0.031(5)	−1.942(8)	O16		0.019(6)	−1.932(9)
O7		−0.027(7)	−1.293(10)	O17		−0.016(7)	−1.314(11)
O8		−0.022(8)	1.358(12)	O18		−0.011(7)	1.334(10)
O9		0.036(7)	1.943(10)	O19		0.015(5)	1.953(8)
O10		2.036(9)	−0.040(10)	O20		1.987(10)	0.006(11)
O21	0.006(3)	−0.018(3)	0.010(7)	O22	−0.017(3)	−0.013(3)	0.005(7)
F1	1.941(7)	−1.933(7)	0.004(3)	F2	−1.920(8)	−1.913(8)	−0.002(3)

Angle between I and II	79.4(3)°	Angle between IV and V	80.5(3)°
I and III	90.3(2)°	IV and VI	89.6(3)°
II and III	90.8(2)°	V and VI	90.3(2)°

$[FO\{MoO(O_2)_2\}_2]^{3-}$ ions the Mo–F_{apical} bond distances are 2.246(6)–2.313(6) Å and are thus somewhat longer than the Mo–F_{apical} bond distances observed in $(NH_4)_2[MoF_2O(O_2)_2]$ [3], $(NH_4)_3[F\{MoFO(O_2)_2\}_2]$ [4] and $(NH_4)_3F[MoF_2O(O_2)_2]$ [5] (2.199(1), 2.196(1) Å and 2.150(2) Å, respectively).

The Mo=O and Mo–O bond distances are normal. As in the above-mentioned ammoniumfluorooxodiperoxomolybdates [3–5] there is a slight but significant asymmetry in the coordination of the peroxo groups. Mo1–O1 and Mo1–O4 (and the corresponding distances Mo2–O6, Mo2–O9, Mo3–O11, Mo3–O14, Mo4–O16 and Mo4–O19) are somewhat longer than the other Mo–O_{peroxo} bond distances. This type of asymmetry has been observed for several other diperoxometallates, too, and has been discussed by, for example, Stomberg et al. [12].

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