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Structure of Tripotassium μ-Fluoro-μ-peroxo-bis(fluorooxoperoxovanadate)(3−) Hydrogen Fluoride Dihydrate

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Abstract. $K_3[V_2F_3O_8].HF.2H_2O$, $M_r = 460{\cdot}2$, triclinic, $P\bar{1}$, $a = 8{\cdot}518$ (5), $b = 12{\cdot}460$ (5), $c = 5{\cdot}981$ (5) Å, $\alpha = 92{\cdot}30$ (5), $\beta = 90{\cdot}90$ (5), $\gamma = 102{\cdot}70$ (5)°, $V = 618{\cdot}56$ Å^3, $Z = 2$, $D_x = 2{\cdot}47$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 26·9 cm^{-1}, $F(000) = 448$, $T = 295$ K, $R = 0{\cdot}042$ for 2512 unique reflections. The core of the structure is a discrete dinuclear fluorooxoperoxo complex of V^v atoms with purely inorganic ligands, $[F(O_2)\{VO(O_2)F\}_2]^{3-}$. The coordination polyhedron of each V atom can be described as a pentagonal bipyramid. Within the dinuclear complex the two chemically equivalent coordination polyhedra share a triangular face formed by an F atom and a peroxo group.

Introduction. The title compound was first synthesized by Schwendt & Joniakova (1983*a*), who investigated its isothermal decomposition by means of weight loss, elemental analyses of solid intermediate products, IR and Raman spectroscopy, and X-ray powder method (Schwendt & Joniakova, 1983*b*). Based on the data obtained they proposed a structure of the complex. Since this prediction was by no means straightforward, it was deemed worthwhile to carry out an X-ray single-crystal structure determination.

Experimental. A crystal, suitable for X-ray crystallography, with the approximate dimensions 0·20 × 0·30 × 0·15 mm, was coated with copal resin to prevent decomposition in air at room temperature. Data were recorded using an automatic three-circle normal-beam single crystal X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters were determined from 18 reflections ($15 \le \theta \le 34°$). The ω–2θ scan method was used to collect intensity data. 2905 integrated intensity values were obtained with the modified Oatley & French (1982) profile analysis procedure. Data were collected for $2\theta \le 73°$, index range: $-14 \le h \le 13$, $-19 \le k \le 20$, $0 \le l \le 6$. One control reflection was monitored every 30 reflections. It showed no significant variation in intensity. 2512 unique reflections having $I > 4\sigma(I)$ were used in the subsequent analysis. Values of I were corrected for Lorentz and polarization effects but no absorption correction was applied. The V atoms were located using the Patterson function and all remaining atoms were located in successive $\Delta\rho$ maps. Calculations were carried out on a BESM-6 computer using the locally modified crystallographic program system *RENTGEN75* (Andrianov, Safina & Tarnopolsky, 1974). Seven scale factors, positional parameters of all atoms and anisotropic thermal parameters of non-H atoms were refined by full-matrix least squares using

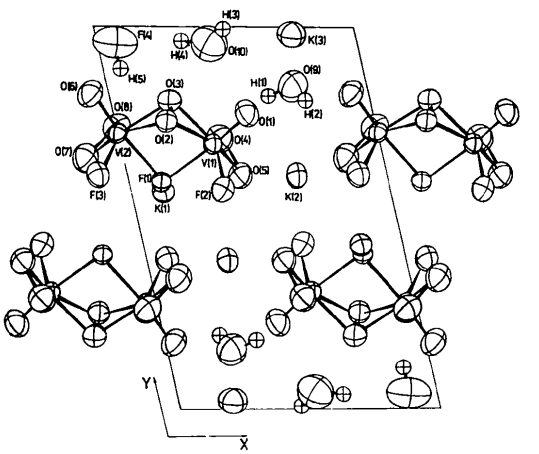

Fig. 1. View of the structure along the *c* axis. Thermal ellipsoids are drawn at the 50% probability level; H atoms are represented by spheres of arbitrary size.

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Table 1. *Positional and equivalent isotropic thermal parameters for non-H atoms*

$B_{eq} = [\mathrm{Det}(\beta_{ik})]^{1/3}\,[1/4\ \mathrm{Det}(a_i^* a_k^*)]^{-1/3}$.

	x	y	z	B_{eq}(Å^2)
V(1)	0·3839 (1)	0·6993 (1)	0·8003 (1)	1·53 (2)
V(2)	0·0296 (1)	0·7289 (1)	0·7926 (1)	1·50 (2)
K(1)	0·1348 (1)	0·5644 (1)	0·2715 (2)	1·98 (3)
K(2)	0·6614 (1)	0·6045 (1)	0·2206 (2)	2·08 (3)
K(3)	0·7610 (2)	0·9681 (1)	0·0688 (3)	3·27 (4)
F(1)	0·1518 (3)	0·6003 (2)	0·7244 (4)	1·6 (1)
F(2)	0·3869 (3)	0·5866 (2)	1·0030 (5)	2·3 (1)
F(3)	−0·0787 (3)	0·6256 (2)	0·9895 (5)	2·4 (1)
F(4)	0·0837 (9)	0·9540 (4)	0·3197 (11)	5·0 (2)
O(1)	0·5433 (3)	0·7818 (3)	0·8977 (7)	2·6 (1)
O(2)	0·2289 (3)	0·7634 (2)	0·9987 (6)	2·0 (1)
O(3)	0·2546 (3)	0·8124 (2)	0·7795 (6)	2·4 (1)
O(4)	0·4107 (4)	0·7077 (3)	0·4938 (7)	3·2 (1)
O(5)	0·4590 (4)	0·6132 (3)	0·5801 (6)	2·6 (1)
O(6)	−0·0395 (4)	0·8331 (3)	0·8737 (7)	2·8 (1)
O(7)	−0·1195 (4)	0·6597 (3)	0·5698 (7)	3·1 (1)
O(8)	0·0163 (4)	0·7357 (3)	0·4811 (7)	3·2 (1)
O(9)	0·7274 (5)	0·8415 (3)	0·4392 (9)	4·1 (2)
O(10)	0·4398 (7)	0·9491 (4)	0·2787 (12)	5·0 (2)

ORFLS (Busing, Martin & Levy, 1962); the function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$ with Cruickshank's weighting scheme: $w = (2|F_o|_{\min} + |F_o| + 2F_o^2/|F_o|_{\min})^{-1}$ (Cruickshank, 1965). The isotropic temperature factor of each H atom was put equal to B_{iso} of the bonded atom. In a separate refinement the site occupancies of hydrogen fluoride and water molecules were refined on 340 unique reflections with $2\theta \le 30°$. Final discrepancy indices were $R = 0{\cdot}042$, $wR = 0{\cdot}053$, $S = 0{\cdot}29$, $(\Delta/\sigma)_{\max} = 0{\cdot}007$, $\Delta\rho_{\max}/\Delta\rho_{\min} = +0{\cdot}59/-0{\cdot}77$ e Å^{-3}. Scattering factors for neutral atoms were taken from Hanson, Herman, Lea & Skillman (1964).

Discussion. Table 1* lists final atomic parameters; the main interatomic distances and bond angles for the title compound are given in Table 2. A projection of the atomic arrangement on the xy plane and the atomic labelling scheme are shown in Fig. 1.

The structure consists of dinuclear complexes $[F(O_2)\{VO(O_2)F\}_2]^{3-}$, K^+ ions, hydrogen fluoride and water molecules. They are held together by electrostatic and hydrogen-bond forces. The dinuclear complex exhibits two pentagonal-bipyramidal polyhedra about V which are joined to each other by sharing a bridging face formed by the O(2), O(3) and F(1) atoms. The complex seems to be the first example of this structural type for peroxo complexes of transition metals. It is noteworthy that although all atoms within the complex occupy non-equivalent positions, the corresponding atoms of the neighbouring polyhedra are related by a pseudo mirror plane which coincides with the bridging face. Each V atom is seven coordinated. The equatorial plane of the V(1) polyhedron is formed by O(2), O(3), O(4), O(5) and F(2) with a maximum deviation from planarity of ± 0·045 Å. The atoms O(2), O(3), O(7), O(8) and F(3) form the equatorial plane of the V(2) polyhedron and are planar within ± 0·042 Å. The dihedral angle between these two planes is 84·9 (3)°. The apical atoms O(1) [V(1) polyhedron] and O(6) [V(2) polyhedron] lie on the same side of the corresponding equatorial planes at distances 1·880 (3) and 1·899 (3) Å, respectively. The V atoms are displaced 0·287 (2) [V(1)] and 0·301 (2) Å [V(2)] from the equatorial planes, towards the apical O atoms. As can be

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *for* $K_3[F(O_2)\{VO(O_2)F\}_2].HF.2H_2O$

V(1)—O(1)	1·598 (4)	V(2)—O(2)	2·038 (4)
V(1)—O(2)	2·055 (4)	V(2)—O(3)	1·974 (4)
V(1)—O(3)	1·976 (4)	V(2)—O(6)	1·600 (4)
V(1)—O(4)	1·856 (5)	V(2)—O(7)	1·872 (5)
V(1)—O(5)	1·873 (4)	V(2)—O(8)	1·871 (5)
V(1)—F(1)	2·119 (3)	V(2)—F(1)	2·124 (3)
V(1)—F(2)	1·896 (4)	V(2)—F(3)	1·879 (4)
O(4)—O(5)	1·441 (5)	O(7)—O(8)	1·447 (5)
		O(2)—O(3)	1·467 (5)
O(1)—V(1)—O(2)	95·3 (2)	O(2)—V(2)—O(3)	42·9 (2)
O(1)—V(1)—O(3)	95·6 (2)	O(2)—V(2)—O(6)	96·1 (2)
O(1)—V(1)—O(4)	102·1 (2)	O(2)—V(2)—O(7)	160·7 (2)
O(1)—V(1)—O(5)	104·0 (2)	O(2)—V(2)—O(8)	128·9 (2)
O(1)—V(1)—F(1)	169·3 (2)	O(2)—V(2)—F(1)	74·6 (2)
O(1)—V(1)—F(2)	96·3 (2)	O(2)—V(2)—F(3)	91·1 (2)
O(2)—V(1)—O(3)	42·6 (2)	O(3)—V(2)—O(6)	94·7 (2)
O(2)—V(1)—O(4)	128·8 (2)	O(3)—V(2)—O(7)	132·2 (2)
O(2)—V(1)—O(5)	160·7 (2)	O(3)—V(2)—O(8)	87·8 (2)
O(2)—V(1)—F(1)	74·3 (2)	O(3)—V(2)—F(1)	78·7 (2)
O(2)—V(1)—F(2)	91·1 (2)	O(3)—V(2)—F(3)	133·2 (2)
O(3)—V(1)—O(4)	87·6 (2)	O(6)—V(2)—O(7)	103·2 (2)
O(3)—V(1)—O(5)	131·7 (2)	O(6)—V(2)—O(8)	101·6 (2)
O(3)—V(1)—F(1)	78·8 (2)	O(6)—V(2)—F(1)	170·7 (2)
O(3)—V(1)—F(2)	133·1 (2)	O(6)—V(2)—F(3)	99·1 (2)
O(4)—V(1)—O(5)	45·5 (2)	O(7)—V(2)—O(8)	45·5 (2)
O(4)—V(1)—F(1)	86·8 (2)	O(7)—V(2)—F(1)	86·2 (2)
O(4)—V(1)—F(2)	133·1 (2)	O(7)—V(2)—F(3)	87·5 (2)
O(5)—V(1)—F(1)	86·5 (2)	O(8)—V(2)—F(1)	84·8 (2)
O(5)—V(1)—F(2)	88·5 (2)	O(8)—V(2)—F(3)	131·7 (2)
F(1)—V(1)—F(2)	81·4 (2)	F(1)—V(2)—F(3)	81·1 (2)
V(1)—O(2)—V(2)	99·3 (2)	V(1)—O(3)—V(2)	104·3 (2)
		V(1)—F(1)—V(2)	94·6 (1)
K(1)—F(2^{i})	2·674 (4)	K(2)—F(3^{iii})	2·598 (4)
K(1)—F(3^{i})	2·711 (4)	K(2)—F(2^{i})	2·620 (4)
K(1)—F(1)	2·724 (4)	K(2)—F(2^{iv})	2·631 (4)
K(1)—F(3^{ii})	2·730 (4)	K(2)—O(7^{v})	2·742 (5)
K(1)—O(8)	2·813 (5)	K(2)—O(5)	2·791 (5)
K(1)—F(1^{ii})	2·824 (4)	K(2)—O(5^{iv})	2·984 (5)
K(1)—O(4)	2·888 (5)	K(2)—O(9)	3·112 (5)
K(1)—O(7^{ii})	2·962 (4)	K(2)—O(4)	3·168 (5)
K(1)—O(2^{i})	2·990 (5)		
K(3)—O(9)	2·753 (6)	K(3)—O(10)	2·994 (7)
K(3)—O(1^{i})	2·780 (5)	K(3)—O(10^{vi})	3·024 (8)
K(3)—F(4^{vi})	2·794 (8)	K(3)—O(6^{vii})	3·034 (5)
K(3)—O(6^{iii})	2·872 (5)	K(3)—F(4^{v})	3·154 (8)
K(3)—O(3^{vii})	2·879 (4)		

Symmetry code: (i) $x, y, z-1$; (ii) $-x, 1-y, 1-z$; (iii) $x+1, y, z-1$; (iv) $1-x, 1-y, 1-z$; (v) $x+1, y, z$; (vi) $1-x, 2-y, -z$; (vii) $1-x, 2-y, 1-z$.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52742 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

seen in Fig. 1, the second apical site in both bipyramids is occupied by the same F atom F(1). It lies 1·819 (2) Å from the equatorial plane of the V(1) complex and 1·812 (2) Å from the equatorial plane of the V(2) complex. The mean bond distance from V atoms to the tetradentate O(2)—O(3) peroxo group [2·011 (2) Å] is significantly longer than the mean bond distance between V atoms and the other equatorial peroxo groups [1·868 (3) Å]. This is easily explained by the weakening of these four V—O bonds as a consequence of the O(2) and O(3) peroxo O atoms being involved in V—O interactions with opposite V atoms within the complex. The additional lengthening of bond distances V(1)—O(2) and V(2)—O(2) [mean 2·047 (3) Å] in comparison with V(1)—O(3) and V(2)—O(3) [mean 1·975 (3) Å] may probably be explained as a *trans* effect. The O(7) and O(5) atoms are *trans* to the O(2) atom in corresponding polyhedra [O(5)—V(1)—O(2) and O(7)—V(2)—O(2) are both 160·7 (2)°], while there are no atoms *trans* to the O(3) atom. The V(1)—F(1) = 2·119 (3) Å and V(2)—F(1) = 2·124 (3) Å bonds are *trans* to V(1)=O(1) and V(2)=O(6), respectively. They are longer than V(1)—F(2) = 1·896 (4) Å and V(2)—F(3) 1·879 (4) Å because F(1) is the bridging apical atom. This lengthening agrees quite well with the general observation that for pentagonal-bipyramidal oxoperoxometallates, the M—L_{apical} bonds (*trans* to the M=O bond) are longer than the M—$L_{equatorial}$ bonds (Szentivanyi, 1983). The V=O and O—O bond distances lie in the expected range.

The potassium ions have irregular O and F atom environments. The individual K—O and K—F distances less than 3·2 Å are listed in Table 2. The remaining intermolecular non-bonded contacts in the structure are all longer than the sum of the van der Waals radii for the two atoms involved (Pauling, 1960).

The water molecules are weakly hydrogen bonded to the peroxo atoms O(4) and O(7), the hydrogen fluoride and to each other [mean 2·97 (1) Å]. The hydrogen fluoride is also weakly hydrogen bonded to the peroxo O atom O(8) with F···O = 2·87 (1) Å. A higher temperature factor for the hydrogen fluoride and water molecules than for the remaining O and F atoms may be explained by weak bonding and/or partial occupancy for these molecules. The least-squares refinement of occupancy factors for hydrogen fluoride and water molecules shows that the F(4) site is partially occupied [0·78 (2)] while the occupancy of the O(10) and O(9) sites differs from unity within 1σ.

The isothermal decomposition of the title compound was shown previously (Schwendt & Joniakova, 1983*a*) to be accompanied by a simultaneous release of water and hydrogen fluoride. This fact may be interpreted as originating from the above-mentioned peculiarities of the structure which contains both H_2O and HF molecules.

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Structures of Lead Chlorite, Magnesium Chlorite Hexahydrate and Silver Chlorite

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Abstract. $Pb(ClO_2)_2$ (I), $M_r = 340·9$, orthorhombic, *Ccca*, $a = 6·004$ (1), $b = 12·504$ (2), $c = 6·010$ (1) Å, $V = 451·2$ (1) Å^3, $Z = 4$, $D_x = 5·02$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0·70930$ Å, $\mu = 38·76$ mm^{-1}, $F(000) = 592$, $T = 300$ (1) K, final $R = 0·030$ for 502 observed unique reflections. $Mg(ClO_2)_2.6H_2O$ (II), $M_r = 267·3$,

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