

Ti1—OT2	1.7242 (7)	K1—O7 <sup>ii</sup>	3.0289 (8)
Ti1—OT1	1.9761 (6)	K2—O1 <sup>viii</sup>	2.6799 (7)
Ti1—O1	2.1455 (6)	K2—OT1	2.7632 (7)
Ti1—O2 <sup>i</sup>	1.9596 (6)	K2—O5 <sup>ix</sup>	2.7990 (7)
Ti1—O5 <sup>ii</sup>	2.0422 (6)	K2—O7 <sup>ii</sup>	2.9030 (7)
Ti1—O6 <sup>iii</sup>	1.9838 (6)	K2—O2 <sup>ii</sup>	2.9496 (7)
Ti2—OT2 <sup>iv</sup>	2.0872 (7)	K2—O8 <sup>ii</sup>	3.0146 (8)
Ti2—OT1	1.7455 (6)	K2—O3 <sup>ii</sup>	3.0137 (8)
Ti2—O3	2.0387 (6)	K2—OT2	3.0325 (8)
Ti2—O4 <sup>v</sup>	1.9744 (6)	K2—O4 <sup>v</sup>	3.1381 (7)
Ti2—O7 <sup>iii</sup>	1.9717 (7)		

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

The intensities were corrected for Lorentz and polarization effects using the program *DREAR* (Blessing, 1987). The structure refinement was carried out using the multipole model least-squares program *MOLLY* (Hansen & Coppens, 1978), which employs generalized atomic scattering factors that are the Fourier transforms of pseudoatom electron density parameterized to model chemical bonding. Following the structure refinement of NaTP, residual electron-density maps indicated that the Na substitution on site 1 was not quite complete. Refining the K content for this site led to the chemical formula Na<sub>1-x</sub>K<sub>x</sub>TiOPO<sub>4</sub> with  $x = 0.008$  (4).

For both compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *DREAR* (Blessing, 1987); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *MOLLY* (Hansen & Coppens, 1978); molecular graphics: *CRIC* (Boudias & Monceau, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DU1171). Services for accessing these data are described at the back of the journal.

## References

- Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
- Belokoneva, E. L., Slovokhotova, O. L., Antipin, M. Yu., Tsirel'son, V. G. & Struchkov, Yu. T. (1992). *Sov. Phys. Dokl.* **37**, 8–10.
- Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
- Boudias, C. & Monceau, D. (1994). *CRIC. CaRIne Cristallographie*. Version 3.0. Distributed by Divergent S. A., Rond Point Guy Denielou, Centre de Transfert, 60200 Compiègne, France.
- Crennell, S. J., Morris, R. E., Cheetham, A. K. & Jarman, R. H. (1992). *Chem. Mater.* **4**, 82–88.
- Crennell, S. J., Owen, J. J., Gray, C. P., Cheetham, A. K., Kaduk, J. A. & Jarman, R. H. (1991). *J. Mater. Chem.* **1**, 113–119.
- DeTitta, G. T. (1985). *J. Appl. Cryst.* **18**, 75–79.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5. Enraf-Nonius, Delft, The Netherlands.
- Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921.
- Marnier, G. (1986). Fr. Patent (CNRS) 2 609 976 (29 July 1986).
- Marnier, G. (1988). US Patent (CNRS) 4 746 396 (24 May 1988).
- Marnier, G., Boulanger, B. & Menaert, B. (1989). *J. Phys. Condens. Mater.* **1**, 4643–4648.
- Phillips, M. L. F., Harrison, W. T. A., Gier, T. E. & Stucky, G. D. (1989). *SPIE Int. Soc. Opt. Eng.* **1104**, 225–231.
- Phillips, M. L. F., Harrison, W. T. A., Stucky, G. D., McCarron, E. G., Calabrese, J. C. & Gier, T. E. (1992). *Chem. Mater.* **4**, 222–233.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Stucky, G. D., Phillips, M. L. F. & Gier, T. E. (1989). *Chem. Mater.* **1**, 492–509.
- Tordjmann, I., Masse, R. & Guitel, J. C. (1974). *Z. Kristallogr.* **139**, 103.

*Acta Cryst.* (1997). **C53**, 1176–1178

## Caesium Pentafluoroterbate, CsTbF<sub>5</sub>

VINCENT GAUMET AND DANIEL AVIGNANT

*Université Blaise Pascal, Laboratoire des Matériaux Inorganiques, URA 444, CNRS, 63177 Aubière CEDEX, France. E-mail: gaumet@ubpcf2.univ-bpclermont.fr*

(Received 24 October 1996; accepted 10 April 1997)

## Abstract

The structure of caesium terbium(IV) pentafluoride has been determined by single-crystal X-ray methods. CsTbF<sub>5</sub> has a layered structure. The layers, which stack along the [100] direction, are built from edge- and corner-sharing (TbF<sub>8</sub>)<sup>4-</sup> dodecahedra and are held together by 11-coordinate Cs<sup>+</sup> ions. CsTbF<sub>5</sub> is closely related to TiZrF<sub>5</sub>.

## Comment

Up to now many fluorinated compounds containing tetravalent terbium have been mentioned in the literature (Hoppe, 1985, and references therein), but because the thermal instability of TbF<sub>4</sub> (Gibson & Haire, 1988) generates some difficulties in growing crystals, all structural studies have been carried out on polycrystalline samples. Recently, we succeeded in growing single crystals of tetravalent terbium complex fluorides. The refinements of the structures of these compounds have been performed with the aim of forming a database of information on tetravalent terbium.

CsTbF<sub>5</sub> was first mentioned as an unknown structure by Hoppe & Rödder (1961). The determination of the crystal structure reported here shows that CsTbF<sub>5</sub> and TiZrF<sub>5</sub> (Avignat, Mansouri, Chevalier & Cousseins, 1981) are closely related. The Tb<sup>4+</sup> ion is surrounded by eight fluorine ions in the form of a dodecahedron with an average Tb—F distance of 2.168 (4) Å. The dodecahedra share one F(3)—F(3) edge (the shortest F—F distance in the structure) with an adjacent dodecahedron and four corners [F(1) twice and F(2) twice] with four additional dodecahedra to form infinite (TbF<sub>5</sub>)<sup>-</sup> layers parallel to the (100) plane. The remaining F(4) corners of each polyhedron, which have the shortest Tb—F distances, are unshared and point out on both sides of the layer. The layers are held together by caesium ions, each of which is surrounded by 11 fluorine ions. The Cs—F distances in the CsF<sub>11</sub> polyhedra range from 2.924 (4) to 3.419 (3) Å. Successive (TbF<sub>5</sub>)<sup>-</sup> layers are shifted relative to each other by  $b/2$ .

It is worth noting that a pseudo quaternary symmetry axis is apparent in the (TbF<sub>5</sub>)<sup>-</sup> isolated layer (in agreement with the *b* and *c* parameters being equal to within less than one s.u.). This pseudo quaternary axis

is parallel to [100] and runs through the centre of the two-dimensional unit cell for the layer lying at  $x = 0$ . The quaternary symmetry is not preserved for the three-dimensional structure because of the relative shift of adjacent layers by  $\mathbf{b}/2$ .

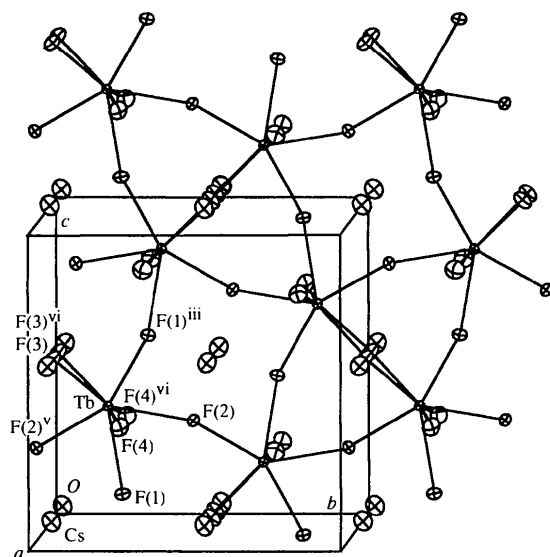


Fig. 1. Partial view (Johnson, 1965) of the  $\text{CsTbF}_5$  structure showing the  $(\text{TbF}_5)^-$  layer perpendicular to the [100] direction and lying at  $x = 0$ . The layer at  $x = \frac{1}{2}$  is displaced by  $\mathbf{b}/2$  relative to the layer shown. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes shown are those defined in Table 2.

## Experimental

Single crystals of the title compound were obtained from polycrystalline samples heated at 860 K for 2 h in a nickel boat under a pure fluorine gas flow and then cooled down slowly to room temperature. Polycrystalline samples were prepared in the solid state by reacting stoichiometric mixtures of  $\text{CsF}$  and  $\text{TbF}_4$  starting fluorides under a pure fluorine atmosphere. The mixtures were heated twice at 770 K for 12 h with an intermediate grinding.

### Crystal data

$\text{CsTbF}_5$

$M_r = 386.82$

Orthorhombic

$Cmca$

$a = 14.067(1) \text{ \AA}$

$b = 8.163(2) \text{ \AA}$

$c = 8.161(2) \text{ \AA}$

$V = 937.1(3) \text{ \AA}^3$

$Z = 8$

$D_x = 5.484 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 6\text{--}16^\circ$

$\mu = 22.87 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.05 \times 0.04 \times 0.02 \text{ mm}$

Colourless

### Data collection

Enraf-Nonius CAD-4 diffractometer

1094 reflections with  $I > 3\sigma(I)$

$\omega/2\theta$  scans

Absorption correction:

empirical via  $\psi$  scans

(North, Phillips &

Mathews, 1968)

$T_{\min} = 0.529$ ,  $T_{\max} = 0.996$

1641 measured reflections

1641 independent reflections

$\theta_{\max} = 40^\circ$

$h = 0 \rightarrow 25$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 14$

3 standard reflections

frequency: 60 min

intensity decay: none

### Refinement

Refinement on  $F$

$R = 0.026$

$wR = 0.028$

$S = 1.339$

1094 reflections

39 parameters

$w = 1/[\sigma^2(F) + (0.02F)^2$

$+ 1]$  (Killean &

Lawrence, 1969)

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 2.27 \text{ e \AA}^{-3}$

(near Tb)

$\Delta\rho_{\min} = -2.60 \text{ e \AA}^{-3}$

(near Cs)

Extinction correction:

$|F_c| = |F_o|(1 + gI_c)$

Extinction coefficient:

$g = 4.0(1) \times 10^{-7}$

Scattering factors from

*International Tables for*

*X-ray Crystallography*

(Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	$x$	$y$	$z$	$U_{eq}$
Cs	0.20754 (4)	0	0	0.0214 (1)
Tb	0	0.16291 (3)	0.33741 (3)	0.0072 (1)
F(1)	0	0.2081 (6)	0.0650 (6)	0.0203 (12)
F(2)	0	0.4355 (5)	0.2923 (5)	0.0167 (8)
F(3)	0.0846 (3)	0	1/2	0.0157 (10)
F(4)	0.1408 (2)	0.2120 (4)	0.2890 (4)	0.0203 (6)

Table 2. Selected geometric parameters ( $\text{\AA}$ )

Cs—Cs <sup>i</sup>	4.2528 (2)	Cs—F(4 <sup>h</sup> )	3.072 (4)
Cs—Cs <sup>ii</sup>	4.2517 (2)	Cs—F(4 <sup>iii</sup> )	3.062 (4)
Cs—Tb	4.2276 (4)	Cs—F(4 <sup>iv</sup> )	3.242 (4)
Cs—Tb <sup>iii</sup>	4.2255 (4)	Cs—F(4 <sup>v</sup> )	3.062 (4)
Tb—Tb <sup>iv</sup>	3.7572 (5)	Cs—F(4 <sup>vi</sup> )	3.242 (4)
Tb—F(1)	2.254 (5)	F(1)—F(2)	2.624 (6)
Tb—F(1 <sup>i</sup> )	2.135 (5)	F(1)—F(2 <sup>iii</sup> )	2.515 (6)
Tb—F(2)	2.255 (4)	F(1)—F(2 <sup>iv</sup> )	2.512 (6)
Tb—F(2 <sup>v</sup> )	2.137 (4)	F(1)—F(3 <sup>iii</sup> )	2.715 (5)
Tb—F(3)	2.224 (2)	F(1)—F(3 <sup>iv</sup> )	2.715 (5)
Tb—F(3 <sup>v</sup> )	2.224 (2)	F(1)—F(4)	2.696 (5)
Tb—F(4)	2.059 (3)	F(1)—F(4 <sup>iii</sup> )	2.696 (5)
Tb—F(4 <sup>iv</sup> )	2.059 (3)	F(2)—F(3 <sup>iii</sup> )	2.717 (4)
Cs—F(1)	3.419 (3)	F(2)—F(3 <sup>iv</sup> )	2.717 (4)
Cs—F(1 <sup>iii</sup> )	3.419 (3)	F(2)—F(4)	2.693 (5)
Cs—F(2 <sup>iii</sup> )	3.417 (2)	F(2)—F(4 <sup>iii</sup> )	2.693 (5)
Cs—F(2 <sup>iv</sup> )	3.417 (2)	F(3)—F(3 <sup>iii</sup> )	2.379 (6)
Cs—F(3 <sup>h</sup> )	2.924 (4)	F(3)—F(4)	2.566 (4)
Cs—F(4)	3.072 (4)	F(3)—F(4 <sup>iii</sup> )	2.566 (4)

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

As no scattering factors for  $\text{Tb}^{4+}$  were available in the literature, we used those of the isoelectronic  $\text{Gd}^{3+}$  ion. Lorentz and polarization corrections were applied to the data. The structure was refined by full-matrix least-squares methods using cationic positions deduced from the structure of  $\text{TlZrF}_5$  (Avignant *et al.*, 1981) and fluorine positions revealed by a subsequent Fourier difference synthesis.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Frenz, 1982). Program(s) used to solve structure: *SDP*. Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP* (Johnson, 1965).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1167). Services for accessing these data are described at the back of the journal.

## References

- Avignant, D., Mansouri, I., Chevalier, R. & Cousseins, J. C. (1981). *J. Solid State Chem.* **38**, 121–127.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Frenz, B. A. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
- Gibson, J. K. & Haire, R. G. (1988). *J. Solid State Chem.* **73**, 524–530.
- Hoppe, R. (1985). *High Oxidation States in Fluorine Chemistry*. In *Inorganic Solid Fluorides, Chemistry and Physics*, edited by P. Hagenmuller. San Diego: Academic Press.
- Hoppe, R. & Rödder, K. M. (1961). *Z. Anorg. Allg. Chem.* **312**, 277–281.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

*Acta Cryst.* (1997). **C53**, 1178–1180

## Re<sub>6</sub>Se<sub>7</sub>Br<sub>4</sub>

CARLOS BASÍLIO PINHEIRO,<sup>a</sup> NIVALDO LÚCIO SPEZIALI<sup>a</sup>  
AND HELMUT BERGER<sup>b</sup>

<sup>a</sup>Departamento de Física–ICEX–UFMG, Cx Postal 702–Belo Horizonte, 30161-970 Brazil, and <sup>b</sup>Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland. E-mail: basilio@fisica.ufmg.br

(Received 19 April 1996; accepted 24 March 1997)

## Abstract

The crystal structure of the semiconductor hexarhenium heptaselenium tetrabromide has been studied by single-crystal X-ray diffraction. The results show that it may be included in the group of Chevrel phases which are very common in molybdenum cluster compounds. Re<sub>6</sub>Se<sub>7</sub>Br<sub>4</sub> crystallizes with well defined Re<sub>6</sub>[Se<sub>7</sub>Br] clusters linked in three dimensions by bromide bridges. Accurate single-crystal X-ray investigations showed that a rhombohedral space group describes the structure best.

## Comment

A number of compounds containing octahedral rhenium clusters have been investigated and related to Chevrel phases (Perrin & Sergent, 1988). The ternary compounds Re<sub>6</sub>X<sub>i</sub>Y<sub>j</sub> (X = Se, S; Y = Cl, Br) crystallize with well defined clusters of Re<sub>6</sub>L<sub>8</sub> (L = X and/or Y). In each cluster, the Re atoms define an octahedron which is located in the centre of a cube defined by the 8 L atoms; the L atoms are called inner ligands. In general, the links between the clusters are made *via* the Y atoms.

The crystal structures of several compounds in the Re<sub>6</sub>Se<sub>i</sub>Br<sub>j</sub> family have been investigated for different types and different numbers of inter-cluster atoms. The 12 single covalent Re–Re bonds in the octahedron involve 24 of the 42 valence electrons (six Re atoms in the 4f<sup>14</sup>5d<sup>5</sup>6s<sup>2</sup> state). The 18 remaining electrons are used in a subtle charge transfer through ionic bonds between the halogen and chalcogen atoms. By controlling the chalcogen number *i* and the halogen number *j* and preserving *i* + 2*j* = 18, structures with Re<sub>6</sub>L<sub>8</sub> clusters linked by halogen bridges in one, two or three dimensions can be obtained, as reported by Perrin & Sergent (1988).

In related studies, the crystal structures of Re<sub>6</sub>Se<sub>5</sub>-Cl<sub>3</sub>Cl<sub>4</sub>Cl<sub>2/2</sub> (Perrin, Leduc & Sergent, 1991) and Re<sub>6</sub>Se<sub>8</sub>Br<sub>4/2</sub> (Speziali *et al.*, 1988) have been reported. In the first compound, successive Re<sub>6</sub>Se<sub>5</sub>Cl<sub>3</sub>Cl<sub>4</sub> units are linked by one-dimensional *trans*-chlorine bridges, while in the second compound, the Re<sub>6</sub>Se<sub>8</sub> clusters are linked in two dimensions *via* Br atoms.

In the title compound, Re<sub>6</sub>[Se<sub>7</sub>Br]Br<sub>3</sub>, the Re<sub>6</sub>[Se<sub>7</sub>Br] clusters are linked *via* halogen bridges in three dimensions. From the X-ray diffraction point of view, Se (*Z* = 34) and Br (*Z* = 35) atoms are very similar, and, as a

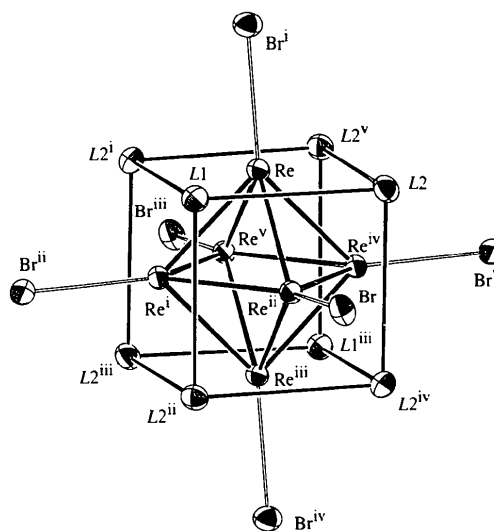


Fig. 1. The Re<sub>6</sub>L<sub>8</sub>Br<sub>3</sub> molecule. Displacement ellipsoids are shown at the 60% probability level. The ternary rotation axis passes through the L1 and L1<sup>iii</sup> atoms.