

## Studies on Peroxomolybdates

### VII. The Crystal Structure of (Tri)ammonium Fluoride Oxoperoxotetrafluoromolybdate(VI), $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$

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The crystal structure of  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$  has been determined from visually estimated X-Ray reflexion intensities, using Patterson and Fourier methods, and refined by the least-squares technique to a final  $R$ -value of 0.129 based on 1079 observed reflexions.

The yellow crystals are orthorhombic, belonging to space group  $Pbca$ , with  $a = 16.521$  (4) Å,  $b = 15.956$  (4) Å,  $c = 6.793$  (2) Å,  $V = 1790.8$  Å<sup>3</sup> and  $Z = 8$ . Each molybdenum atom is surrounded by three oxygen atoms and four fluorine atoms in a pentagonal bipyramidal arrangement, the equatorial plane containing the two peroxidic oxygen atoms and three of the fluorine atoms. The apical positions are occupied by a double-bonded oxygen atom and the remaining fluorine atom. Molybdenum is displaced 0.23 Å out of the equatorial plane towards the oxygen atom.

Average bond distances are: Mo—O<sub>peroxo</sub> 1.91 Å, Mo=O 1.67 Å, Mo—F<sub>equatorial</sub> 1.97 Å, Mo—F<sub>apical</sub> 2.03 Å and (O—O)<sub>peroxo</sub> 1.36 Å.

Peroxo-fluoro complexes of transition metals have been known for quite a long time. Piccini,<sup>1,2</sup> *e.g.*, prepared complexes of both molybdenum and tungsten by dissolving oxo-fluoromolybdates or -tungstates in warm hydrogen peroxide, or by treating solutions of molybdates or tungstates in dilute hydrofluoric acid with hydrogen peroxide. The products isolated were formulated as  $2\text{MF} \cdot \text{MoO}_3\text{F}_2 \cdot \text{H}_2\text{O}$ ,  $2\text{MF} \cdot \text{WO}_3\text{F}_2 \cdot \text{H}_2\text{O}$  ( $M = \text{alkali metal}$ ) and  $3\text{NH}_4\text{F} \cdot \text{MoO}_3\text{F}_2$ . For niobium, compounds with formulae such as  $2\text{KF} \cdot \text{NbO}_2\text{F}_3 \cdot \text{H}_2\text{O}$  and  $3\text{NaF} \cdot \text{NbO}_2\text{F}_3 \cdot \text{H}_2\text{O}$  were obtained by Piccini<sup>2</sup> and Balke *et al.*,<sup>3</sup> respectively.

Since the alkali metal peroxo-fluoromolybdates differ in stoichiometry from the ammonium compound, it seemed possible that there might be a difference in the configuration of ligands about molybdenum in these two types of compounds. This is true of the peroxomolybdates which can exhibit 6-, 7-, or 8-coordinated molybdenum, *e.g.* in  $\text{K}_4[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]$ ,<sup>4</sup>  $\text{K}_2[\text{O}(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2] \cdot (\text{H}_2\text{O})_2$ ,<sup>5</sup> and  $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ ,<sup>6</sup> respectively. In order to ascertain whether or not this was the case, it was decided to investigate the crystal structure

of  $3\text{NH}_4\text{F}\cdot\text{MoO}_3\text{F}_2$  and to compare the results with those obtained by Weiss for  $\text{K}_2[\text{MoO}(\text{O}_2)\text{F}_4](\text{H}_2\text{O})$ .<sup>7</sup> The results of the investigation of the structure of ammonium peroxo-fluoromolybdate are presented in this paper. In the course of an extensive investigation of the formation and structure of transition metal peroxo complexes the crystal structures of some sodium peroxo-fluoroniobates have also been determined and a report on these investigations will be published.

## EXPERIMENTAL

*Preparation of crystals.* Crystals of ammonium peroxo-fluoromolybdate were prepared by the method proposed by Piccini.<sup>1</sup> 7 g ammonium fluoride and 35 ml 5 % hydrogen peroxide were added to a solution obtained by dissolving 10 g ammonium heptamolybdate in 5 ml concentrated hydrofluoric acid. The crystals obtained were yellow and needle-shaped, the needle-axis being parallel to the crystallographic *c*-axis.

*Analysis.* Molybdenum was determined gravimetrically as molybdenum trioxide, according to Piccini.<sup>1</sup> The peroxide content was established by titration with a standardized permanganate solution. The Kjeldahl method<sup>8</sup> was used to determine the nitrogen content. (Found: Mo 33.2; O<sub>peroxide</sub> 10.7; N 14.8. Calc. for  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$ : Mo 32.7; O<sub>peroxide</sub> 10.9; N 14.3).

*X-Ray methods.* Approximate cell dimensions were obtained from rotation and Weissenberg photographs and more accurate ones from X-ray powder photographs (Guinier camera) with  $\text{CuK}\alpha$  radiation, using lead nitrate ( $a=7.8566$  Å at 21°C)<sup>9</sup> as an internal standard.

For the single crystal work multiple-film (5 films) equi-inclination Weissenberg photographs were taken for crystals of approximate dimensions  $0.06 \times 0.06 \times 0.2$  mm<sup>3</sup> with rotation about [001] (layer lines 0–6) and [010] (layer line 0) using  $\text{CuK}\alpha$  radiation. Owing to decomposition, five crystals were used.

The relative intensities of the reflexions were estimated visually by comparison with a standard scale (obtained by the rotating sector method) and were corrected for Lorentz' and polarization effects. Errors due to absorption and extinction were not taken into consideration. The  $|F_o|$ -values were brought on to an absolute scale by comparison with the finally calculated structure factors. A total of 1079 independent reflexions was obtained.

*Computing methods.* All computational work, including least-squares refinement of the cell dimensions, Lorentz' and polarization corrections, Fourier summations, structure factor least-squares refinement, calculation of interatomic distances and angles, and calculation of planes to fit sets of atoms, was performed on the electronic computer IBM 360/65 using the set of crystallographic programmes, *viz.* POWDER, DATAP2, DRF, LALS, DISTAN, and PLANEFIT, in use at this department.<sup>10</sup>

The atomic scattering factors for molybdenum, oxygen, and fluorine used in the calculation of the structure factors were taken from Volume III of the *International Tables for X-Ray Crystallography*, 1962. The scattering factors for ammonium were those calculated by Davis and Whitaker.<sup>11</sup>

## UNIT CELL AND SPACE GROUP

The unit cell parameters were obtained from the measured  $\sin^2\theta$ -values by a least-squares procedure using 66 observed lines in the Guinier powder photograph.  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$  was found to be orthorhombic with  $a=16.521$  (4) Å,  $b=15.956$  (4),  $c=6.793$  (2) Å, and  $V=1790.8$  Å<sup>3</sup> (The errors given in parentheses are  $10^3\sigma$ ).

Calculated and observed  $\sin^2\theta$ -values are given in Table 1.

Table 1. Observed lines in the powder photograph of  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$ .  
 $\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$ .

$hkl$	$10^5 \times \sin^2\theta_{\text{obs}}$	$10^5 \times \sin^2\theta_{\text{calc}}$	$I_{\text{obs}}$	$d_{\text{obs}}$
0 2 0	924	932	vst	8.013
2 1 0	1094	1103	vvst	7.364
1 1 1	1728	1736	w	5.860
0 2 1	2212	2218	vvst	5.179
2 1 1	2381	2388	vvst	4.992
1 2 1	2423	2435	w	4.948
2 3 0	2957	2967	vvst	4.479
4 0 0	3467	3478	vst	4.137
0 4 0	3709	3729	st	4.000
3 2 1	4161	4174	w	3.776
4 2 0	4397	4410	st	3.673
0 4 1	5001	5014	vst	3.444
0 0 2	5135	5142	st	3.399
3 3 1}	5347	5339}	m	3.331
1 0 2}		5360}		
4 3 0}	5575	5575}	m	3.262
1 1 2}		5592}		
4 2 1	5687	5696	vst	3.230
0 2 2	6043	6075	w	3.133
2 1 2	6226	6245	st	3.087
2 2 2}	6946	6944}	vw	2.923
3 4 1}		6971}		
3 0 2	7084	7099	m	2.894
1 5 1	7314	7329	w	2.848
1 3 2	7448	7457	w	2.822
5 2 1	7626	7652	m	2.789
2 5 1	7959	7981	m	2.730
3 2 2	8023	8031	st	2.719
0 6 0	8377	8390	m	2.661
4 4 1	8485	8492	w	2.644
4 0 2	8600	8620	m	2.627
6 2 0	8737	8757	vw	2.606
5 3 1	8805	8817	vw	2.596
3 5 1	9062	9068	m	2.559
3 3 2	9188	9196	vw	2.541
6 1 1	9333	9344	m	2.521
4 2 2	9538	9552	st	2.494
0 6 1	9660	9675	vw	2.478
6 3 0	9905	9923	w	2.447
5 4 1	10439	10448	vw	2.384
3 4 2	10805	10827	vw	2.343
1 5 2	11185	11186	vw	2.303
4 6 0	11852	11867	st	2.237
1 1 3	12007	12020	m	2.223
7 1 1	12162	12169	vw	2.209
2 7 0	12272	12289	m	2.199
0 2 3	12495	12502	vw	2.179
2 1 3	12665	12673	w	2.164
1 7 1}	12908	12922}	w	2.144
3 5 2}		12925}		
4 6 1	13123	13153	m	2.126
6 1 2	13190	13201	m	2.121
2 2 3	13377	13372	vw	2.106
2 7 1	13552	13574	st	2.092
8 0 0	13906	13911	m	2.066

Table 1. Continued.

8 1 0	14158	14144	vvw	2.047
3 2 3	14429	14459	m	2.028
0 8 0	14908	14915	m	1.9949
6 3 2	15051	15065	m	1.9854
4 1 3}	15266	15281}	w	1.9715
0 4 3}		15299}		
1 4 3	15492	15516	m	1.9570
4 2 3	15957	15980	m	1.9282
8 2 1	16113	16129	m	1.9189
0 8 1	16178	16201	m	1.9150
5 5 2}	16395	16403}	vvw	1.9017
1 8 1}		16418}		
7 2 2}	16739	16725}	vvw	1.8823
1 7 2}		16779}		
4 6 2	16997	17010	m	1.8683
5 1 3}	17228	17238}	m	1.8556
3 4 3}		17255}		
2 7 2	17441	17431	vvw	1.8444
8 4 0	17613	17640	w	1.8353
7 5 1	17751	17763	w	1.8282
7 3 2	17866	17891	w	1.8223
4 4 3	18767	18777	vvw	1.7780
8 4 1	18909	18926	st	1.7713
8 0 2	19046	19054	m	1.7650
6 1 3	19630	19628	st	1.7385
4 8 1	19684	19678	st	1.7361
8 2 2	19964	19986	vvw	1.7239

The systematically absent reflexions are  $0kl$  with  $k=2n+1$ ,  $h0l$  with  $l=2n+1$  and  $hk0$  with  $h=2n+1$ . These conditions are characteristic of space group  $Pbca$ .

The density of the crystals, determined by weighing a sample in air and in benzene, is  $2.09 \text{ g/cm}^3$ . The density calculated with  $Z=8$  is  $2.17 \text{ g/cm}^3$ .

### STRUCTURE DETERMINATION

*Atomic positions.* The Patterson function  $P(uvw)$  showed the following large maxima in the asymmetric unit:

$u$	$v$	$w$	Peak heights (arbitrary units)	
0	0	0	999	
0.246	$\frac{1}{2}$	0	500	(elongated in the $w$ -direction)
0	0.334	$\frac{1}{2}$	450	
$\frac{1}{2}$	0	0.10	330	
0.245	0.170	$\frac{1}{2}$	230	
0	0	0.32	201	
0.26	$\frac{1}{2}$	0.10	170	(within the range of the peak with height 500)
$\frac{1}{2}$	0.34	0.39	160	
0.26	0.16	0.40	110	(within the range of the peak with height 230)

The expected vectors between molybdenum atoms occupying position 8c of space group *Pbca* are:

<i>u</i>	<i>v</i>	<i>w</i>	Relative peak height
0	0	0	8
$\pm[\frac{1}{2}-2x]$	$\frac{1}{2}$	0 ]	4
$\pm[0]$	$\frac{1}{2}-2y$	$\frac{1}{2}$ ]	4
$\pm[\frac{1}{2}]$	0	$\frac{1}{2}-2z$ ]	4
$\pm[\frac{1}{2}-2x]$	$\pm 2y$	$\frac{1}{2}$ ]	2
$\pm[\pm 2x]$	$\frac{1}{2}$	$\frac{1}{2}-2z$ ]	2
$\pm[\frac{1}{2}]$	$\frac{1}{2}-2y$	$\pm 2z$ ]	2
$\pm[2x]$	$\pm 2y$	$\pm 2z$ ]	1

Comparison between expected and observed peaks indicates that molybdenum occupies the general eight-fold position 8c with  $x=0.13$ ,  $y=0.08$  and  $z=0.20$ . A Fourier summation of the observed structure factors in which the

Table 2a. Atomic coordinates (expressed in fractions of the cell edges) for  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$ . All atoms occupy the general 8-fold position 8c of space group *Pbca*. The numbers in parentheses are the standard deviations of the last significant figures.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.1290 (1)	0.0833 (1)	0.2041 (3)
O <sub>1</sub>	0.1749 (12)	0.3948 (11)	0.4912 (25)
O <sub>2</sub>	0.3594 (15)	0.4646 (16)	0.2260 (39)
O <sub>3</sub>	0.4282 (14)	0.4846 (12)	0.1264 (31)
F <sub>1</sub>	0.0727 (8)	0.0740 (7)	0.4695 (18)
F <sub>2</sub>	0.1411 (7)	0.2003 (9)	0.3050 (20)
F <sub>3</sub>	0.2256 (9)	0.0702 (9)	0.3555 (26)
F <sub>4</sub>	0.0229 (7)	0.1342 (9)	0.1195 (18)
F <sub>5</sub>	0.3670 (7)	0.2941 (11)	0.4770 (19)
N <sub>1</sub>	0.2642 (11)	0.3043 (13)	0.1597 (30)
N <sub>2</sub>	0.3863 (11)	0.0630 (14)	0.1936 (33)
N <sub>3</sub>	0.0049 (11)	0.3123 (11)	0.2296 (26)

Table 2b. Anisotropic temperature parameters  $U_{ij}$  (with the standard deviations of the last significant figures in parentheses). The expression used is  $\exp[-(2\pi^2)(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+klb^*c^*U_{12}+lhc^*a^*U_{13}+hka^*b^*U_{23})]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mo	0.042 (0)	0.053 (0)	0.052 (0)	-0.003 (0)	0.010 (0)	0.001 (0)
O <sub>1</sub>	0.098 (1)	0.059 (1)	0.076 (5)	-0.013 (1)	0.060 (4)	-0.023 (3)
O <sub>2</sub>	0.142 (1)	0.079 (1)	0.125 (8)	-0.030 (2)	0.003 (6)	-0.007 (5)
O <sub>3</sub>	0.132 (1)	0.072 (1)	0.075 (4)	0.023 (2)	0.016 (4)	-0.040 (4)
F <sub>1</sub>	0.070 (0)	0.065 (1)	0.037 (3)	0.022 (1)	-0.007 (2)	0.005 (2)
F <sub>2</sub>	0.065 (0)	0.059 (1)	0.076 (4)	-0.014 (1)	-0.019 (2)	-0.030 (3)
F <sub>3</sub>	0.067 (1)	0.085 (1)	0.094 (5)	0.035 (1)	-0.026 (3)	-0.043 (3)
F <sub>4</sub>	0.049 (0)	0.086 (1)	0.060 (3)	0.013 (1)	-0.007 (2)	0.003 (3)
F <sub>5</sub>	0.059 (0)	0.107 (1)	0.055 (3)	-0.030 (1)	0.002 (2)	0.044 (3)
N <sub>1</sub>	0.054 (1)	0.069 (1)	0.089 (7)	0.007 (1)	0.017 (3)	-0.038 (3)
N <sub>2</sub>	0.051 (1)	0.078 (1)	0.079 (7)	0.026 (1)	-0.016 (4)	-0.024 (4)
N <sub>3</sub>	0.058 (1)	0.067 (1)	0.071 (5)	-0.002 (1)	0.012 (3)	0.023 (4)



Table 3. Continued.

H 2	15	-10	14 15	15	H 4 3	4 38	-35	14 20	-32	7 24	28
1 119	1'6		15 10	-2'	7 06	-00	7 14	20	-1	8 22	-18
3 1	-17		16 30	33	7 42	-17	7 25	-24	15 15	-11	9 24
5 62	-40		17 30	34	7 27	78	8 25	25	14 7	8	1 0 6
6 47	10	1	18 14	-12	7 70	-74	9 29	29	17 16	19	11 14
4 71	-52	2	19 24	13'	4 0r	85	11 0	-3	18 10	-6	12 13
5 62	-40	3			5 56	4'	11 11	11			17 17
6 47	10	4			6 33	-38	12 16	-17			14 13
7 55	-4'	5			7 5	44	13 16	-21			15 13
8 71	18	6			8 81	-7			1 81	111	16 9
9 27	18	7			9 35	-28			2 79	-84	15 9
10 6	45	8			10 25	23			3 91	-113	
11 22	11	9			11 25	-22			4 4	-3	H 9 4
12 36	-20	10			12 59	43			5 94	-00	1 73
13 22	-03	11			13 48	16			6 81	67	2 95
14 19	7	12			14 18	-14			7 91	60	3 99
15 20	-2	13			15 17	14			8 0	-4	4 0
16 20	10	14			16 29	-21			9 37	36	5 53
17 0	-4	15			17 28	-21			10 73	-21	6 26
18 0	-4	16			18 22	-21			11 73	-21	7 53
					19 0				12 0	0	8 21
					20 0				13 22	-17	9 25
					21 0				14 32	31	10 24
					22 0				15 63	52	11 32
					23 0				16 0	-13	12 0
					24 0				17 13	18	13 20
					25 0				18 10	-13	14 11
					26 0				19 0	-4	15 33
					27 0				20 0	-4	
					28 0				21 18	22	
					29 0				22 22	-25	
					30 0				23 27	27	
					31 0				24 17	18	
					32 0				25 18	10	
					33 0				26 22	10	
					34 0				27 22	10	
					35 0				28 22	10	
					36 0				29 22	10	
					37 0				30 22	10	
					38 0				31 22	10	
					39 0				32 22	10	
					40 0				33 22	10	
					41 0				34 22	10	
					42 0				35 22	10	
					43 0				36 22	10	
					44 0				37 22	10	
					45 0				38 22	10	
					46 0				39 22	10	
					47 0				40 22	10	
					48 0				41 22	10	
					49 0				42 22	10	
					50 0				43 22	10	
					51 0				44 22	10	
					52 0				45 22	10	
					53 0				46 22	10	
					54 0				47 22	10	
					55 0				48 22	10	
					56 0				49 22	10	
					57 0				50 22	10	
					58 0				51 22	10	
					59 0				52 22	10	
					60 0				53 22	10	
					61 0				54 22	10	
					62 0				55 22	10	
					63 0				56 22	10	
					64 0				57 22	10	
					65 0				58 22	10	
					66 0				59 22	10	
					67 0				60 22	10	
					68 0				61 22	10	
					69 0				62 22	10	
					70 0				63 22	10	
					71 0				64 22	10	
					72 0				65 22	10	
					73 0				66 22	10	
					74 0				67 22	10	
					75 0				68 22	10	
					76 0				69 22	10	
					77 0				70 22	10	
					78 0				71 22	10	
					79 0				72 22	10	
					80 0				73 22	10	
					81 0				74 22	10	
					82 0				75 22	10	
					83 0				76 22	10	
					84 0				77 22	10	
					85 0				78 22	10	
					86 0				79 22	10	
					87 0				80 22	10	
					88 0				81 22	10	
					89 0				82 22	10	
					90 0				83 22	10	
					91 0				84 22	10	
					92 0				85 22	10	
					93 0				86 22	10	
					94 0				87 22	10	
					95 0				88 22	10	
					96 0				89 22	10	
					97 0				90 22	10	
					98 0				91 22	10	
					99 0				92 22	10	
					100 0				93 22	10	

Table 3. Continued

1	17	-14	5	70	72	H	8	5	3	0	-3	5	23	21	H	5	6	4	0	4	
2	5	5	6	0	-8	0	0	4	4	0	-4	0	0	3	1	21	-24	5	22	-14	
3	14	-11	7	51	41	1	61	50	5	0	-4	7	30	-28	2	0	-7	6	0	-3	
4	0	7	8	0	-2	2	0	5	6	0	6	8	0	2	3	21	22	7	52	44	
5	18	15	9	64	-59	3	44	42	7	0	-6	9	30	-21	4	0	-3	8	0	-2	
			10	0	4	4	0	-2	8	0	-1	10	0	3	5	0	9	9	32	24	
	H	1	5	11	40	-34	5	61	9	0	3	11	27	23	6	0	1	10	0	3	
1	22	37	12	0	3	6	0	4	6	0	4	12	0	-1	7	26	-28	11	37	-30	
2	0	-18	13	39	36	7	28	-24	H	13	5	13	0	9	8	0	1	0	0	0	
3	63	-89	14	0	-14	8	0	3	1	43	26	14	0	5	9	20	-14	H	10	6	
4	24	-5	15	0	15	9	59	43	2	0	-10	15	17	-18	10	0	-6	0	18	13	
5	46	-38				10	0	-3	3	33	-29				11	20	22	1	0	-8	
6	21	33				11	39	26	4	0	-4				12	0	1	2	0	-6	
7	71	66	H	5	5	12	0	-1	5	24	-20	H	2	6	5	5	18	3	18	-12	
8	0	-5	2	0	17	13	26	-28	6	0	5	1	29	-40	6	0	7	4	0	-7	
9	41	34	3	75	87	7	0	3	7	35	36	2	0	-7	0	6	5	5	19	9	
10	0	8	4	23	18	H	0	5	8	0	-1	3	19	-19	0	23	-22	6	0	1	
11	44	-47	5	44	48	1	0	0	9	23	18	4	0	2	1	50	40	7	15	8	
12	0	-8	6	71	-15	2	0	-3	H	14	5	5	35	47	2	0	-4	8	0	5	
13	29	-23	7	0	3	3	0	0	0	0	0	6	0	-3	3	37	35	9	17	-11	
14	0	1	8	0	-4	4	0	9	0	0	-8	7	29	24	4	0	7	10	0	-2	
15	36	32	9	37	-10	4	0	1	1	34	-25	8	0	-7	5	42	-47	11	15	-10	
			10	0	-2	6	0	3	2	0	-5	9	59	-40	6	0	5				
	H	2	4	11	52	48	7	0	-3	1	28	-23	10	0	6	7	36	-31	H	11	6
1	43	-77	4	42	0	-7	8	0	1	4	0	6	11	19	-18	8	0	-6	1	0	7
2	0	-7	13	23	18	9	0	-2	5	26	24	12	0	-1	9	47	47	2	0	4	
3	37	-51	15	39	-37	11	0	5	10	0	-8	13	23	22	10	0	-6	3	21	-7	
4	16	18				12	0	1	7	18	14	14	0	-2	11	29	25	4	0	0	
5	76	89				13	0	-2	8	0	-3	15	12	7	12	0	4	5	0	-5	
6	23	18	H	6	5	13	0	0	9	18	-27	13	30	-31	13	0	7	7	26	20	
7	67	53	1	2	0	-1	5	H	15	5		1	28	-32	H	7	6	8	0	-3	
8	0	11	2	0	-8	C	0	9	1	0	-10	2	21	-22	1	19	15	9	13	0	
9	55	-49	3	4	-4	1	48	41	2	0	-9	3	48	62	2	0	10				
10	0	9	4	0	-12	2	0	4	3	0	3	4	0	3	3	36	-29	H	12	6	
11	23	-31	5	0	-9	3	47	33	4	0	6	5	33	36	4	0	-2	0	0	5	
12	0	1	6	0	-17	4	0	-3	0	16	5	6	0	6	5	28	-22	1	35	-25	
13	46	-44	7	5	-45	5	46	-45	H	16	5	7	41	-95	6	0	-1	0	0	1	
14	0	-7	8	0	10	6	0	1	1	19	-14	8	0	4	7	24	22	3	27	-23	
15	22	24	9	0	-5	7	27	-28	2	0	-1	9	33	-31	8	0	-2	4	0	-5	
			11	0	3	8	0	3	3	18	-16	10	0	-7	9	16	11	5	93	35	
	H	3	5	11	0	-11	0	55	43	H	6	11	39	45	10	0	3	6	0	-2	
1	19	18	12	0	-7	10	0	-7	1	0	6	12	0	1	11	20	-20	0	0	7	
2	0	-3	13	0	-1	11	27	24	2	0	-43	13	22	18	12	0	7	8	0	8	
3	0	-3	14	0	3	12	0	-3	2	0	-13	14	0	6	13	14	-11	9	24	-37	
4	0	-1	15	0	-1	13	21	-24	3	26	-22	15	21	-37							
5	0	-6				5	61	64	4	22	-24										
6	0	-6				6	0	-11	5	0	14										
7	34	27	H	7	5	1	35	33	6	0	-2	H	4	6	-11	1	22	20	2	0	-5
8	0	-5	2	45	27	7	40	45	7	40	45	1	28	29	7	0	2	3	16	8	
9	0	-4	3	49	30	3	42	-35	8	0	12	2	0	4	2	15	4	4	0	1	
10	0	-6	4	20	16	4	0	-4	9	41	-43	3	25	24	4	0	1	5	16	11	
11	0	-6	5	34	26	5	32	-25	10	0	-3	4	0	8	5	20	-18	6	0	3	
12	0	-4	6	0	-11	6	0	2	11	31	-32	5	32	-33	6	0	8	7	12	-10	
13	0	-6	7	48	-41	7	37	36	12	0	-15	6	0	7	18	-11	8	0	0	0	
14	0	-7	8	0	11	8	0	-7	13	37	37	7	30	-25	8	0	-4	0	0	0	
15	0	4	9	33	-27	9	26	21	14	0	-3	8	0	0	9	22	21	0	0	4	
			10	46	36	11	29	-24	15	14	18	10	0	-2	10	11	15	0	14	-9	
	H	4	5	11	0	-11	0	-24	H	1	6	10	0	0	11	0	2	2	0	2	
1	58	-74	12	0	-5	0	12	5	1	15	-19	11	16	8	H	9	6	3	0	-2	
2	35	-37	14	0	-5	0	0	-1	2	0	-7	12	0	1	1	0	0	4	0	-1	
3	51	-51	15	20	-21	1	0	-1	3	25	33	13	23	-23	2	7	10	5	11	11	
4	22	-24				2	0	5	4	0	2				3	37	-33				

Table 4. Bond distances and angles in  $(\text{NH}_4)_2\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$ . The numbers in parentheses are the standard deviations of the last significant figures.

	Distance (Å)		Distance (Å)
Mo-O <sub>1</sub>	1.67 (2)	Mo-F <sub>2</sub>	2.00 (1)
Mo-O <sub>2</sub>	1.91 (3)	Mo-F <sub>3</sub>	1.91 (2)
Mo-O <sub>3</sub>	1.91 (2)	Mo-F <sub>4</sub>	2.01 (1)
Mo-F <sub>1</sub>	2.03 (1)	O <sub>2</sub> -O <sub>3</sub>	1.36 (3)
	Angle (°)		Angle (°)
O <sub>1</sub> -Mo-F <sub>1</sub>	172.1 (7)	F <sub>2</sub> -Mo-F <sub>3</sub>	80.5 (6)
O <sub>1</sub> -Mo-F <sub>2</sub>	93.2 (7)	F <sub>2</sub> -Mo-F <sub>4</sub>	78.9 (5)
O <sub>1</sub> -Mo-F <sub>3</sub>	96.3 (8)	F <sub>2</sub> -Mo-O <sub>2</sub>	152.8 (9)
O <sub>1</sub> -Mo-F <sub>4</sub>	93.7 (8)	F <sub>2</sub> -Mo-O <sub>3</sub>	156.1 (8)
O <sub>1</sub> -Mo-O <sub>2</sub>	103.3 (10)	F <sub>3</sub> -Mo-F <sub>4</sub>	157.6 (6)
O <sub>1</sub> -Mo-O <sub>3</sub>	99.1 (9)	F <sub>3</sub> -Mo-O <sub>2</sub>	76.4 (9)
F <sub>1</sub> -Mo-F <sub>2</sub>	79.0 (5)	F <sub>3</sub> -Mo-O <sub>3</sub>	118.1 (8)
F <sub>1</sub> -Mo-F <sub>3</sub>	84.1 (6)	F <sub>4</sub> -Mo-O <sub>2</sub>	120.6 (8)
F <sub>1</sub> -Mo-F <sub>4</sub>	83.4 (5)	F <sub>4</sub> -Mo-O <sub>3</sub>	79.9 (8)
F <sub>1</sub> -Mo-O <sub>2</sub>	84.5 (9)	O <sub>2</sub> -Mo-O <sub>3</sub>	41.7 (10)
F <sub>1</sub> -Mo-O <sub>3</sub>	87.7 (7)		



signs of the Fourier coefficients were determined by the contribution from the molybdenum atoms was undertaken. This showed large peaks at the above position and minor peaks, which were taken to be fluorine, oxygen, and nitrogen sites. On introducing these into a structure factor calculation an  $R$ -value of 0.23 was obtained.

*Structure refinement.* The structure was refined by the structure factor least-squares method using 1079 observed reflexions. For each reflexion the weight  $w$  was computed according to  $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$  with  $a = 1.0$ ,  $c = 0.005$ , and  $d = 0.00009$ . Anisotropic temperature parameters were

Table 5. Packing distances in  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$ . Distances less than 3.7 Å are included. (The first atom symbols refer to the coordinates given in Table 2. After the second atom symbols, the unit cell translations in the  $a$ ,  $b$ , and  $c$  directions are given in brackets, the number following being that of the symmetry operation performed on the original coordinates of the atom as given in the *International Tables for X-ray Crystallography*, Vol. I).

$\text{F}_5-\text{O}_1$	( 0 0 0)1	3.56 Å	$\text{N}_2-\text{O}_2$	( 0 0 0)7	3.67
$-\text{O}_2$	( 0 0 0)1	3.21	$-\text{O}_3$	( 1 -1 0)3	3.53
$-\text{F}_4$	( 0 0 0)8	3.68	$-\text{O}_3$	( 0 0 0)7	3.11
$-\text{F}_5$	( 0 0 0)7	3.67	$-\text{F}_1$	( 0 0 -1)4	2.75
$-\text{N}_1$	( 0 0 0)1	2.75	$-\text{F}_1$	( 0 0 0)8	3.28
$-\text{N}_1$	( 0 0 0)7	2.62	$-\text{F}_3$	( 0 0 0)1	2.87
$-\text{N}_2$	( 0 0 0)7	2.73	$-\text{F}_3$	( 0 0 -1)4	3.63
$-\text{N}_3$	( 0 0 0)2	3.47	$-\text{F}_4$	( 0 0 0)8	2.83
$-\text{N}_3$	( 0 0 0)8	2.69	$\text{N}_3-\text{O}_1$	( 0 0 0)1	3.57
$\text{N}_1-\text{O}_1$	( 0 0 0)1	3.06	$-\text{O}_2$	(-1 0 0)8	3.43
$-\text{O}_1$	( 0 0 -1)7	3.69	$-\text{O}_3$	(-1 0 0)8	3.18
$-\text{O}_2$	( 0 0 0)1	3.04	$-\text{F}_1$	( 0 0 -1)7	2.77
$-\text{F}_2$	( 0 0 0)1	2.81	$-\text{F}_2$	( 0 0 0)1	2.92
$-\text{F}_2$	( 0 0 -1)7	3.15	$-\text{F}_2$	( 0 0 -1)7	3.66
$-\text{F}_3$	( 0 0 -1)7	2.95	$-\text{F}_4$	( 0 0 0)1	2.95
$\text{N}_2-\text{O}_1$	( 0 -1 0)6	3.51	$-\text{F}_4$	( 0 0 0)7	2.80
$-\text{O}_2$	( 0 0 -1)7	3.24			

included for all atoms in the final cycles of refinement. The refinement converged after about ten cycles to the parameters given in Table 2, the ultimate  $R$ -value being 0.129. Observed and calculated structure factors are given in Table 3. Calculated bond distances and angles with their standard deviations are given in Table 4 and some packing distances in Table 5. All bond distances were found to be within their normal range. The result obtained from the refinement was checked by calculating a three-dimensional electron density difference map. This showed only small residual maxima, the largest maximum having a magnitude of about 25 % of the height of a nitrogen peak in the  $\text{F}_o$ -synthesis.

#### DESCRIPTION AND DISCUSSION

The crystals of the compound investigated, formulated as  $3\text{NH}_4\text{F} \cdot \text{MoO}_3\text{F}_2$  by Piccini,<sup>1</sup> consist of ammonium ions, fluoride ions and oxoperoxotetrafluoromolybdate(VI) ions packed as illustrated in Fig. 1. The formula is

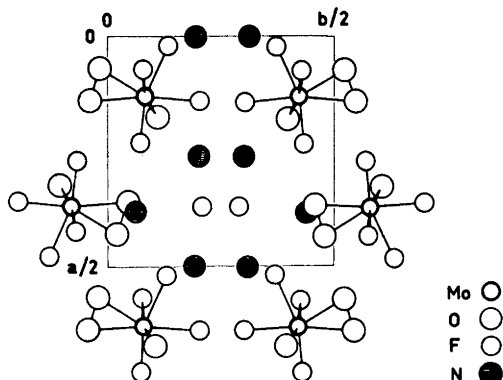


Fig. 1. The crystal structure of  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$  projected on the plane (001)

$(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$  and the systematic name (tri)ammonium fluoride oxo-peroxotetrafluoromolybdate(VI). The configuration about a molybdenum atom is illustrated in Figs. 2 and 3.

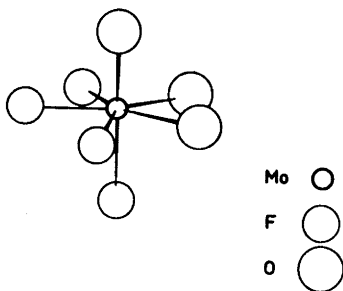


Fig. 2. The configuration about the molybdenum atom in the complex ion  $[\text{MoO}(\text{O}_2)\text{F}_4]^{2-}$ .

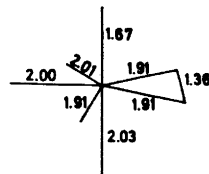


Fig. 3. Bond distances in the  $[\text{MoO}(\text{O}_2)\text{F}_4]^{2-}$  ion.

Molybdenum is 7-coordinated by a pentagonal bipyramidal arrangement of ligands. The atoms  $\text{O}_1$  and  $\text{F}_1$  are apically situated, while  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{F}_2$ ,  $\text{F}_3$ , and  $\text{F}_4$  form the equatorial plane. The two oxygen atoms  $\text{O}_2$  and  $\text{O}_3$  of the peroxo group are equally remote from the central molybdenum atom, 1.91 Å, and the bond distances imply that these Mo–O bonds are single bonds. They agree well with the Mo– $\text{O}_{\text{peroxo}}$  distances found in other 7-coordinated peroxomolybdates (see Table 6), as well as with those obtained for the 8-coordinated tetraperoxomolybdate(VI) ion in  $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ ,<sup>6</sup> (1.93 and 2.00 Å).

The Mo– $\text{O}_1$  bond is 1.67 Å and is thus significantly shorter than the Mo– $\text{O}_{\text{peroxo}}$  bonds, indicating considerable double-bond character. As may

Table 6. Comparison between corresponding distances in  $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$  and other 7-coordinated peroxomolybdates.

Compound	Mo—O <sub>peroxo</sub> (Å)	Mo—F (Å)	Mo=O (Å)	(O—O) <sub>peroxo</sub> (Å)	Mo-equatorial plane (Å)	Ref.
$\text{K}_2[\text{MoO}(\text{O}_2)\text{F}_4](\text{H}_2\text{O})$	1.94—1.95	2.00—2.03	1.64	1.44	0.18	7
$\text{K}_2[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$	1.93—1.96		1.68	1.44—1.47	0.35	13
$\text{K}_2[\text{O}(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2](\text{H}_2\text{O})_2$	1.94—1.98		1.66	1.45—1.52	0.38—0.39	5
$(\text{pyH})_2[\text{O}(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$	1.96—1.98		1.68	1.44—1.46	<sup>a</sup>	19
$(\text{pyH})_2[(\text{O}_2)_2\text{OMo}(\text{OOH})_2\text{MoO}(\text{O}_2)_2]$	1.92—1.96		1.67	1.47—1.48	<sup>a</sup>	19
$(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$	1.91	1.91—2.03	1.67	1.36	0.23	This paper

<sup>a</sup> Not given in the paper cited. A more detailed description will probably be given elsewhere.

be seen from Table 6, it does not differ significantly from corresponding Mo = O distances observed in other peroxomolybdates. Moreover, values between 1.69 and 1.71 Å were found in the 6-coordinated diperoxotetramolybdate  $\text{K}_4[\text{Mo}_4\text{O}_{12}(\text{O}_2)_2]$ .<sup>4</sup>

The distances between molybdenum and  $\text{F}_1$ ,  $\text{F}_2$ , and  $\text{F}_4$  are all identical within the limits of experimental error and do not differ significantly from the Mo—F values observed in  $\text{K}_2[\text{MoO}(\text{O}_2)\text{F}_4](\text{H}_2\text{O})$  (see Table 6). The Mo— $\text{F}_3$  bond distance is, however, shorter than the other Mo—F bond lengths (0.1 Å), a phenomenon not observed for the potassium salt.

The (O—O)<sub>peroxo</sub> distance is rather short (1.36 Å) compared with the value of 1.44 Å found in  $\text{K}_2[\text{MoO}(\text{O}_2)\text{F}_4](\text{H}_2\text{O})$ . Since the standard deviations are 0.03 Å in both investigations, the discrepancy between these two observations is not, however, significant. Short (O—O)<sub>peroxo</sub> distances of 1.40 Å were also observed in both  $[\text{CrO}(\text{O}_2)_2\text{py}]$ ,<sup>14</sup>  $[\text{CrO}(\text{O}_2)_2\text{phen}]$ ,<sup>15</sup> and  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$ .<sup>16</sup> The value 1.36 Å ought, however, to be considered to be significantly different from the value 1.49 Å found in hydrogen peroxide.<sup>17</sup>

Within the limits of experimental error all five equatorial atoms lie in a plane. The equation of this plane, A, as determined by the least-squares method, is

$$\text{A:} \quad 0.4691 X + 0.1316 Y - 0.8733 Z = -0.2613$$

where X, Y, and Z are the atomic coordinates expressed in Å, referred to the original axes. The distances from certain atoms to the plane are

A—O <sub>2</sub>	−0.06 Å	A—F <sub>3</sub>	0.05 Å	A—O <sub>1</sub>	1.89 Å
O <sub>3</sub>	0.04	F <sub>4</sub>	0.01	F <sub>1</sub>	−1.80
F <sub>2</sub>	−0.03	Mo	0.23		

The molybdenum atom is thus displaced 0.23 Å from the equatorial plane in the direction of the double-bonded oxygen atom, O<sub>1</sub>. This means that the distances from the apically situated oxygen and fluorine atoms to the plane are almost equal, *i.e.* 1.89 and 1.80 Å, respectively. A similar displacement of the metal atom from the equatorial plane has been observed in a number of 7-coordinated transition metal oxoperoxo compounds. A displacement of 0.35

Å was observed in  $K_2[O(WO(O_2)_2(H_2O))_2](H_2O)_2$ ,<sup>18</sup> of 0.27 Å in  $[CrO(O_2)_2phen]$ <sup>15</sup> and of 0.31 Å in  $[CrO(O_2)_2dipy]$ .<sup>16</sup> Further examples are cited in Table 6.

In most 7-coordinated peroxy complexes there is a mirror plane perpendicular to the equatorial plane. To investigate whether or not this is the case for the  $[MoO(O_2)F_4]^{2-}$  ion, the equation of the best plane, **B**, through the atoms Mo, O<sub>1</sub>, F<sub>1</sub>, and F<sub>2</sub> was determined. This was found to be

$$\mathbf{B}: \quad 0.8733 X - 0.2545 Y + 0.4153 Z = 2.0807$$

As the angle between the planes **A** and **B** is 89.8° they are, even here, perpendicular to one another within the limits of experimental error. The distances of some atoms from the plane **B** are:

<b>B</b> —Mo	0.02 Å	<b>B</b> —F <sub>2</sub>	0.00 Å	<b>B</b> —F <sub>3</sub>	1.89 Å
O <sub>1</sub>	-0.01	O <sub>2</sub>	0.73	F <sub>4</sub>	-1.96
F <sub>1</sub>	-0.01	O <sub>3</sub>	-0.63		

The distances between the plane **B** and the oxygen atoms O<sub>2</sub> and O<sub>3</sub> of the peroxy group, on the one hand, and F<sub>3</sub> and F<sub>4</sub>, on the other, are less than 0.1 Å. From the above evidence it can be concluded that the complex ion has approximately C<sub>s</sub> symmetry. This situation was not found in the complex anion of  $K_2[MoO(O_2)F_4](H_2O)$ . The distances of O<sub>2</sub> and O<sub>3</sub> from the plane corresponding to **B** are 0.53 and 0.91 Å, respectively, and thus differ by as much as 0.4 Å.

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