Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Bis(tetramethylammonium) di-$\mu$-fluoro-bis[aquatetrafluorohafnate(IV)]

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Received 26 October 2005
Accepted 19 December 2005

**Key indicators**

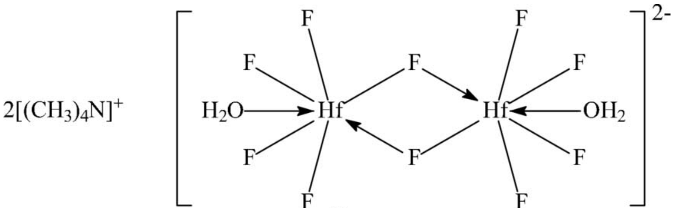
Single-crystal X-ray study
$T$ = 295 K
Mean $\sigma$(N–C) = 0.007 Å
$R$ factor = 0.021
$wR$ factor = 0.055
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The $Hf^{IV}$ atoms in the centrosymmetric title compound, $(C_4H_{12}N)_2][Hf_2F_{10}(H_2O)_2]$, are bridged by two F atoms. The $Hf^{IV}$ atoms show pentagonal–bipyramidal coordination. The dianions are linked by water–fluorine hydrogen bonds into layers.

## Comment

Fluorocomplexes of zirconium and hafnium feature coordination numbers 6, 7 and 8 resulting from monomeric, dimeric, tetrameric and polymeric formulations; the oligomeric formulations involve fluorine bridging (Davidovich, 1998). The Zr atom in the bis(tetramethylammonium) di[aquapentaflurozirconate(IV)] salt shows pentagonal–bipyramidal coordination arising from such bridging. One of the equatorial sites is occupied by the coordinated water molecule (Bukvetskii *et al.*, 1985). The analogous hafnium(IV) salt, (I) (Fig. 1), adopts a similar structure. However, the two compounds are not isostructural although both belong to the same space group.



(I)

The dianion of (I) lies on an inversion centre and the two metal sites are nearly symmetrically bridged by two F atoms. Strong hydrogen bonds between water and F atoms (Table 2) lead to a layer motif.

## Experimental

The title compound was synthesized by treating a small quantity of oxonium hexafluorohafnate(V) with 20% aqueous tetramethylammonium hydroxide in an approximate 1:1 molar stoichiometry. The oxonium salt was synthesized by the procedure reported for oxonium hexafluorozirconate (Davidovich *et al.*, 1987). Hydrofluoric acid was added until the mixture registered a pH in the acid range. The crystalline compound that separated from solution was washed with acetone and then dried to constant weight. Elemental analysis, calculated: C 13.14, H 3.86, N 3.83, Hf 48.82%; found: C 13.02, H 3.71, N 3.70, Hf 48.76%.

*Crystal data*

$(C_4H_{12}N)_2][Hf_2F_{10}(H_2O)_2]$
$M_r = 731.30$
Orthorhombic, *Pbca*
$a = 9.919$ (1) Å
$b = 9.687$ (1) Å
$c = 19.656$ (2) Å
$V = 1888.6$ (4) Å$^3$
$Z = 4$
$D_x = 2.572$ Mg m$^{-3}$

Mo *Kα* radiation
Cell parameters from 754 reflections
$\theta = 27.0$–$44.7°$
$\mu = 11.08$ mm$^{-1}$
$T = 295$ (2) K
Sphere, colourless
0.16 × 0.16 × 0.16 mm

*Data collection*

Bruker SMART 1000 area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.141$, $T_{\max} = 0.170$
11359 measured reflections

2168 independent reflections
1942 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 27.6°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -20 \rightarrow 25$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.055$
$S = 1.09$
2168 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 3.7908P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.91$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.81$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0026 (1)

## Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Hf1—F1 | 2.141 (2) | Hf1—F5 | 1.991 (2) |
| Hf1—F1$^{i}$ | 2.173 (2) | Hf1—F4 | 1.992 (2) |
| Hf1—F2 | 1.975 (3) | Hf1—O1 | 2.230 (3) |
| Hf1—F3 | 1.987 (2) | | |
| F1—Hf1—F1$^{i}$ | 65.4 (1) | F2—Hf1—F3 | 79.8 (1) |
| F1—Hf1—F2 | 139.7 (1) | F2—Hf1—F4 | 91.3 (1) |
| F1—Hf1—F3 | 140.5 (1) | F2—Hf1—F5 | 90.7 (1) |
| F1—Hf1—F4 | 88.5 (1) | F2—Hf1—O1 | 150.9 (1) |
| F1—Hf1—F5 | 87.0 (1) | F3—Hf1—F4 | 91.5 (1) |
| F1—Hf1—O1 | 69.3 (1) | F3—Hf1—F5 | 93.4 (1) |
| F1$^{i}$—Hf1—F2 | 74.4 (1) | F3—Hf1—O1 | 71.2 (1) |
| F1$^{i}$—Hf1—F3 | 154.1 (1) | F5—Hf1—F4 | 175.0 (1) |
| F1$^{i}$—Hf1—F4 | 87.8 (1) | F4—Hf1—O1 | 89.2 (1) |
| F1$^{i}$—Hf1—F5 | 88.3 (1) | F5—Hf1—O1 | 91.3 (1) |
| F1$^{i}$—Hf1—O1 | 134.7 (1) | | |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

## Table 2
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···F4$^{ii}$ | 0.85 (1) | 1.84 (2) | 2.643 (4) | 156 (5) |
| O1—H2···F5$^{iii}$ | 0.85 (1) | 1.84 (2) | 2.660 (4) | 162 (4) |

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

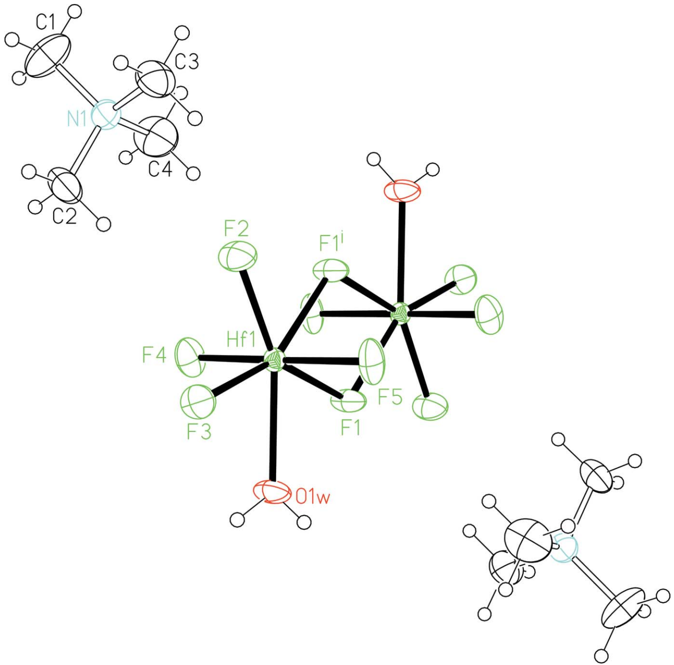


**Figure 1**
A plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The symmetry code (i), which applies also to unlabelled atoms, is as in Table 1.

The water H atoms were located in a difference Fourier map and refined with distance restraints of O—H = 0.85 (1) and H···H = 1.39 (1) Å; their displacement parameters were freely refined. The remaining H atoms were placed in calculated positions, with C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, and were included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXS97*.

The authors thank the Institute of Chemistry of the Far East Division of the Russian Academy of Sciences, the Institute of Problems of Chemical Physics of the Russian Academy of Sciences and the University of Malaya for supporting this study. We acknowledge Dr V. B. Logvinova for assistance with the synthesis.

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*Acta Cryst.* (2006). E**62**, m196–m197 Gerasimenko *et al.* • $(C_4H_{12}N)_2][Hf_2F_{10}(H_2O)_2]$ **m197**