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The Crystal Structure of Potassium Pentafluoroperoxotantalate(V)–Potassium Hydrogen Difluoride, $K_2[Ta(O_2)F_5].KHF_2$

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Crystals of $K_2[Ta(O_2)F_5].KHF_2$ are orthorhombic, space group $Pna2_1$ with $a=6{\cdot}999$, $b=13{\cdot}848$, $c=9{\cdot}094$ Å, $Z=4$. The compound is sensitive to air and X-rays. The structure was determined from film data by Patterson and Fourier methods and refined by full-matrix least-squares to $R=0{\cdot}095$. The structure is composed of discrete $[Ta(O_2)F_5]^{2-}$, HF_2^- and K^+ ions. Ta–F distances range from 1·88 (6) to 1·95 (4) Å. Ta–O distances are 2·02 (9) and 2·05 (14) Å. The O–O length in the peroxo group is 1·64 (16) Å. F···F in the HF_2^- ion is 2·25 (7) Å.

Experimental

The space group was determined from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The diffraction symmetry and systematic absences indicated space groups $Pnma$ or $Pna2_1$. The solution of the Patterson map and number of molecules in the unit cell ($Z=4$) are in agreement with $Pna2_1$. The subsequent refinement showed that this choice was appropriate.

Cell parameters for the Ta compound were determined from rotation Straumanis photographs round a, b and c. A least-squares treatment of 24 $0kl$, 24 $h0l$ and 19 $hk0$ high-angle reflexions was performed after taking into account the angular dependence of systematic aberration in the form $\Delta d/d=\cos^2\theta/\theta+\cos^2\theta/\sin\theta$ (Popović, 1974). The density was measured at 25 °C pycnometrically with decalin.

Three crystals shaped into spheres were used for the collection of the intensities with radii: 0·0140 for $0kl$–$4kl$, 0·0109 for $h0l$, and 0·0146 cm for $hk0$–$hk1$ reflexions. Equi-inclination Weissenberg photographs were taken with filtered Cu $K\alpha$ radiation and the multiple-film technique. 517 independent reflexions were recorded and their intensities measured by a microdensitometer. The recorded films were of poor quality due to the decomposition of the crystals. The intensities were corrected for absorption (Bond, 1967). Scale factors were determined for the reflexions of each layer line separately and further improved in the course of refinement.

Crystal data

$K_2[Ta(O_2)F_5].KHF_2$ crystals are sensitive to air and X-ray radiation. From the similar cell parameters and analogous chemical formula of the Ta and Nb compounds, isomorphism is presumed.

$K_2[Ta(O_2)F_5].KHF_2$	$K_2[Nb(O_2)F_5].KHF_2$
Symmetry: orthorhombic, space group $Pna2_1$	
a = 6·999 (1)* Å	a = 6·98 (1) Å
b = 13·848 (2)	b = 13·86 (2)
c = 9·094 (1)	c = 9·07 (1)
V = 881·41 Å^3	V = 877·5 Å^3
D_x = 3·50 g cm^{-3}	D_x = 2·85 g cm^{-3}
D_m = 3·45	D_m = 2·82
μ = 106·3 cm^{-1} for Cu $K\alpha$ radiation	
Z = 4	

Structure determination and refinement

The Patterson map was successfully solved in $Pna2_1$ and the coordinates of the Ta and three K atoms were determined. A Fourier synthesis based on the coordinates of those atoms revealed the positions of seven F atoms. A difference synthesis was used to locate the two O atoms of the peroxo group.

The structure (excluding the H atom) was refined by minimizing $\sum w(|F_o|-|F_c|)^2$ by full-matrix least-squares calculations based on 501 observable reflexions. Isotropic full-matrix refinement led to $R=0{\cdot}105$. Application of the Hughes modified weighting function and anisotropic thermal parameters for Ta gave $R=0{\cdot}095$.

Scattering factors given by Cromer & Waber (1965) and anomalous dispersion corrections for Ta and K (Cromer, 1965) were used.

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* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

Table 1. *Final positional* ($\times 10^4$) *and isotropic thermal parameters*

	x	y	z	B (Å^2)
Ta	2646 (4)	708 (2)	0	
K(1)	2713 (20)	994 (12)	5049 (50)	2·1 (2)
K(2)	7274 (43)	1458 (16)	2312 (31)	2·6 (5)
K(3)	2374 (44)	3420 (17)	7818 (32)	2·4 (5)
F(1)	5363 (48)	794 (27)	−112 (109)	2·5 (7)
F(2)	2738 (70)	2062 (38)	−453 (50)	4·7 (1·0)
F(3)	3063 (137)	788 (55)	−2112 (119)	6·0 (2·2)
F(4)	2943 (84)	587 (36)	2048 (67)	1·4 (9)
F(5)	3214 (48)	−663 (29)	190 (62)	2·7 (7)
F(6)	5262 (53)	2737 (29)	3711 (61)	1·7 (7)
F(7)	−218 (60)	2450 (30)	6143 (57)	2·1 (7)
O(1)	195 (117)	431 (58)	1098 (105)	3·3 (1·4)
O(2)	−40 (203)	347 (93)	−696 (145)	6·3 (3·6)

Anisotropic thermal parameters ($\times 10^4$ Å^2)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ta	109 (6)	32 (1)	40 (2)	3 (3)	16 (24)	13 (3)

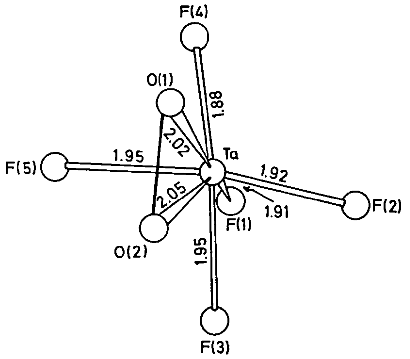

Fig. 1. The Ta coordination sphere.

Atomic and thermal parameters are listed in Table 1; interatomic distances and angles in Table 2.* The calculations were done on a UNIVAC 1106 Computer with the X-RAY 72/73 system.

Description and discussion of the structure

The Ta atom is coordinated by five F atoms and one O_2 group (Fig. 1). The remaining two F atoms are not involved in the coordination sphere, but form HF_2^-. Thus the existence of a double salt in the structure is confirmed. The coordination polyhedra are connected only by means of Coulomb interactions (Fig. 2).

The coordination polyhedron around Ta can be described as an irregular octahedron with one corner located in the middle of the peroxo bond (Fig. 1). The rectangular section of the octahedron [F(1), F(2), F(5), *T*] is nearly perpendicular to the crystallographic c axis, but the F(3)–Ta–F(4) angle is 164°. The deviations from the best plane are listed in Table 3. Ta–F distances range from 1·88 (6) to 1·95 (4) Å. The Ta–O distances are 2·02 (9) and 2·05 (14) Å. The intra-ionic F...F distances range from 2·33 (11) to 3·06 (8) Å, the shortest being in agreement with the distance of 2·357 (4) Å in the structure of K_2NbF_7 (Brown & Walker, 1966).

The F...F distance in HF_2^- of 2·25 (7) Å is in agreement with the value of 2·26 Å in KHF_2 (*International Tables for X-ray Crystallography*, 1968).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31379 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

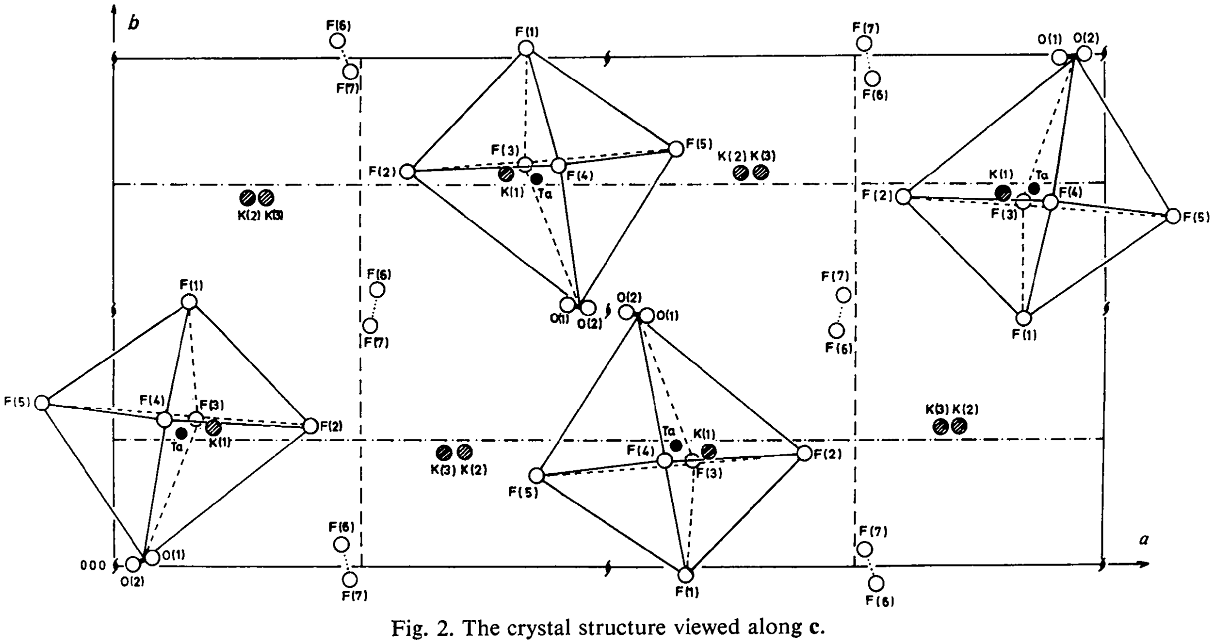

Fig. 2. The crystal structure viewed along **c**.

Table 2. *Interatomic distances and angles*

Within the Ta polyhedron

Ta——F(1)	1·91 (3) Å
Ta——F(2)	1·92 (5)
Ta——F(3)	1·95 (11)
Ta——F(4)	1·88 (6)
Ta——F(5)	1·95 (4)
Ta——O(1)	2·02 (9)
Ta——O(2)	2·05 (14)
F(1)···F(2)	2·56 (6)
F(1)···F(3)	2·43 (13)
F(1)···F(4)	2·61 (10)
F(1)···F(5)	2·53 (5)
F(2)···F(3)	2·33 (11)
F(2)···F(4)	3·06 (8)
F(3)···F(5)	2·90 (11)
F(4)···F(5)	2·43 (7)

F(1)–Ta–F(2)	83 (2)°
F(1)–Ta–F(3)	78 (4)
F(1)–Ta–F(4)	87 (3)
F(1)–Ta–F(5)	82 (2)
F(1)–Ta–O(1)	152 (4)
F(1)–Ta–O(2)	156 (5)
F(2)–Ta–F(3)	74 (3)
F(2)–Ta–F(4)	107 (2)
F(2)–Ta–F(5)	165 (2)
F(2)–Ta–O(1)	109 (3)
F(2)–Ta–O(2)	102 (4)
F(3)–Ta–F(4)	164 (3)
F(3)–Ta–F(5)	96 (3)
F(3)–Ta–O(1)	129 (4)
F(3)–Ta–O(2)	81 (5)
F(4)–Ta–F(5)	79 (2)
F(4)–Ta–O(1)	66 (3)
F(4)–Ta–O(2)	113 (4)
F(5)–Ta–O(1)	87 (3)
F(5)–Ta–O(2)	89 (4)
O(1)–Ta–O(2)	48 (5)

Within peroxo group

O(1)——O(2) 1·64 (16) Å

Within HF_2^-

F(6)···F(7) 2·25 (7) Å

K(1)···F,O ≤3·24 Å

K(1)···F(1)	2·82 (4)
K(1)···F(3)	2·61 (12)
K(1)···F(4)	2·79 (7)
K(1)···F(5)	2·89 (4)
K(1)···F(6)	3·24 (5)
K(1)···F(6^i)	2·74 (5)
K(1)···F(7)	2·78 (5)
K(1)···F(7^i)	3·04 (5)
K(1)···O(1)	2·99 (9)
K(1)···O(2)	2·72 (14)

K(2)···F,O ≤3·27 Å

K(2)···F(1)	2·74 (9)
K(2)···F(2)	3·26 (6)
K(2)···F(3)	3·27 (6)
K(2)···F(4)	3·16 (8)
K(2)···F(5)	2·86 (6)
K(2)···F(6)	2·69 (5)
K(2)···F(6^i)	2·60 (5)
K(2)···O(1)	2·73 (9)

K(3)···F,O ≤3·21 Å

K(3)···F(1)	2·59 (8)
K(3)···F(2)	2·46 (6)
K(3)···F(3)	3·21 (10)
K(3)···F(4)	3·09 (5)
K(3)···F(5)	2·74 (6)
K(3)···F(7)	2·57 (5)
K(3)···F(7^i)	2·72 (5)
K(3)···O(2)	2·83 (14)

Symmetry operation

(i) $(xyz) \rightarrow \frac{1}{2}+x, \frac{1}{2}-y, z$

Table 3. *Distances from the least-squares plane*

F(1)	0·04 (5) Å
F(2)	−0·04 (5)
F(5)	−0·06 (5)
T	0·04 (5)

One corner of the octahedron (*T*) is located in the centre of the peroxo bond.

The three symmetrically independent potassium atoms have different environments (Figs. 3, 4 and 5). K(1) is surrounded by eight F and two O atoms at distances ranging from 2·61 (12) to 3·24 (5) Å, K(2) and K(3) by seven F and one O atom. The K(2)...F,O and K(3)...F,O distances lie in the range 2·60 (5) to 3·27 (6) Å and 2·46 (6) to 3·21 (10) Å, respectively.

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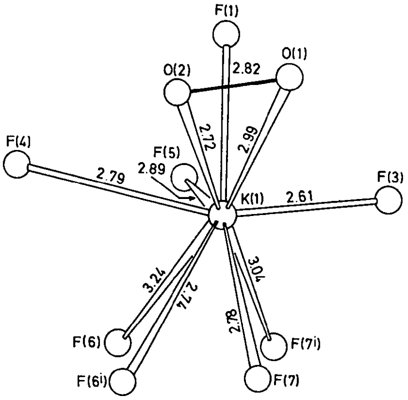

Fig. 3. Environment around K(1).

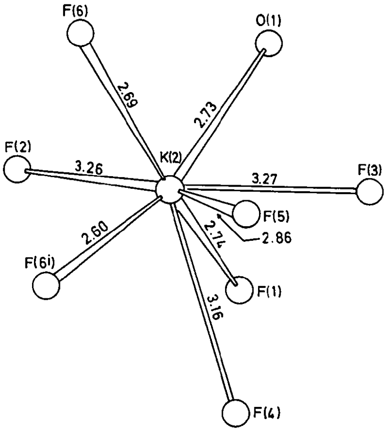

Fig. 4. Environment around K(2).

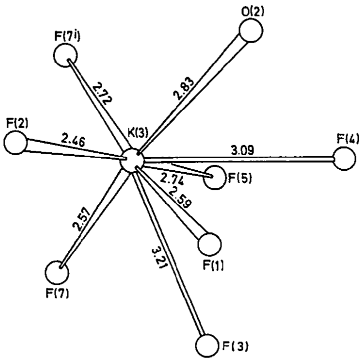

Fig. 5. Environment around K(3).

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