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Studies on peroxomolybdates
XVII. Synthesis and structure of tri(ammonium) fluoride difluorooxodiperoxomolybdate(VI), $(NH_4)_3F[MoF_2O(O_2)_2]$

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Abstract

The crystal structure of tri(ammonium) fluoride difluorooxodiperoxomolybdate(VI), $(NH_4)_3F[MoF_2O(O_2)_2]$, was determined using single-crystal X-ray diffraction methods. The yellow compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 6.745(3)$ Å, $b = 8.718(3)$ Å, $c = 15.427(5)$ Å and $Z = 4$. Reflection intensities were recorded at room temperature on a Syntex $P2_1$ diffractometer using Mo Kα radiation. Full-matrix least-squares refinement yielded a final R value of 0.026 for 1474 observed ($I > 3\sigma(I)$) reflections. In the complex anion the coordination geometry is pentagonal bipyramidal. Bond distances are as follows: $Mo{=}O_{apical}$ 1.679(3) Å, $Mo{-}O_{peroxo}$ 1.915(4)–1.969(3) Å, $Mo{-}F_{equatorial}$ 1.960(3) Å, $Mo{-}F_{apical}$ 2.150(2) Å and $(O{-}O)_{peroxo}$ 1.471(6)–1.481(5) Å. The powder photograph of the title compound was recorded at room temperature and was indexed.

1. Introduction

The formation of peroxomolybdates was first recognized in 1861 [1]. A comprehensive investigation of the solid compounds formed in the system $M^+{-}MoO_4^{2-}{-}H_2O_2{-}H^+{-}H_2O$ ($M^+ \equiv NH_4^+, K^+$), performed in this department, has shown the existence of oxoperoxo mono-, di-, tri-, tetra-, penta-, hepta-, octa- and decamolybdates [2–4]. The addition of fluoride to the above system usually reduces the nuclearity to one or two. In the system $NH_4^+{-}MoO_4^{2-}{-}H_2O_2{-}HF{-}H_2O$ five crystalline phases have been characterized by X-ray diffraction methods, *i.e.* $(NH_4)_3F[MoF_4O(O_2)]$ [5, 6], $(NH_4)_2[MoF_2O(O_2)_2]$ [7], $(NH_4)_3[F\{MoFO(O_2)_2\}_2]$ [8], $(NH_4)_3[FO\{MoO(O_2)_2\}_2]\cdot\frac{1}{2}H_2O$ [9] and $(NH_4)_3F[MoF_2O(O_2)_2]$. The structure of the last compound will be presented in this paper.

2. Experimental details

2.1. Preparation of $(NH_4)_3F[MoF_2O(O_2)_2]$

Ammonium fluoride (2 g) and ammonium heptamolybdate (1 g) were dissolved in 6% hydrogen peroxide (30 mL) and hydrogen fluoride was added to adjust the pH to 2–3. The solution was left to evaporate at room temperature (a stream of air was passed over the solution to increase the evaporation speed). Plate-formed yellow crystals were obtained within a few hours. The peroxide content was checked by iodometric titration (found: O_2^{2-}, 22.4%; calculated for $(NH_4)_3F[MoF_2O(O_2)_2]$, 22.29%).

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 [10]. Observed lines in the powder photograph are given in Table 1; they were indexed after the structure determination. 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-monochromated Mo $K\alpha$ 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. Data were collected at room temperature. There was a slight increase in the intensity of two of the test reflections and a slight decrease in the intensity of one of them.

3. Structure determination

The structure was solved by Patterson and electron density calculations. The false mirror plane introduced in the initial molybdenum-phased electron density map could be resolved by a few trial models. Full-matrix least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms yielded an R value of 0.055. With anisotropic thermal parameters for these atoms R became 0.031. From the subsequent electron density difference map (maximum electron density 0.69 e $Å^{-3}$) all the hydrogen atoms were localized. Introduction of these with isotropic thermal parameters reduced R to 0.026.

Calculations were carried out on an IBM 3081 computer with programmes in use in this department. Atomic scattering factors were taken from ref. 11. Further details concerning the refinement are summarized in Table 2.

4. Results and discussion

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

TABLE 1

Observed lines in the powder photograph of $(NH_4)_3F[MoF_2O(O_2)_2]$ at room temperature registered with a Guinier–Hägg camera, using Cu $K\alpha_1$ radiation ($\lambda = 1.54060$ Å) and silicon (NBS standard) as internal standard

d_{obs} (Å)	d_{calc} (Å)	$h\ k\ l$	I_{obs}	F_{calc}	d_{obs} (Å)	d_{calc} (Å)	$h\ k\ l$	I_{obs}	F_{calc}
7.7208	7.7215	0 0 2	29.6	86	2.1388	2.1388	0 1 7	1.9	99
7.5961	7.5955	0 1 1	24.0	85	2.1200	2.1196	2 3 2	1.7	63
6.2006	6.1922	1 0 1	3.0	34	2.0993	2.0993	3 1 2	2.7	64
5.0493	5.0858	1 0 2	100.0	134	2.0201	2.0205	2 2 5	4.0	40
	5.0494	1 1 1		148		2.0204	1 3 5		73
4.4334	4.4333	0 1 3	40.8	158	2.0045	2.0044	1 4 2	3.2	78
4.3950	4.3937	1 1 2	8.6	53	1.9938	1.9934	2 1 6	1.9	70
4.3638	4.3619	0 2 0	16.4	171	1.9854	1.9852	3 2 1	2.2	71
3.8604	3.8607	0 0 4	3.1	86	1.9375	1.9377	3 2 2	1.4	61
3.7980	3.7978	0 2 2	7.8	98	1.8995	1.8993	3 1 4	3.8	96
3.5662	3.5659	1 2 1	5.3	58	1.8538	1.8561	1 0 8	5.6	94
3.3801	3.3796	2 0 0	7.6	91		1.8535	2 2 6		87
3.3536	3.3524	1 0 4	13.0	134	1.8188	1.8202	3 0 5	1.6	66
3.3112	3.3110	1 2 2	26.8	132		1.8197	2 4 1		40
[a]	3.1514	2 1 0		101	1.7351	1.7355	3 3 2	1.5	60
3.0886	3.0878	2 1 1	3.3	49		1.7337	0 5 1		48
2.9180	2.9178	2 1 2	5.9	74	1.7263	1.7264	2 4 3	2.0	83
2.8098	2.8092	1 0 5	2.8	76	1.7077	1.7079	1 2 8	1.9	84
2.6870	2.6877	2 1 3	2.7	52	1.7006	1.7011	2 2 7	2.6	66
2.6738	2.6740	1 1 5	7.0	84		1.7010	1 3 7		64
2.6330	2.6321	1 3 1	3.3	65	1.6794	1.6798	3 2 5	4.0	50
2.5246	2.5247	2 2 2	12.0	102		1.6798	4 0 1		74
	2.5244	1 3 2		55		1.6794	1 5 1		64
2.3712	2.3712	2 2 3	6.0	93	1.6748	1.6762	2 0 8	1.6	49
2.2297	2.2295	3 0 1	1.7	73		1.6742	2 3 6		82
2.2167	2.2167	0 2 6	3.9	124	1.6173	1.6172	3 3 4	1.6	85
2.2041	2.2043	2 3 0	3.2	91	1.5068	1.5070	2 1 9	2.8	72
2.1975	2.1969	2 2 4	2.4	38		1.5067	4 2 3		70
	2.1967	1 3 4		58	1.4832	1.4825	3 2 7	2.0	70
2.1812	2.1822	2 3 1	2.9	58		1.4821	1 5 5		68
	2.1809	0 4 0		102	1.3969	1.3975	3 4 5	2.1	67

[a]Coincides with standard line.

The crystals of $(NH_4)_3F[MoF_2O(O_2)_2]$ consist of ammonium ions, fluoride ions and difluorooxodiperoxomolybdate(VI) ions. Besides ionic bonding, the structure is further stabilized by extensive hydrogen bonding; 11 out of 12 hydrogen atoms participate in hydrogen bonding. The fluoride ion is involved in the strongest hydrogen bonds ($N\cdots F^-$ distances range between 2.620(4) and 2.686(4) Å).

In the complex anion molybdenum is seven-coordinated in the pentagonal bipyramidal way and the complex has almost C_s symmetry as observed for other seven-coordinated fluorooxoperoxomolybdates [5–9]. The equatorial plane in the bipyramid is defined by the atoms O1–O4 and F1. The maximum deviation of these atoms from the equatorial plane is 0.048(3) Å (O4). The

TABLE 2

Crystal and experimental data for $(NH_4)_3F[MoF_2O(O_2)_2]$

M_r	287.05	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$ (No. 19)	
Unit cell dimensions[a] (a, b, c (Å); V (Å^3))	a=6.745(3)	[6.759(1)]
	b=8.718(3)	[8.724(1)]
	c=15.427(5)	[15.443(2)]
	V=907.1(6)	
Z	4	
D_c (g cm^{-3})	2.102	
μ (Mo Kα) (mm^{-1})	1.48	
Crystal size (mm)	0.10×0.26×0.28	
Crystal colour; habit	Yellow; prismatic	
Number of reflections for cell determination (θ range (deg))	15 ($2.7<\theta<15.2$)	
Diffractometer	Syntex $P2_1$	
Radiation	Mo Kα	
Temperature (°C)	20	
Scan mode	ω–2θ	
2θ range (deg)	$3.5<2\theta<60.0$	
2θ scan speed (deg min^{-1})	3.9–19.5	
Total number of reflections measured	1576	
Number of observed independent reflections ($I>3\sigma(I)$)	1474	
Test reflections (standard deviation (%))	0 0 4 (1.7); 0 4 0 (4.1); 2 0 0 (2.5)	
Corrections	Lorentz, polarization and absorption	
Number of parameters refined	157	
Weights calculated according to	$w=(10+\|F_0\|+0.002\|F_0\|^2+0.001\|F_0\|^3)^{-1}$	
R (R_w)	0.026 (0.032)	
Maximum residual electron density (e Å^{-3})	0.36	

[a]Cell dimensions obtained from the powder photograph are given in square brackets.

largest deviation of the atoms Mo, F1, F2 and O5 from the plane, which they define, is 0.020(3) Å (O5). The midpoints between O1 and O4 on the one hand and O2 and O3 on the other coincide within 0.008 Å with this plane, which forms an angle of 89.72(9)° with the equatorial plane.

The molybdenum atom is displaced 0.285(2) Å from the equatorial plane towards the double-bonded oxygen atom O5. In the three other fluorooxodiperoxomolybdates studied the observed displacements are 0.311–0.365 Å [7–9]. These displacements are significantly larger than that observed in the fluorooxomonoperoxomolybdate $(NH_4)_3F[MoF_4O(O_2)]$ [6].

The anions in $(NH_4)_3F[MoF_2O(O_2)_2]$ and $(NH_4)_2[MoF_2O(O_2)_2]$ are very similar; this is evident from Table 4 in this paper and from Table 3 in ref. 7. The largest difference is shown by the Mo–F2 distance, being 2.150(2) Å in $(NH_4)_3F[MoF_2O(O_2)_2]$ and 2.199(1) Å in $(NH_4)_2[MoF_2O(O_2)_2]$. The reason

TABLE 3

Atomic fractional coordinates and thermal parameters for $(NH_4)_3F[MoF_2O(O_2)_2]$; $T = 293$ K, $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$

Atom	x	y	z	B_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.18894(4)	0.25770(3)	0.33636(1)	2.269(6)	0.0287(1)	0.0289(1)	0.0286(1)	−0.0085(2)	0.0023(2)	0.0020(2)
F1	0.1273(4)	0.4553(3)	0.3907(2)	3.89(6)	0.048(1)	0.040(1)	0.059(1)	−0.014(2)	0.038(2)	−0.030(2)
F2	0.4389(3)	0.3919(3)	0.2949(1)	3.14(4)	0.0336(9)	0.0377(9)	0.048(1)	−0.009(2)	0.021(2)	−0.005(2)
F3	0.5296(4)	0.2077(3)	0.0362(2)	3.72(5)	0.043(1)	0.050(1)	0.048(1)	0.024(2)	0.007(2)	−0.013(2)
O1	0.0840(5)	0.3379(4)	0.2262(2)	4.07(7)	0.045(1)	0.067(2)	0.042(1)	0.004(3)	−0.008(3)	0.027(3)
O2	0.1877(6)	0.1889(4)	0.2179(2)	4.34(8)	0.066(2)	0.061(2)	0.037(1)	−0.017(4)	0.006(3)	−0.034(3)
O3	0.3818(7)	0.1018(4)	0.3596(3)	5.23(9)	0.065(2)	0.054(2)	0.079(2)	0.039(3)	−0.010(4)	0.031(4)
O4	0.3721(5)	0.2120(5)	0.4317(2)	4.99(8)	0.056(2)	0.085(2)	0.048(1)	−0.018(4)	−0.033(3)	0.048(3)
O5	−0.0186(5)	0.1749(4)	0.3742(2)	4.20(8)	0.049(2)	0.052(2)	0.059(2)	−0.041(3)	0.028(3)	−0.001(3)
N1	0.2835(5)	0.4341(4)	0.0660(2)	3.09(7)	0.039(2)	0.035(1)	0.043(2)	0.003(3)	0.003(3)	−0.011(2)
N2	0.6831(5)	0.2074(4)	0.1969(2)	3.25(7)	0.037(1)	0.046(2)	0.040(1)	0.011(3)	−0.001(3)	−0.011(2)
N3	0.7086(6)	0.4732(5)	0.4272(3)	3.48(8)	0.038(2)	0.047(2)	0.048(2)	−0.005(3)	0.003(3)	0.016(3)
H1(N1)	0.17(1)	0.39(1)	0.017(5)	5(1)						
H2(N1)	0.385(9)	0.371(7)	0.055(4)	2(1)						
H3(N1)	0.252(9)	0.438(6)	0.115(4)	2(1)						
H4(N1)	0.31(1)	0.513(8)	0.056(4)	3(1)						
H1(N2)	0.646(7)	0.220(5)	0.148(3)	0(1)						
H2(N2)	0.818(7)	0.233(5)	0.202(3)	1(1)						
H3(N2)	0.664(9)	0.113(7)	0.216(4)	2(1)						
H4(N2)	0.60(1)	0.284(7)	0.225(4)	3(1)						
H1(N3)	0.618(9)	0.434(6)	0.386(4)	2(1)						
H2(N3)	0.658(9)	0.555(7)	0.444(4)	2(1)						
H3(N3)	0.810(9)	0.505(7)	0.398(4)	3(1)						
H4(N3)	0.741(9)	0.413(6)	0.469(4)	2(1)						

TABLE 4

Distances (Å) and angles (deg) in $(NH_4)_3F[MoF_2O(O_2)_2]$

Distances

Mo–O1	1.969(3)	O1–O2	1.481(5)	O5···O3	2.784(6)
Mo–O2	1.923(3)	O3–O4	1.471(6)	O5···O4	2.799(5)
Mo–O3	1.915(4)	O2···O3	2.659(5)	O5···F1	2.648(4)
Mo–O4	1.962(3)	F1···O1	2.751(4)	F2···O1	2.660(4)
Mo–O5	1.679(3)	F1···O4	2.762(5)	F2···O2	2.723(4)
Mo–F1	1.960(3)	O5···O1	2.776(5)	F2···O3	2.746(5)
Mo–F2	2.150(2)	O5···O2	2.786(5)	F2···O4	2.668(4)
				F2···F1	2.628(4)

Angles

F1–Mo–O1	88.9(1)	F2–Mo–O4	80.8(1)
F1–Mo–O4	89.5(2)	F2–Mo–F1	79.3(1)
O1–Mo–O2	44.7(2)	F2–Mo–O5	172.3(1)
O2–Mo–O3	87.7(2)	O5–Mo–F1	93.0(1)
O3–Mo–O4	44.6(2)	O5–Mo–O1	98.8(2)
F2–Mo–O1	80.4(1)	O5–Mo–O2	101.1(2)
F2–Mo–O2	83.7(1)	O5–Mo–O3	101.3(2)
F2–Mo–O3	84.8(1)	O5–Mo–O4	100.2(2)

Hydrogen bonds

N–H···X	N···X	N–H	H···X	∠N–H···X
N1–H1(N1)···F3	2.635(4)	1.14(8)	1.52(8)	167(7)
N1–H2(N1)···F3	2.620(4)	0.90(6)	1.75(6)	164(6)
N1–H3(N1)···O1	2.937(5)	0.79(6)	2.23(6)	149(6)
N2–H1(N2)···F3	2.686(4)	0.80(4)	1.90(4)	167(4)
N2–H2(N2)···O1	2.968(5)	0.94(5)	2.05(5)	165(4)
N2–H3(N2)···F2	2.873(4)	0.88(6)	2.06(6)	153(5)
N2–H4(N2)···F2	2.755(4)	0.96(6)	1.82(6)	166(5)
N3–H1(N3)···F2	2.823(5)	0.94(6)	1.89(6)	169(5)
N3–H2(N3)···F3	2.661(5)	0.83(6)	1.86(6)	161(6)
N3–H3(N3)···F1	2.884(5)	0.86(6)	2.19(6)	138(5)
N3–H4(N3)···O4	2.926(5)	0.86(6)	2.08(6)	169(5)

for this difference does not seem to be due to hydrogen bonding; in both compounds F2 is hydrogen bonded to three hydrogen atoms at 2.755(4)–2.873(4) and 2.767(2)–2.857(2) Å respectively. In $(NH_4)_3[VF_2O(O_2)_2]$, in which the complex anion shows the same geometry and general features as the $[MoF_2O(O_2)_2]^{2-}$ ions, the V–F2 distance is considerably longer, namely 2.306(1) Å. This is in line with the general observation made that peroxovanadates have a tendency towards pentagonal pyramidal six-coordination; this has been discussed by Stomberg in *e.g.* ref. 12.

In the system M^+–MoO_4^{2-}–H_2O_2–HF–H_2O ($M^+ \equiv NH_4^+$, K^+) the most fluoride-rich solid phase seems to be $M_3F[MoF_4O(O_2)]$ [5, 6], which appears at a high concentration of fluoride and at low pH. This may be compared to the most fluoride-rich fluoroperoxometallates in group 5, $[NbF_5(O_2)]^{2-}$ and $[TaF_5(O_2)]^{2-}$ being easily formed (see *e.g.* ref. 7 and references cited

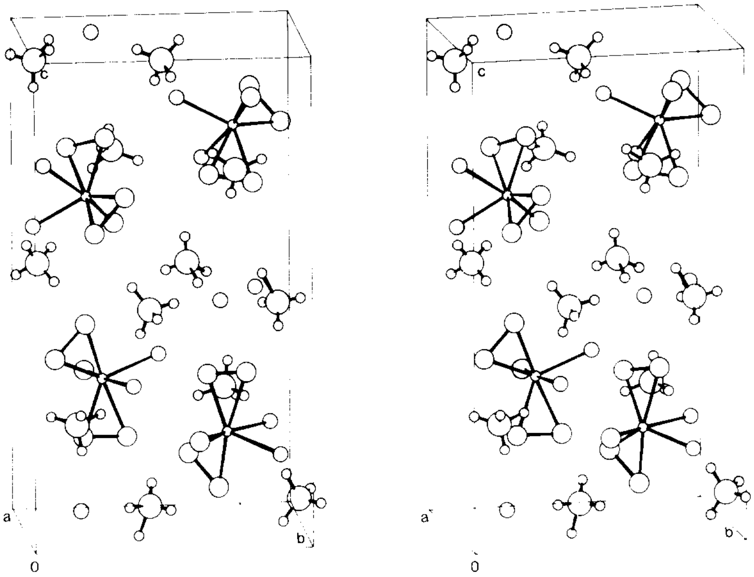

Fig. 1. Stereoscopic view of the unit cell of $(NH_4)_3F[MoF_2O(O_2)_2]$.

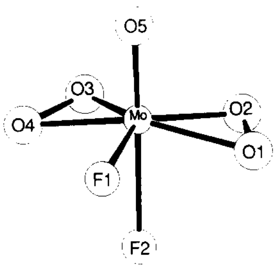

Fig. 2. The anion $[MoF_2O(O_2)_2]^{2-}$.

therein). Both molybdenum and vanadium form difluorodiperoxomolybdates (see above).

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References

1 G. Werther, *J. Prakt. Chem.*, *83* (1861) 198.
2 R. Stomberg and L. Trysberg, *Acta Chem. Scand.*, *23* (1969) 314.
3 I. Persdotter, L. Trysberg and R. Stomberg, *Acta Chem. Scand. A*, *40* (1986) 83.
4 L. Trysberg, unpublished result, 1979.

5 I. Larking and R. Stomberg, *Acta Chem. Scand.*, *24* (1970) 2043.
6 R. Stomberg, *Acta Chem. Scand. A*, *42* (1988) 284.
7 R. Stomberg, *J. Crystallogr. Spectrosc. Res.*, *18* (1988) 659.
8 R. Stomberg, *J. Less-Common Met.*, *144* (1988) 109.
9 R. Stomberg, to be published.
10 K. E. Johansson, T. Palm and P.-E. Werner, *J. Phys. E: Sci. Instrum.*, *13* (1980) 1289.
11 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974.
12 R. Stomberg, *Acta Chem. Scand. A*, *38* (1984) 801.