# Dipotassium heptafluorotantalate(V), $\beta$-K$_2$TaF$_7$, at 509 K

## Vratislav Langer,[a] Ľubomír Smrčok[b] and Miroslav Boča[b]*

[a]Environmental Inorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and [b]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic

Correspondence e-mail: uachsmrk@savba.sk

Upon heating to 509 K, monoclinic $\alpha$-K$_2$TaF$_7$ ($P2_1/c$) transforms to orthorhombic $\beta$-K$_2$TaF$_7$ ($Pnma$) which is composed of discrete K$^+$ cations and TaF$_7{}^{2-}$ anions. In the anion, the Ta atom is sevenfold coordinated by F atoms, with the Ta—F distance varying from 1.88 (2) to 1.965 (19) Å. The two independent K$^+$ cations are surrounded by F atoms positioned within 2.740 (17)–2.979 (10) and 2.989 (17)–3.15 (5) Å. Ta, both K and one of the four F atoms are located on a mirror plane, Wyckoff position 4$c$.

## Comment

K$_2$TaF$_7$, also known as K-salt, is one of the components for electrodeposition of pure tantalum metal. Tantalum is used in electroplating of cheaper metal substrates by a compact thin layer. The thin tantalum oxide layer, which is formed on the surface, has exceptional thermodynamic stability and acts as an effective corrosion barrier. The corrosion resistance of tantalum can be compared to that of a glass.

The low-temperature crystal structure of K$_2$TaF$_7$ was reported for the first time by Hoard (1939) and was later independently confirmed by English *et al.* (1983) and Torardi *et al.* (1987). K$_2$TaF$_7$ has also been investigated using NMR, IR and Raman spectroscopy (Heyns, 1982; Reynhardt *et al.*, 1981; English *et al.*, 1983). Analysis of the NMR experiments suggests that the TaF$_7{}^{2-}$ anion undergoes a rapid floppy reorientation above 260 K during which the shape of the TaF$_7{}^{2-}$ anion changes. Since K$_2$TaF$_7$ is used for molten-salt applications, knowledge of the structural changes during heating below the melting temperature is desirable in order to propose an accurate model of solid–liquid phase transitions. The model of the phase transition $\alpha$-K$_2$TaF$_7$ $\longleftrightarrow$ $\beta$-K$_2$TaF$_7$ proposed by Agulyansky *et al.* (1982) and Agulyansky (2003)
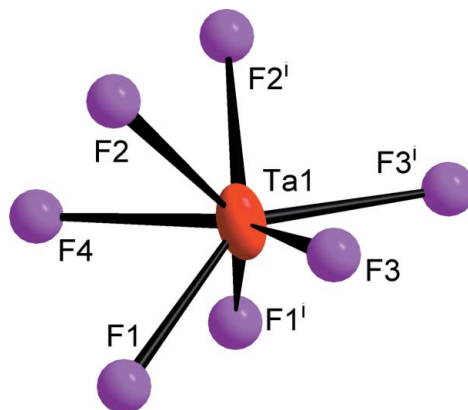


**Figure 1**
The environment around the Ta atom. Displacement ellipsoids (spheres for the isotropic F atoms) are drawn at the 50% probability level. [Symmetry code: (i) $x, \frac{1}{2} - y, z$.]
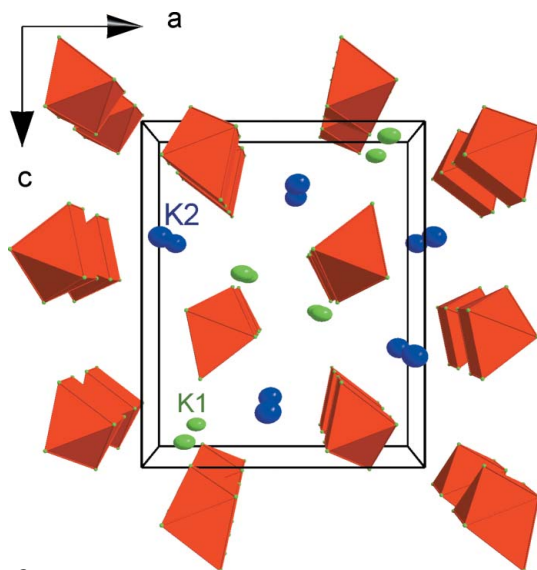
**Figure 2**
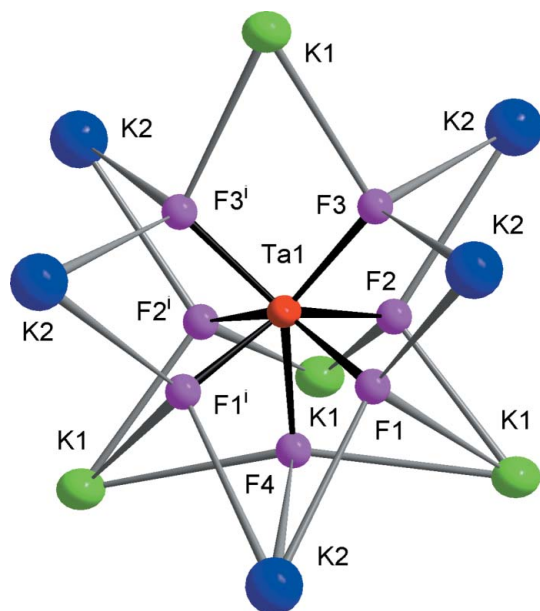Polyhedral representation of the crystal structure of $\beta$-K$_2$TaF$_7$, viewed along the $b$ axis.



**Figure 3**
The {TaF$_7$} polyhedron and surrounding K$^+$ ions. [Symmetry code: (i) $x$, $\frac{1}{2} - y$, $z$.]

was based on knowledge derived only from X-ray powder diffraction data, IR spectroscopy and differential thermal analysis. The reported powder diffraction pattern taken at ~500 K was not, however, indexed. In order to allow an interpretation of high-temperature powder diffraction data, the crystal structure of the $\beta$-phase was determined from single-crystal X-ray data measured at 509 K.

The crystal structure of $\beta$-K$_2$TaF$_7$ is composed of discrete K$^+$ cations and TaF$_7^{2-}$ anions. The TaF$_7$ polyhedron is shown in Fig. 1 and the packing of the polyhedra is displayed in Fig. 2. In the anion, the Ta atom is sevenfold coordinated by F atoms, with Ta—F distances between 1.88 (2) and 1.965 (19) Å. Those values are in reasonable agreement with the range 1.919 (3)–

1.976 (2) Å observed for the TaF$_7$ polyhedron in the low-temperature $\alpha$-phase (Torardi *et al.*, 1987). In relation to the $\alpha$-phase, the polyhedral volumes in the $\beta$-phase are increased by a factor of ~1.2. The two K cations are surrounded by F atoms positioned within 2.740 (17)–2.979 (10) and 2.989 (17)–3.15 (5) Å, respectively. The K—F distances are longer than those in the $\alpha$-phase, and the number of atoms formally coordinating the K$^+$ cations increases from nine to ten (K1) and eleven (K2), respectively.

In addition to one strong bond to Ta, each F atom is electrostatically bonded to three K$^+$ cations (Fig. 3).

## Experimental

The crystal was selected from a bottle of 99.5% pure K$_2$TaF$_7$ produced by the Institute of Chemistry, Kola Science Centre of the Russian Academy of Sciences, Apatity, Russia.

*Crystal data*

| | |
|---|---|
| K$_2$TaF$_7$ | Mo $K\alpha$ radiation |
| $M_r = 392.15$ | Cell parameters from 801 |
| Orthorhombic, $Pnma$ | reflections |
| $a = 9.8155\ (15)$ Å | $\theta = 2.7$–$28.3°$ |
| $b = 5.8212\ (8)$ Å | $\mu = 17.30$ mm$^{-1}$ |
| $c = 12.0041\ (18)$ Å | $T = 509\ (2)$ K |
| $V = 685.89\ (17)$ Å$^3$ | Rod, colorless |
| $Z = 4$ | $0.82 \times 0.28 \times 0.28$ mm |
| $D_x = 3.798$ Mg m$^{-3}$ | |

*Data collection*

| | |
|---|---|
| Siemens SMART CCD diffractometer | 771 independent reflections |
| $\omega$ scans | 443 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002) | $R_{\mathrm{int}} = 0.062$ |
| | $\theta_{\mathrm{max}} = 28.3°$ |
| $T_{\mathrm{min}} = 0.025$, $T_{\mathrm{max}} = 0.085$ | $h = -13 \rightarrow 5$ |
| 2231 measured reflections | $k = -4 \rightarrow 5$ |
| | $l = -14 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.123P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.071$ | $+ 12.4367P]$ |
| $wR(F^2) = 0.220$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{\mathrm{max}} < 0.001$ |
| 771 reflections | $\Delta\rho_{\mathrm{max}} = 1.48$ e Å$^{-3}$ |
| 34 parameters | $\Delta\rho_{\mathrm{min}} = -2.42$ e Å$^{-3}$ |

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Ta—F4 | 1.95 (5) | K1—F1$^{ii}$ | 2.88 (2) |
| Ta—F1 | 1.88 (2) | K1—F4$^{vii}$ | 2.979 (10) |
| Ta—F1$^i$ | 1.88 (2) | K1—F4 | 2.979 (10) |
| Ta—F3$^i$ | 1.94 (3) | K2—F2$^{vi}$ | 2.989 (17) |
| Ta—F3 | 1.94 (3) | K2—F2$^{viii}$ | 2.989 (17) |
| Ta—F2 | 1.965 (19) | K2—F1$^{ix}$ | 3.02 (2) |
| Ta—F2$^i$ | 1.965 (19) | K2—F1$^x$ | 3.02 (2) |
| K1—F2$^{ii}$ | 2.740 (17) | K2—F3$^{ix}$ | 3.12 (3) |
| K1—F2 | 2.740 (17) | K2—F3$^x$ | 3.12 (3) |
| K1—F2$^{iii}$ | 2.779 (19) | K2—F4 | 3.15 (5) |
| K1—F2$^{iv}$ | 2.779 (19) | K2—F3$^{vi}$ | 3.04 (3) |
| K1—F3$^v$ | 2.78 (3) | K2—F3$^{viii}$ | 3.04 (3) |
| K1—F3$^{vi}$ | 2.78 (3) | K2—F1$^i$ | 3.08 (2) |
| K1—F1 | 2.88 (2) | K2—F1 | 3.08 (2) |

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

The single crystal was heated in a stream of hot nitrogen. Only one series of $\omega$ scans could succesfully be indexed and integrated. After this measurement, the crystal suddenly did not diffract any more. Analysis of systematic extinctions and the intensity statistics led to the space group *Pnma*, a supergroup of $P2_1/c$ in which the structure of $\alpha$-$K_2TaF_7$ is described (Torardi *et al.*, 1987). The values of the cell parameters (*a*, *b* and *c*) are within 94–115% of those of the $\alpha$-phase, but the cell setting is $a_\beta = c_\alpha$, $b_\beta = a_\alpha$, $c_\beta = b_\alpha$. [Note that the angle $\beta$ in the $\alpha$-phase is very close to 90°.] Ta and both $K^+$ cations were refined anisotropically, while F atoms were refined isotropically without any restraints. The highest peak and deepest hole in the final Fourier map were 0.27 Å from F4 and 0.72 Å from Ta1, respectively.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *PLATON* (Spek, 2003).

## References

Agulyansky, A. (2003). *J. Fluorine Chem.* **123**, 155–161.
Agulyansky, A., Bessonova, V., Kuznetsov, V. & Sklokina, N. (1982). *Zh. Neorg. Khim.* **27**, 679–682.
Brandenburg, K. (2000). *DIAMOND*. Version 2.1.d. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
English, R. B., Heyns, E. C. & Reynhardt, E. C. (1983). *J. Phys. C*, **16**, 829–840.
Heyns, A. M. (1982). *J. Mol. Struct.* **79**, 391–394.
Hoard, J. L. (1939). *J. Am. Chem. Soc.* **61**, 1252–1259.
Reynhardt, E. C., Pratt, J. C., Watton, A. & Petch, E. H (1981). *J. Phys. C: Solid State Phys.* **14**, 4701–4715.
Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Torardi, C. C., Brixner, L. H. & Blasse, G. (1987). *J. Solid State Chem.* **67**, 21–25.