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K₃TaF₈ from laboratory X-ray powder data

**Ľubomír Smrčok,^{a,*} Radovan Černý,^b Miroslav Boča,^a
Iveta Macková^a and Blanka Kubíková^a**

^aInstitute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic, and ^bLaboratory of Crystallography, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland
Correspondence e-mail: lubomir.smrcek@savba.sk

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The crystal structure of tripotassium octafluoridotantalate, K₃TaF₈, determined from laboratory powder diffraction data by the simulated annealing method and refined by total energy minimization in the solid state, is built from discrete potassium cations, fluoride anions and monocapped trigonal-prismatic [TaF₇]^{2−} ions. All six atoms in the asymmetric unit are in special positions of the *P*6₃*mc* space group: the Ta and one F atom in the 2*b* (3*m*) sites, the K and two F atoms in the 6*c* (*m*) sites, and one F atom in the 2*a* (3*m*) site. The structure consists of face-sharing K₆ octahedra with a fluoride anion at the center of each octahedron, forming chains of composition [FK₃]²⁺ running along [001] with isolated [TaF₇]^{2−} trigonal prisms in between. The structure of the title compound is different from the reported structure of Na₃TaF₈ and represents a new structure type.

Comment

In the course of our investigation of the compounds formed in the K–Ta–F system, we have synthesized the title compound, (I), crystallizing in the binary KF–K₂TaF₇ system as a congruently melting product of the two components (Boča *et al.*, 2007; Netriová *et al.*, 2009). The existence of this compound has been suggested previously (Efros & Lantratov, 1963; Kovalev *et al.*, 1973), but up until now no structural data have been reported.

Since (I) has been obtained only in the form of a fine powder, its structure was solved from laboratory X-ray powder data (Fig. 1). All six atoms in the asymmetric unit were found to be in special positions of the *P*6₃*mc* space group: atoms Ta1 and F3 in the 2*b* position, atoms K1, F2 and F4 in the 6*c* position, and, finally, atom F1 in the 2*a* position.

The structure is composed of monocapped [TaF₇]^{2−} trigonal prisms (Fig. 2) and octahedra of K⁺ cations, each with an F[−] anion at the center. The F-centered K₆ octahedra share faces to create infinite chains of composition [FK₃]²⁺ along the *c* axis (Fig. 3). The discrete [TaF₇]^{2−} anions are located between the

cationic chains. The individual Ta–F bond distances in the monocapped trigonal prisms (Table 1) are in good agreement with the range of 1.919 (3)–1.976 (2) Å found for the similar polyhedron in the low-temperature phase of K₂TaF₇ (Torardi & Brixner, 1987). The arrangement of the K atoms in (I) is dictated by the presence of the eighth fluoride anion. While in K₂TaF₇, two independent K⁺ cations are nine-coordinated (K–F < 3.0 Å) by the F[−] anions, all of which are shared with the Ta^V atoms, in (I) the F1 anions bond exclusively to the unique K1 cation and the remaining seven fluoride anions are shared with atom Ta1. The [FK₆] octahedra show only a slight deviation from ideal geometry, as the individual K1–F1 bond distances (Table 1) are close to one another and the deviations from the ideal octahedral K–F–K bond angles are less than 2°. These K–F bond distances agree well with the octahedral K–F distances (2.674 Å) in the structure of carobbiite, KF (Wyckoff, 1963). Different bonding conditions in (I) and K₂TaF₇ also lead to different K⋯K separations, which are

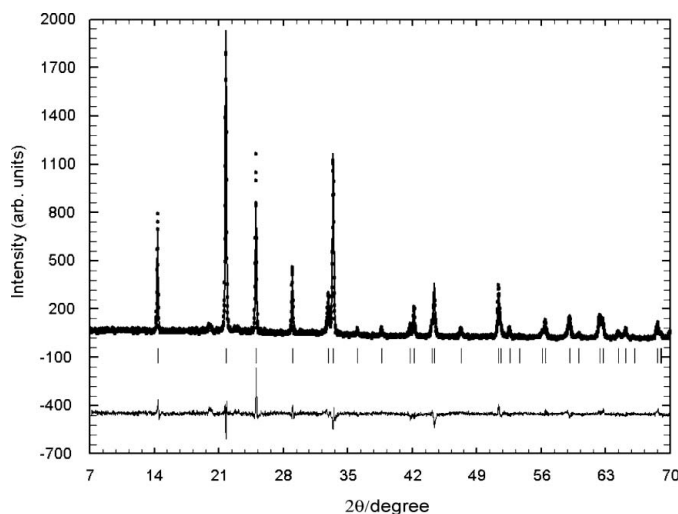


Figure 1

The results of Rietveld refinement. Data are given as filled circles, the calculated profile as a solid line and the difference profile as a solid line below. Vertical markers above the difference profile indicate the calculated Bragg reflection positions.

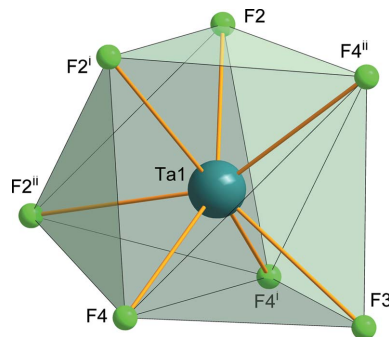
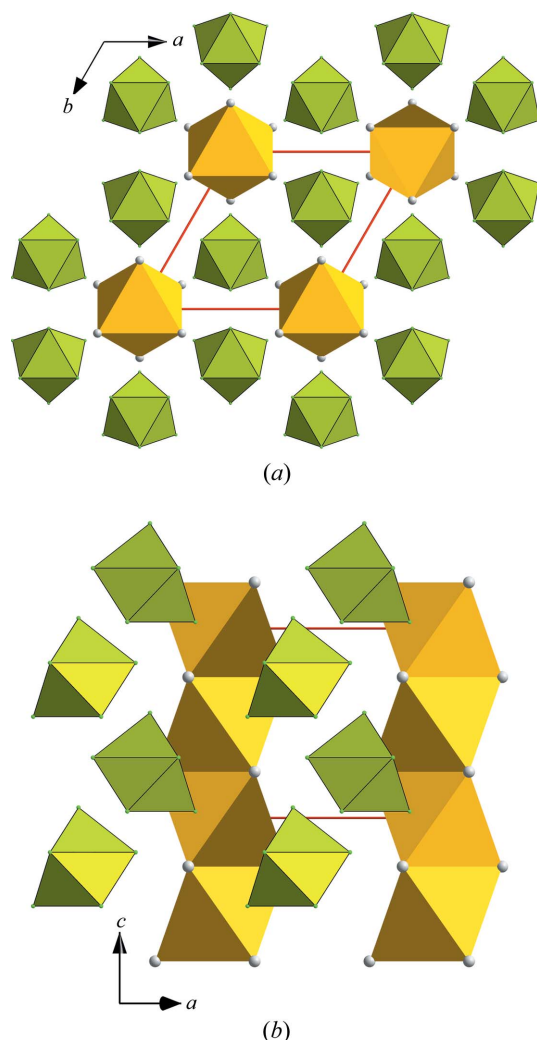


Figure 2

The [TaF₇]^{2−} polyhedron. The triangles F2/F2'/F4'' and F3/F4/F4' form the bases of a distorted trigonal prism capped by atom F2'. [Symmetry codes: (i) $-y + 1, x - y, z$; (ii) $-x + y + 1, -x + 1, z$.]

**Figure 3**

(a) A polyhedral representation of the structure of (I) as viewed along the c axis. (The smaller $[\text{TaF}_7]^{2-}$ polyhedra are shown in green in the electronic version of the paper, while the larger $[\text{FK}_6]$ octahedra are yellow.) (b) A polyhedral representation of the structure of (I) as viewed along the b axis. The F-centered K_6 octahedra share faces to form infinite chains of composition $[\text{FK}_3]^{2+}$ running along $[001]$, with isolated $[\text{TaF}_7]^{2-}$ anions positioned in between the chains.

reduced from 4.08 Å in K_2TaF_7 to 3.83 Å in (I). To our knowledge, K_3TaF_8 belongs to a new structure type.

Our structure determination has ruled out the hypothesis of eightfold fluoride coordination of the Ta atoms as identified in the structure of trisodium octafluorotantalate, Na_3TaF_8 (Hoard *et al.*, 1956). In the Na_3TaF_8 structure, solved only from the $h0l$ and $hk0$ projections calculated using film data with no refinement having been carried out, the $[\text{TaF}_8]^{3-}$ groups are suggested to have a configuration of a square antiprism, with the sodium cations surrounded by six fluoride anions forming an octahedron. However, the uncertainties in the choice of the unit cell, indicating possible problems with pseudosymmetry (*i.e.* a monoclinic β angle of *ca* 121°), a rather low number of structure factors and the absence of any refinement throw some doubts on the accuracy of the structure of that compound.

Experimental

K_2TaF_7 (2.613 g) and KF (0.387 g) were placed in a Pt crucible, gently mixed and the crucible hermetically sealed. The system was heated to 1123 K in a furnace for 30 min and then cooled slowly at a rate of 1 K min⁻¹ to 973 K and at a rate of 5 K min⁻¹ to 473 K. After the system had cooled to room temperature, a white polycrystalline sample was removed and powdered under a dry nitrogen atmosphere.

Crystal data

K_3TaF_8	$Z = 2$
$M_r = 450.25$	Cu $K\alpha_1$ radiation
Hexagonal, $P6_3mc$	$\lambda = 1.78892$ Å
$a = 8.2533$ (4) Å	$\mu = 285.81$ mm ⁻¹
$c = 6.3196$ (4) Å	$T = 298$ K
$V = 372.79$ (3) Å ³	Flat sheet, 8×0.1 mm

Data collection

Stoe Stadi P diffractometer	Scan method: step
Specimen mounting: between two Mylar foils	$2\theta_{\min} = 7.12^\circ$, $2\theta_{\max} = 69.98^\circ$,
Data collection mode: transmission	$2\theta_{\text{step}} = 0.02^\circ$

Refinement

$R_p = 12.725$	$S = 1.6$
$R_{wp} = 15.870$	$\chi^2 = 2.560$
$R_{\text{exp}} = 12.490$	3144 data points
$R_{\text{Bragg}} = 0.1$	4 parameters

Table 1

Selected bond lengths (Å).

Ta1—F2	1.9953 (1)	K1—F1 ^{iv}	2.7517 (2)
Ta1—F3	1.9844 (1)	K1—F4 ^v	2.7614 (2)
Ta1—F4	1.9643 (1)	K1—F3 ^{vi}	2.8175 (2)
K1—F4 ⁱⁱⁱ	2.6427 (2)	K1—F2	2.8869 (2)
K1—F1	2.6848 (2)		

Symmetry codes: (iii) $x - y + 1, x, z - \frac{1}{2}$; (iv) $x - y, x, z + \frac{1}{2}$; (v) $-y + 1, x - y + 1, z - 1$; (vi) $x, y, z - 1$.

The X-ray powder diffraction pattern was indexed using the program *ITO* (Visser, 1969) via the positions of 20 diffraction peaks. The accuracy of the lattice parameters was improved by several cycles of LeBail decomposition of the pattern as implemented in the *FULLPROF* code (Rodríguez-Carvajal, 1993). The systematic absences suggested extinction symbol $P\bar{c}$. A satisfactory structure solution was obtained in the space group $P6_3mc$ using the *FOX* program (Favre-Nicolin & Černý, 2002).

The solved structure was then expanded to $P1$ symmetry and the atoms moved from the respective special positions and refined using total energy minimization with the *VASP* code (Kresse & Furthmüller, 1996; Kresse & Hafner, 1993). The main advantage of such an approach is that the contributions of the atoms to the electron-density distribution are not weighted by their scattering power, in contrast to X-ray diffraction. Secondly, this approach provides a remedy to the chronic difficulty of standard powder refinements, which is the lack of information extractable from a powder pattern (see, for example, Smrčok *et al.*, 2007, 2008).

Geometry analysis using the *PLATON* program (Spek, 2009) revealed that the symmetry of the optimized structure could be increased to $P6_3mc$ as the r.m.s. deviations between the atomic coordinates of the $P1$ structural units, expected to be symmetrically equivalent in $P6_3mc$, were negligible. Furthermore, the typical deviation of the optimized fractional coordinates from the expected

special positions was only 0.004 in the $P1$ model. In the final step, the optimized atomic coordinates were transformed back to the $P6_3mc$ space group and introduced into a Rietveld refinement; three groups (Ta, K and one for all F atoms) of isotropic displacement parameters plus the scale parameter were refined, keeping the profile and atomic parameters fixed. The refined values of the isotropic displacement parameters, *i.e.* $0.080(2) \text{ \AA}^2$ for Ta, $0.090(3) \text{ \AA}^2$ for K and $0.091(5) \text{ \AA}^2$ for F, do not show any anomalies that would indicate possible problems with the structural model. The overall fit ($R_{wp} = 0.16$) is shown in Fig. 1.

Theoretical calculations were carried out using the *VASP* package (Kresse & Furthmüller, 1996; Kresse & Hafner, 1993). The calculations were based on the density functional theory with periodic boundary conditions using the generalized gradient approximation in the exchange-correlation functional (Perdew *et al.*, 1992). The interactions between ions and electrons were described using the projector augmented wave method (Kresse & Joubert, 1999) with a plane-wave cutoff of 400 eV. The optimization of the structure was performed by the method of conjugated gradient in $4k$ points (Teter *et al.*, 1989; Bylander *et al.*, 1990).

Data collection: *X-POW* (Stoe & Cie, 1994); cell refinement: *ITO* (Visser, 1969); data reduction: *X-POW*; program(s) used to solve structure: *FOX* (Favre-Nicolin & Černý, 2002); program(s) used to refine structure: *VASP* (Kresse & Furthmüller, 1996; Kresse & Hafner, 1993) and *FULLPROF* (Rodriguez-Carvajal, 1993); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3230). Services for accessing these data are described at the back of the journal.

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