Redetermination of Na₃TaF₈

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-412 96 Göteborg, Sweden, and [b]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic
Correspondence e-mail: langer@chalmers.se

The crystal structure of trisodium octafluoridotantalate, Na_3TaF_8, has been redetermined using diffractometer data collected at 153 K, resulting in more accurate bond distances and angles than obtained from a previous structure determination based on film data. The structure is built from layers running along [101], which are formed by distorted $[TaF_8]$ antiprisms and $[NaF_6]$ rectangular bipyramids sharing edges and corners. The individual layers are separated by eight-coordinated Na ions. Two atoms in the asymmetric unit are in special positions: the Ta atom is on a twofold axis in Wyckoff position 4e and one of the Na ions lies on an inversion centre in Wyckoff site 4d.

Comment

As part of our structure investigations of compounds containing Ta—F bonds (Langer *et al.*, 2006; Smrčok *et al.*, 2008, 2010), we present here a new structure determination providing well determined atomic coordinates essential for future spectral and quantum chemistry studies. The structure of trisodium octafluoridotantalate was reported previously to be solved in a face-centred pseudo-orthorhombic cell (though the correct monoclinic space group $C2/c$ was recognized) using Patterson and Fourier techniques from the $h0l$ and $hk0$ projections obtained from film data, but with no subsequent refinement carried out (Hoard *et al.*, 1954). The coordinates were given for both pseudo-orthorhombic and monoclinic cells, but unfortunately those in the true monoclinic space group are incorrect, as the authors did not realise that the coordinate systems have different origins. The monoclinic coordinates (Hoard *et al.*, 1954) transform approximately to the equivalent solution as presented here by transformation of the unit cell ($-a$, $-b$, $a + c$), with a shift of origin by ($\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{2}$).

The structure of Na_3TaF_8 can be regarded as consisting of layers built by sharing corners and/or edges of $[TaF_8]$ antiprisms (Ta1 is on a twofold rotation axis, Wyckoff position 4e) and deformed $[NaF_6]$ rectangular bipyramids (Na1 lies on an inversion centre at position 4d) (Fig. 1). The Na2 ions, which

like all the F atoms appear in general positions of the $C2/c$ space group, are sandwiched between the layers and their formal coordination number is eight. The individual Ta—F bond distances in the antiprism (Table 1 and Fig. 2) are longer than those in the monocapped $[TaF_7]$ trigonal prisms in K_2TaF_7 [1.919 (3)–1.976 (2) Å; Torardi & Brixner, 1987], but comparable to the Ta—F bond distances in the $[TaF_7]$ prism in K_3TaF_8 (energy minimization data: 1.964–1.995 Å; Smrčok *et al.*, 2010). The longest Ta—F bond distances involve F1 and F4 shared by the shorter basal edge of the Na1 polyhedron (Fig. 3). Somewhat shorter Ta—F bonds involve F3 atoms, which are shared by the corners of Na1–F bipyramids and the $[TaF_7]$ antiprism, while the shortest Ta—F bonds involve F2 atoms engaged only in a bond to the interlayer Na2 ion. This variation in the Ta—F bond lengths is of the same order as in the antiprisms of $[IF_8]$, $[WF_8]$ and $[ReF_8]$, but is remarkably
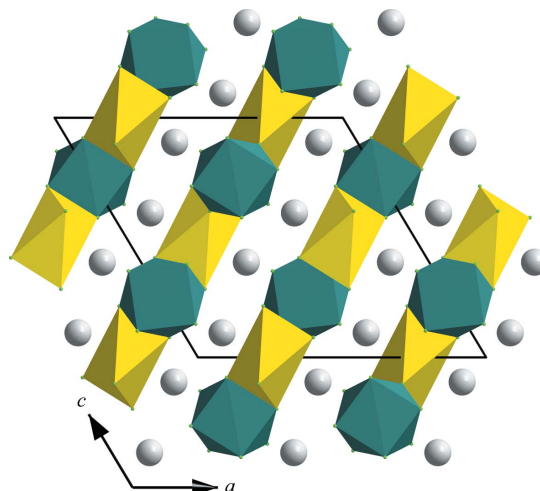

Figure 1
Polyhedral representation of the title structure, viewed along the *b* axis. The $[TaF_8]$ polyhedra are dark (dark green in the electronic version of the paper), the $[NaF_6]$ rectangular bipyramids around Na1 ions are light grey (yellow) and the Na2 ions are depicted as large spheres.
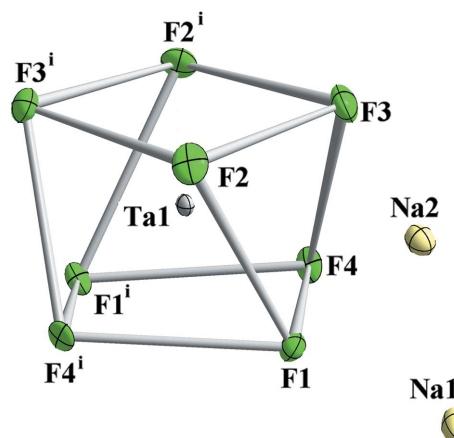

Figure 2
The numbering scheme for the title compound, with displacement ellipsoids drawn at the 50% probability level. Slightly deformed F2/F3/F2^i/F3^i and F1/F4/F1^i/F4^i squares form the upper and lower bases of the distorted $[TaF_8]$ antiprism. The F···F separations in the lower and upper bases are 2.354 (5)/2.415 (4) and 2.365 (6)/2.406 (3) Å, respectively. [Symmetry code: (i) $-x + 1$, y, $-z + \frac{3}{2}$.]
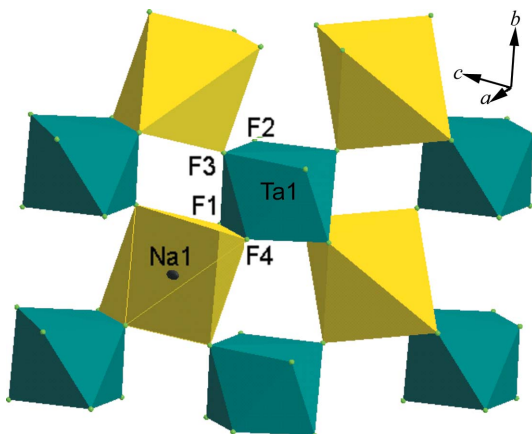
Figure 3
A layer consisting of [TaF$_8$] antiprisms joined to [NaF$_6$] polyhedra.

smaller than that in [XeF$_8$] (Adam *et al.*, 1996). The F···F contact distances within the bases of the antiprism (Fig. 2) are slightly shorter than those separating the atoms of the respective bases, *i.e.* 2.469 (5) Å [F3—F4 and F3^i—F4^i; symmetry code: (i) $-x + 1$, y, $-z + \frac{3}{2}$] or 2.484 (4) Å (F1—F2 and F1^i—F2^i).

The values of the Na—F distances span the reference value of 2.317 Å reported for NaF (Deshpande, 1961), but the majority of them are longer. Because all of the distances are shorter than the sum of the van der Waals radii for Na and F (3.74 Å), they can be considered to be bonded distances. The coordination polyhedron around the hexacoordinate Na1 ion is a distorted rectangular bipyramid with two sets of Na—F bond distances (Table 1). The polyhedron around the Na2 ion is a highly distorted cube, with the span of Na—F distances being greater (0.350 Å) than in the polyhedron around the Na1 ion (0.208 Å).

Experimental

A solution of HF [weight fraction (w) = 5.4×10^{-4}, 327.5 ml] was prepared by dilution of concentrated HF (w = 0.40, 0.5 ml) with distilled water. This solution (30 ml) was used as the solvent for NaF (0.152 g, 3.62 mmol) and TaF$_5$ (0.25 g, 0.91 mmol). The latter compound was weighted in a dry-box into a hermetically sealed transport ampoule before dissolving it in HF solution. Evaporation from this solution at room temperature for 5 d yielded a solid phase. When this had formed in a sufficient amount, it was filtered off, washed with acetone and dried under vacuum at 333 K for 30 min. All experiments were carried out using platinum or plastic dishes.

Crystal data

Na$_3$TaF$_8$	V = 589.25 (12) Å^3
M_r = 401.92	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 11.5203 (14) Å	μ = 18.98 mm^{-1}
b = 5.3453 (6) Å	T = 153 K
c = 11.1540 (13) Å	$0.24 \times 0.18 \times 0.07$ mm
β = 120.919 (2)°	

Table 1
Selected bond lengths (Å).

Ta1—F1	2.002 (3)	Na2—F1^{iii}	2.428 (3)
Ta1—F2	1.981 (3)	Na2—F2	2.557 (4)
Ta1—F3	1.991 (3)	Na2—F2^{iv}	2.264 (4)
Ta1—F4	2.036 (3)	Na2—F3	2.614 (4)
Na1—F1	2.231 (3)	Na2—F3^{ii}	2.506 (4)
Na1—F3^{ii}	2.234 (3)	Na2—F4^v	2.299 (3)
Na1—F4	2.439 (3)	Na2—F4^{ii}	2.382 (3)
Na2—F1	2.375 (3)	Na2—Na1^{vi}	3.405 (2)

Symmetry codes: (ii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 2$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $-x + 1, -y + 2, -z + 2$; (v) $x, -y + 1, z + \frac{1}{2}$; (vi) $x, y + 1, z$.

Data collection

Siemens SMART CCD area-detector diffractometer	4688 measured reflections
	1030 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	961 reflections with $I > 2\sigma(I)$
T_{min} = 0.092, T_{max} = 0.350	R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024	58 parameters
$wR(F^2)$ = 0.051	$\Delta\rho_{max}$ = 1.93 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = -3.00 e Å^{-3}
1030 reflections	

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

References

Adam, S., Ellern, A. & Seppelt, K. (1996). *Chem. Eur. J.* **2**, 398–402.
Brandenburg, K. (2009). *DIAMOND.* Version 3.2c. Crystal Impact GbR, Bonn, Germany.
Bruker (2003). *SMART* (Version 5.63) and *SAINT* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
Deshpande, V. T. (1961). *Acta Cryst.* **14**, 794.
Hoard, J. L., Martin, W. J., Smith, M. E. & Whitney, J. F. (1954). *J. Am. Chem. Soc.* **76**, 3820–3823.
Langer, V., Smrčok, Ľ. & Boča, M. (2006). *Acta Cryst.* E**62**, i91–i93.
Sheldrick, G. M. (2003). *SADABS.* Version 2.03. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Smrčok, Ľ., Brunelli, M., Boča, M. & Kuchárik, M. (2008). *J. Appl. Cryst.* **41**, 634–636.
Smrčok, Ľ., Černý, R., Boča, M., Macková, I. & Kubíková, B. (2010). *Acta Cryst.* C**66**, i16–i18.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Torardi, C. C. & Brixner, L. H. (1987). *J. Solid State Chem.* **67**, 21–25.