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The Crystal Structure of Tripotassium Pentafluoroperoxotantalate(V) Hydrogendifluoride, $K_3[HF_2][TaF_5(O_2)]$. A Redetermination at 290 and 170 K

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Crystals of $K_3[HF_2][TaF_5(O_2)]$ are orthorhombic, space group *Pnam* (No. 62), with $a = 6.976(4)$ Å, $b = 13.82(1)$ Å, $c = 9.072(4)$ Å at 290 K and $a = 6.957(3)$ Å, $b = 13.61(1)$ Å, $c = 9.082(7)$ Å at 170 K. $Z = 4$. Reflexion intensities were registered with an automatic single crystal X-ray diffractometer using Mo$K\alpha$ radiation. Least-squares refinement of structural and thermal parameters yielded a final R-value of 0.049 for 1203 observed reflexions at 290 K and of 0.073 for 1429 observed reflexions at 170 K, using different crystals.

The structure was originally solved by Ružić-Toroš *et al.* using 517 independent reflexions collected by the Weissenberg film technique. The space group $Pna2_1$ was selected. The present reinvestigation has shown, however, that the structure can be refined in space group *Pnam*. The principal features of the coordination geometry and the packing of the ions arrived at by Ružić-Toroš *et al.* are correct, however.

The present investigation has shown that the structure of $K_3[HF_2][TaF_5(O_2)]$ is the same at 290 K and 170 K, the largest discrepancy between bond distances being less than 2.3σ. It is not isomorphous with that of $Na_3[HF_2][NbF_5(O_2)]$.

Peroxo oxygen bond distances are normally 1.49 Å or somewhat shorter in transition metal peroxo compounds.[2-6] Rare exceptions among peroxofluorometallates, a class of compounds being studied at this department, are the dinuclear complex in $K_6[TaF_5(O_2)][O\{TaF_4(O_2)\}_2] \cdot H_2O$,[7] and, possibly, $[TaF_5(O_2)]^{2-}$ in $K_3[HF_2][TaF_5(O_2)]$.[1] O – O distances of 1.69(3) and 1.75(3) Å in the former and of 1.64(16) Å in the latter were observed. In view of the large e.s.d.'s in $K_3[HF_2][TaF_5(O_2)]$, it was thought worthwhile to perform a reinvestigation using diffractometer data.

Ružić-Toroš *et al.*[1] mention that their recorded films were of poor quality due to the decomposition of the crystal. Therefore, it seemed profitable to collect the intensity data at low temperature and, for comparison, at room temperature as well.

EXPERIMENTAL

Preparation. Tantalum(V) oxide was dissolved in an excess of boiling 38 % hydrofluoric acid. The stoichiometric amount of potassium in the form of the hydroxide and an excess of hydrogen peroxide were added. By evaporation of the solvent at room temperature, well-developed, transparent prismatic crystals were obtained. They were crystallographically identified as $K_3[HF_2][TaF_5(O_2)]$.[1]

Data collection. Complete sets of intensities were recorded at 290 K and at 170 K, for different crystals (crystal size $0.09 \times 0.11 \times 0.14$ mm and $0.13 \times 0.14 \times 0.39$ mm, respectively), with a SYNTEX $P2_1$ automatic four-circle single crystal X-ray diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. The crystals were coated with a thin layer of epoxy resin. The $\omega - 2\theta$ scan method was used, and the 2θ scan speed was allowed to vary between $3 - 20°$/min, depending on the intensity of the measured reflexion. Data were collected for $2\theta \leqslant 65°$. Three test reflexions, measured after each fiftieth reflexion, showed no significant difference in intensity during the data collection at 170 K. At 290 K, the intensities of the test reflexions decreased linearly with time, however. The intensity data were corrected for this. Weissenberg photographs, taken as a check measure before and after the data collection, also showed the slight decrease in intensity. These photographs were of rather good quality, unlike those described by Ružić-Toroš *et al.* A profile analysis based on the Lehmann-Larsen method[8] was applied to the

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96-step profile collected for each reflexion. Those reflexions having $I_o \geqslant 3\sigma(I_o)$ (1203 reflexions at 290 K and 1429 at 170 K) were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz, polarization and absorption effects.

The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

CRYSTAL DATA

Tripotassium pentafluoroperoxotantalate(V) hydrogendifluoride, $K_3[HF_2][TaF_5(O_2)]$. F.W.= 464.24. Space group *Pnam* (No. 62; non-standard setting). General positions: $\pm(x,y,z)$; $\pm(\bar{x},\bar{y},\frac{1}{2}+z)$; $\pm(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,z)$. At 290 K: $a=6.976(4)$ Å, $b=13.82(1)$ Å, $c=9.072(4)$ Å, $V=874.4(9)$ Å^3, $Z=4$, $D_c=3.53$ g cm^{-3}. At 170 K: $a=6.957(3)$ Å, $b=13.61(1)$ Å, $c=9.082(7)$ Å, $V=859.9(9)$ Å^3, $Z=4$, $D_c=3.59$ g cm^{-3}. μ(Mo$K\alpha$)=14.7 mm^{-1}, λ(Mo$K\alpha$)=0.71069 Å.

Lists of structure factors and thermal parameters are available from the author upon request.

STRUCTURE REFINEMENT

Block-diagonal least-squares refinement of positional and isotropic thermal parameters, starting with those given by Ružić-Toroš *et al.*, led to an *R*-value of 0.089. Further refinement, introducing anisotropic thermal parameters, reduced the *R*-value to 0.069. F(2) and O(2) showed large anisotropy, however, and the peroxo oxygen bond distance was unacceptably short (1.20 Å). Further refinement along these lines did not seem profitable. A closer examination of the atomic positions at this point showed, however, that the symmetry was almost that of space group *Pnam*, the average discrepancy being 0.09 Å ($=3\sigma$), and the largest 0.25 Å. The latter value applied to O(2), probably due to strong coupling to O(1). The arguments put forward by Ružić-Toroš *et al.* for choosing space group $Pna2_1$ – the number of molecules in the unit cell and the Patterson map – do not seem convincing. Further refinement was, therefore, performed according to space group *Pnam*, which turned out to lead to an acceptable structure proposal.

Full-matrix least-squares refinement of overall scale factors and positional and anisotropic thermal parameters for all non-hydrogen atoms yielded *R*-values of 0.049 and 0.073 for 1203 observed reflexions at 290 K and 1429 at 170 K, respectively. The weighting scheme used was that of Cruickshank:[9] $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$ with $a=50$, $c=0.006$ and $d=0.0003$ for the data collected at 290 K and $a=30$, $c=0.004$ and $d=0.0001$ for those at 170 K. The scattering factors for Ta, K^+, F and O were taken from the *International Tables for X-Ray Crystallography, Vol. IV* (1974), as were the dispersion corrections.

The highest peaks in the difference syntheses calculated after the last refinement cycles, 6 and 7 e/Å^3 at 290 and 170 K, respectively, appeared at less than 1.1 Å from Ta, while the peaks at larger distances than 1.1 Å from Ta or K were smaller than 3.5 e/Å^3.

Calculations were carried out on an IBM 3033 computer using the crystallographic programmes described by Lindgren.[10]

Table 1. Atomic coordinates for $K_3[HF_2][TaF_5(O_2)]$ at 290 and 170 K. Space group *Pnam*. $U_{eq}=\frac{1}{3}(U_{11}+U_{22}+U_{33})$.

		290 K				170 K			
Atom	Site	x	y	z	U_{eq}/Å^2	x	y	z	U_{eq}/Å^2
Ta	4*c*	0.26481(7)	0.07050(4)	$\frac{1}{4}$	0.025	0.26473(10)	0.07003(5)	$\frac{1}{4}$	0.022
K(1)	4*c*	0.2288(4)	0.5983(2)	$\frac{1}{4}$	0.031	0.2293(5)	0.5986(2)	$\frac{1}{4}$	0.016
K(2)	8*d*	0.2328(3)	0.3481(2)	0.0234(2)	0.038	0.2261(4)	0.3488(2)	0.0217(2)	0.022
F(1)	4*c*	0.5522(12)	0.0780(6)	$\frac{1}{4}$	0.035	0.5532(13)	0.0796(7)	$\frac{1}{4}$	0.019
F(2)	4*c*	0.2664(18)	0.2070(7)	$\frac{1}{4}$	0.067	0.2653(22)	0.2077(7)	$\frac{1}{4}$	0.041
F(3)	8*d*	0.3181(14)	0.0691(7)	0.0382(7)	0.062	0.3208(15)	0.0691(6)	0.0391(6)	0.033
F(4)	4*c*	0.3226(15)	−0.0671(6)	$\frac{1}{4}$	0.041	0.3246(15)	−0.0698(6)	$\frac{1}{4}$	0.019
F(5)	8*d*	0.0000(9)	0.2362(5)	0.6264(8)	0.051	−0.0042(12)	0.2340(5)	0.6271(9)	0.027
O	8*d*	0.0119(13)	0.0464(8)	0.1734(13)	0.068	0.0102(14)	0.0478(8)	0.1706(12)	0.033

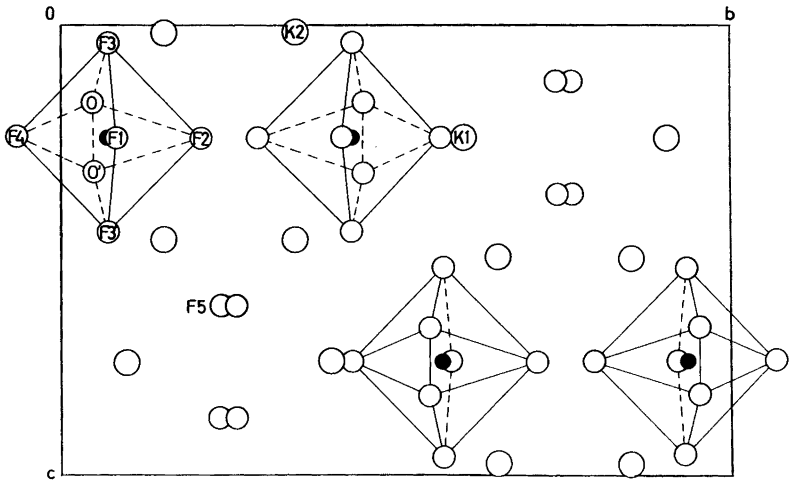

Fig. 1. The crystal structure of $K_3[HF_2][TaF_5(O_2)]$ viewed along the *a*-direction. Full circles represent tantalum atoms.

Table 2. Bond distances and angles in $K_3[HF_2]$-$[TaF_5(O_2)]$ at 290 and 170 K.

	Distance/Å at 290 K	170 K
Ta–F(1)	2.007(8)	2.011(9)
Ta–F(2)	1.886(10)	1.873(10)
Ta–F(3)	1.957(6)	1.955(7)
Ta–F(4)	1.943(9)	1.948(8)
Ta–O	1.925(10)	1.936(10)
O–O′	1.389(24)	1.443(22)
F(5)···F(5)′	2.242(15)	2.233(16)
	Angle/° at 290 K	**170 K**
F(1)–Ta–F(2)	86.7(5)	86.2(5)
F(1)–Ta–F(3)	79.1(3)	78.5(3)
F(1)–Ta–F(4)	81.0(4)	81.4(4)
F(1)–Ta–O	157.5(4)	157.4(3)
F(2)–Ta–F(3)	90.5(3)	90.3(3)
F(2)–Ta–F(4)	167.7(5)	167.5(6)
F(2)–Ta–O	100.2(5)	99.1(5)
F(3)–Ta–F(3)′	158.0(6)	157.0(6)
F(3)–Ta–F(4)	87.2(3)	87.2(3)
F(3)–Ta–O	79.5(4)	79.4(4)
F(3)–Ta–O′	121.8(4)	123.1(4)
F(4)–Ta–O	91.2(4)	92.5(4)
O–Ta–O′	42.3(7)	43.7(6)

RESULTS AND DISCUSSION

The positional parameters as well as U_{eq} are given in Tables 1. The unit cell content projected on (100) is shown in Fig. 1 and the anion in Fig. 2. Bond distances and angles are given in Table 2 and coordination distances to the potassium ions in Table 3.

The crystals of tripotassium pentafluoroperoxotantalate(V) hydrogendifluoride consist of potassium ions, pentafluoroperoxotantalate(V) ions and hydrogendifluoride ions held together by ionic forces. K(1) and K(2) are surrounded by ten and eight nearest fluorine and oxygen atoms at distances ranging from 2.666(6) to 3.006(7) Å and from 2.584(7) to 3.124(10) Å, respectively, at 290 K and from 2.678(7) to 2.981(8) Å and from 2.572(8) to 3.066(9) Å, respectively, at 170 K. These distances may be compared with the radii sum of 2.7 Å. $K_3[HF_2]$-$[TaF_5(O_2)]$ is not isomorphous with $Na_3[HF_2]$-$[NbF_5(O_2)]$.[4]

$[TaF_5(O_2)]^{2-}$ has a pentagonal bipyramidal arrangement of ligands, a configuration met with in several transition metal peroxo complexes (see, *e.g.*, Refs. 2–7, 11–14). In Table 4 are listed the lengths of the edges of the coordination polyhedron. These agree well with the corresponding ones in other pentafluoroperoxometallates.[5] The distances from the equatorial plane, defined by F(1), F(3), F(3)′, O and O′, to these atoms and to Ta, F(2) and F(4) are given in Table 5. This plane is perpendicular

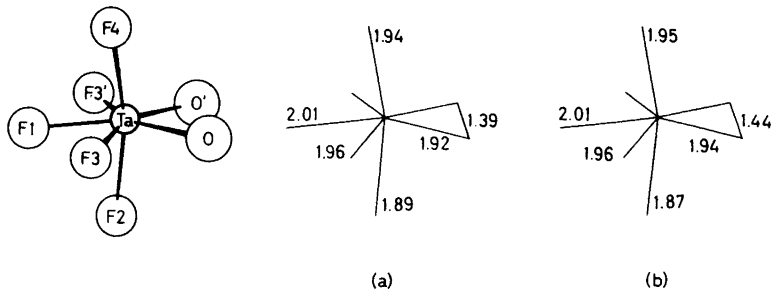

Fig. 2. The ion $[TaF_5(O_2)]^{2-}$. Bond distances at (a) 290 K and (b) 170 K.

to the crystallographic mirror plane through F(1), F(2), F(4) and the midpoint between O and O'. Besides, the angles F(1)–Ta–F(2) and F(1)–Ta–F(4) are approximately equal. The equatorial plane is, therefore, almost a mirror plane. Hence, the point symmetry of $[TaF_5(O_2)]^{2-}$ is almost C_{2v}.

The $Ta-F_{equatorial}$ bond distances, 1.957–2.007 Å at 290 K and 1.955–2.011 Å at 170 K are somewhat longer than the $Ta-F_{apical}$ bond distances, 1.886–1.943 Å and 1.873–1.948 Å, respectively. This compares well with the corresponding distances in a number of pentafluoroperoxoniobates[3-6,14] as well as in $K_6[TaF_5(O_2)][O\{TaF_4(O_2)\}_2]\cdot H_2O$.[7]

The Ta–O distances 1.925 and 1.936 Å, respectively, are normal Ta–O single bond distances, observed ones in $K_6[TaF_5(O_2)][O\{TaF_4(O_2)\}_2]\cdot H_2O$ being 1.86–1.99 Å.[7]

Table 3. Coordination distances to the potassium ions in $K_3[HF_2][TaF_5(O_2)]$.

	Distance/Å at 290 K	170 K
$K(1)\cdots F(3)^{i,ii}$	2.666(6) ×2	2.678(7) ×2
$K(1)\cdots F(1)^{iii}$	2.729(9)	2.717(10)
$K(1)\cdots F(4)^{iii}$	2.867(11)	2.842(11)
$K(1)\cdots O^{iv,v}$	2.894(11) ×2	2.882(11) ×2
$K(1)\cdots F(5)^{vi,vii}$	2.910(7) ×2	2.881(8) ×2
$K(1)\cdots F(5)^{viii,ix}$	3.006(7) ×2	2.981(8) ×2
$K(2)\cdots F(5)^{v}$	2.584(7)	2.572(8)
$K(2)\cdots F(1)^{iii}$	2.619(6)	2.587(6)
$K(2)\cdots F(5)^{x}$	2.622(7)	2.614(8)
$K(2)\cdots F(4)^{ii}$	2.770(5)	2.728(4)
$K(2)\cdots O^{iv}$	2.786(11)	2.777(11)
K(2)···F(2)	2.843(7)	2.839(7)
$K(2)\cdots F(3)^{iii}$	3.114(10)	3.037(10)
$K(2)\cdots F(3)^{ii}$	3.124(10)	3.066(9)

Symmetry codes

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

Table 4. The lengths of the edges of the pentagonal bipyramidal coordination polyhedron in $K_3[HF_2]$-$[TaF_5(O_2)]$. The designation of the edges conforms to Fig. 3 in Ref. 5. Compare with Table 5 in Refs. 5 and 6.

Edge		Distance/Å at 290 K	170 K
a, b	F(1)···F(3)	2.524(10)	2.511(10)
c, e	F(3)···O	2.483(13)	2.486(14)
d	O···O'	1.389(24)	1.443(22)
f, h	F(2)···F(3)	2.730(11)	2.716(11)
g	F(2)···F(1)	2.675(14)	2.655(16)
i, j	F(2)···O	2.926(15)	2.899(16)
k, m	F(4)···F(3)	2.689(10)	2.692(9)
l	F(4)···F(1)	2.565(13)	2.582(13)
n, o	F(4)···O	2.764(14)	2.805(14)

Table 5. Displacements of the atoms from the least-squares equatorial plane in $[TaF_5(O_2)]^{2-}$. Defining atoms are F(1), F(3), F(3)', O and O'.

Atom	Distance/Å at 290 K	170 K
F(1)	0.040	0.026
F(2)	−1.970	−1.941
F(3), F(3)'	−0.035	−0.023
F(4)	1.837	1.857
O, O'	0.019	0.010
Ta	−0.099	−0.082

The peroxo oxygen bond distance is 1.389(24) Å at 290 K and 1.443(16) Å at 170 K and does not deviate significantly from other observations,[2-6,12] although the distance obtained at 290 K seems a bit short. In fact, it is the author's experience that such short distances are often observed when, as in this case, the substance disintegrates during the collection of the data.

The tantalum atom is displaced about 0.1 Å from the equatorial plane. Such small displacements have been observed for other pentafluoroperoxometallates as well as for other transition metal compounds, when, as in this case, the apical positions are occupied by identical ligands.

The F···H···F distance, 2.242 Å at 290 K and 2.233 Å at 170 K, does not differ significantly from the observed values of 2.283 and 2.292 Å in $Na_3[HF_2][NbF_5(O_2)]$[4] or 2.294 Å found in KHF_2 by the neutron diffraction method.[15,16]

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