Table 2. *Selected geometric parameters (Å)*

| | | | |
|---|---|---|---|
| V1—O5 | 1.634 (1) | V2—V3$^{vi}$ | 2.968 (1) |
| V1—O4 | 1.887 (1) | V2—V3$^{v}$ | 2.968 (1) |
| V1—O1$^{i}$ | 1.946 (1) | V3—O6 | 1.639 (1) |
| V1—O1$^{ii}$ | 1.946 (1) | V3—O3$^{vii}$ | 1.909 (1) |
| V1—O1 | 2.031 (1) | V3—O3$^{viii}$ | 1.909 (1) |
| V1—O6$^{iii}$ | 2.817 (1) | V3—O7 | 1.914 (1) |
| V1—Li$^{i}$ | 2.896 (2) | V3—O2 | 2.001 (1) |
| V1—Li$^{ii}$ | 2.896 (2) | V3—O3$^{iv}$ | 2.469 (1) |
| V2—O7 | 1.858 (1) | Li—O1 | 1.952 (3) |
| V2—O7$^{iv}$ | 1.920 (1) | Li—O6$^{vi}$ | 2.127 (2) |
| V2—O2$^{v}$ | 1.869 (1) | Li—O6$^{v}$ | 2.127 (2) |
| V2—O2$^{vi}$ | 1.869 (1) | Li—O4$^{vi}$ | 2.461 (2) |
| V2—O3 | 2.037 (1) | Li—O4$^{v}$ | 2.461 (2) |
| V2—O5 | 2.109 (1) | Li—V1$^{i}$ | 2.896 (2) |
| V2—V2$^{iv}$ | 2.851 (1) | Li—V1$^{ii}$ | 2.896 (2) |

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

The structure was solved by difference Fourier syntheses using the atomic coordinates of $V_6O_{13}$ (Wilhelmi, Waltersson & Kilborg, 1971). Refinement of the occupancy factor for the Li site confirmed that the site was fully occupied.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *STOEDATRED*, *LSQLIN*, *ABSSTOE* (Lundgren, 1983). Program(s) used to solve structure: *FORDUP* (Lundgren, 1983). Program(s) used to refine structure: *DUPALS* (Lundgren, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *DISTAN* (Lundgren, 1983).

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Lists of displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# β-BaTbF$_6$

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## Abstract

The single-crystal structure of the quenchable high temperature form of barium terbium hexafluoride has been refined. This structure is built from infinite chains of edge-sharing $[TbF_8]^{4-}$ dodecahedra linked together by the $Ba^{2+}$ ions and is isostructural with β-$BaZrF_6$.

## Comment

Since their pioneering work on ionic radii determination in which Shannon & Prewitt (1969) claimed that there were no available crystallographic data concerning tetravalent terbium in fluorinated media, no report has appeared on this subject. On the other hand, many fluorinated combinations containing tetravalent terbium have been mentioned (Hoppe, 1985, and references therein). All these compounds, however, have been characterized by X-ray powder diffraction only. Single-crystal studies were needed but there were problems in growing crystals because of the relative thermal instability of $TbF_4$ (Gibson & Haire, 1988). As these problems have now been at least partially overcome, we have undertaken an extensive study of the single-crystal structures of tetravalent terbium fluorides.

$BaTbF_6$ was originally reported with an unknown structure (Feldner & Hoppe, 1983). It can be inferred now that this still unknown structure is a low temperature form, subsequently called α-$BaTbF_6$, since a recent study has shown that $BaTbF_6$ undergoes a phase transition at high temperature to an orthorhombic form of the β-$BaZrF_6$ type (Mehlhorn & Hoppe, 1976). β-$BaTbF_6$ is the first representative of a high temperature polymorph of a $Tb^{IV}$-containing fluoride and also one of the first $Tb^{IV}$ fluorinated compounds obtained as a single crystal. It is isostructural with β-$BaZrF_6$.

Each $Tb^{4+}$ ion is surrounded by eight $F^-$ ions, four of which are shared in pairs with adjacent $Tb^{4+}$ ions to form infinite chains running along the [100] direction. These chains are linked together by the $Ba^{2+}$ ions. The Tb—F bond distances are divided into two groups: bonds to bridging F atoms are 2.271 (2) Å and bonds to non-bridging F atoms involved in shared edges within the chains are 2.081 (3) Å. Comparison of the bond

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lengths within the eight-vertex polyhedra shows that the dodecahedron surrounding the $Tb^{4+}$ ion is slightly less distorted than those around the $Zr^{4+}$ ions in $\beta$-$BaZrF_6$.

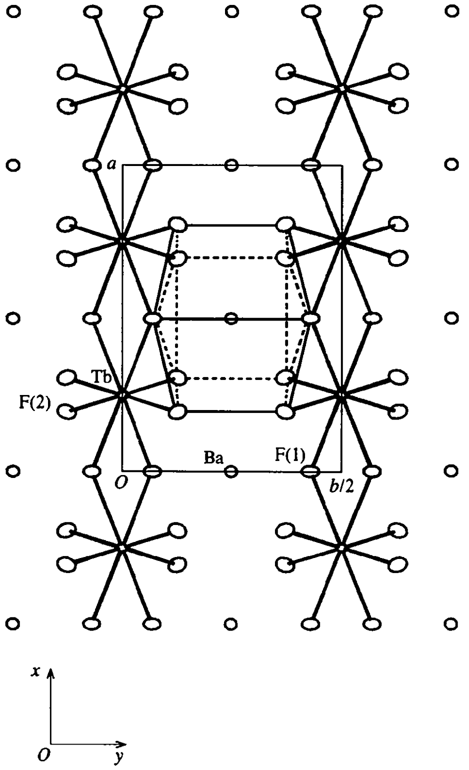

Fig. 1. A (001) projection of the $[TbF_8]^{4-}$ dodecahedra chains linked by Ba–F polyhedra. Displacement ellipsoids are plotted at the 50% probability level.

## Experimental

Single crystals of $\beta$-$BaTbF_6$ were obtained by solid-state reaction of a stoichiometric mixture of the starting fluorides $BaF_2$ and $TbF_4$ in a nickel boat under a pure fluorine atmosphere. This mixture was heated overnight successively at 773, 873 and 973 K, grinding in between. Colorless prismatic crystals were isolated from the sample and identified as $\beta$-$BaTbF_6$ by X-ray powder diffraction of the ground crystals.

*Crystal data*

$BaTbF_6$
$M_r = 410.25$
Orthorhombic
*Cmma*
$a = 7.761\,(1)$ Å
$b = 11.513\,(3)$ Å
$c = 5.5234\,(9)$ Å
$V = 493.57\,(17)$ Å$^3$
$Z = 4$
$D_x = 5.523$ Mg m$^{-3}$
$D_m$ not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–19°
$\mu = 22.75$ mm$^{-1}$
$T = 293$ K
Prismatic
0.09 × 0.09 × 0.05 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.211$, $T_{max} = 0.321$
888 measured reflections
888 independent reflections

779 reflections with $I > 3\sigma(I)$
$\theta_{max} = 40°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 1.2%

*Refinement*

Refinement on *F*
$R = 0.026$
$wR = 0.030$
$S = 1.615$
769 reflections
24 parameters
$w = 1.0$ for $F_o < 0.8F_o(\max)$, $w = [0.8F_o(\max)/F_o]^{-2}$ for $F_o \geq 0.8F_o(\max)$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 2.358$ e Å$^{-3}$ (close to Tb)
$\Delta\rho_{min} = -2.797$ e Å$^{-3}$ (close to Tb)
Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 6.6\,(2) \times 10^{-7}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ba | 0 | 1/4 | 0.44358 (9) | 0.00895 (6) |
| Tb | 1/4 | 0 | 0 | 0.00589 (5) |
| F(1) | 0 | 0.4300 (4) | 0.1557 (8) | 0.0162 (7) |
| F(2) | 0.3060 (4) | 0.3719 (3) | 0.2541 (6) | 0.0205 (5) |

Table 2. *Selected geometric parameters (Å)*

| | | | |
|---|---|---|---|
| Ba—Ba$^{i}$ | 3.9304 (1) | Tb—F(1$^{iv}$) | 2.271 (2) |
| Ba—Tb | 4.2489 (3) | Tb—F(2$^{v}$) | 2.081 (3) |
| Ba—F(1) | 2.613 (4) | F(1)—F(1$^{vi}$) | 2.356 (7) |
| Ba—F(2$^{ii}$) | 2.651 (4) | F(1)—F(2) | 2.527 (3) |
| Ba—F(2) | 2.951 (3) | F(1)—F(2$^{vii}$) | 2.800 (5) |
| Tb—Tb$^{iii}$ | 3.8807 (1) | F(1)—F(2$^{viii}$) | 2.786 (5) |

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

Data collection and cell refinement were carried out using *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction and other calculations were performed using *MolEN* (Fair, 1990). Lorentz and polarization corrections were applied to the data. The structure was refined by full-matrix least squares using the atomic positions of the isotypic $\beta$-$BaZrF_6$ phase (Mehlhorn & Hoppe, 1976) as the starting model. Molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BR1157). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Trisodium Trimetaphosphimate Monohydrate

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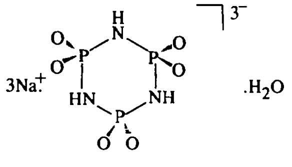
## Abstract

The trimetaphosphimate anion $(PO_2NH)_3^{3-}$ in trisodium *cyclo*-tri-$\mu$-imido-triphosphate monohydrate, $Na_3(PO_2NH)_3.H_2O$, exhibits a chair conformation. Two trimetaphosphimate rings are linked to one another by six N—H···O hydrogen bonds forming pairs. These units are interconnected by O—H···O hydrogen bonds through water molecules forming columns.

## Comment

In contrast to the well known structural chemistry of trimetaphosphates (Durif, 1995), only very few structural details about trimetaphosphimates are known despite the fact that many salts of trimetaphosphimic acid were known more than 100 years ago (Stokes, 1895). These compounds have been mainly characterized by IR spectroscopy (Pustinger, Cave & Nielsen, 1959) and powder diffraction (Herzog & Nielsen, 1958). In contrast to $H_3(PO_2NH)_3.2H_2O$ and $(NH_4)H_2(PO_2NH)_3.CH_3OH$, where the P–N rings show a distorted boat conformation (Olthof, Migchelsen & Vos, 1965), the title compound, (I) (Fig. 1), $Na_3(PO_2NH)_3.4H_2O$ and $(NH_4)_3(PO_2NH)_3.H_2O$ exhibit distorted chair conformations (Attig & Mootz, 1976; Stock & Schnick, 1996).



(I)

As may be seen from the bond lengths and valence angles, the phosphimate ring in $Na_3(PO_2NH)_3.H_2O$ exhibits approximate $3m$ symmetry. Whereas in $(NH_4)_3(PO_2NH)_3.H_2O$ and $Na_3(PO_2NH)_3.4H_2O$, three-dimensional networks of $(PO_2NH)_3^{3-}$ anions and water molecules are formed by N—H···O and O—H···O hydrogen bonds, in $Na_3(PO_2NH)_3.H_2O$, rings are linked pairwise to one another by six N—H···O bonds [N···O 2.964 (2), 3.053 (2) and 3.121 (2) Å]. These units are

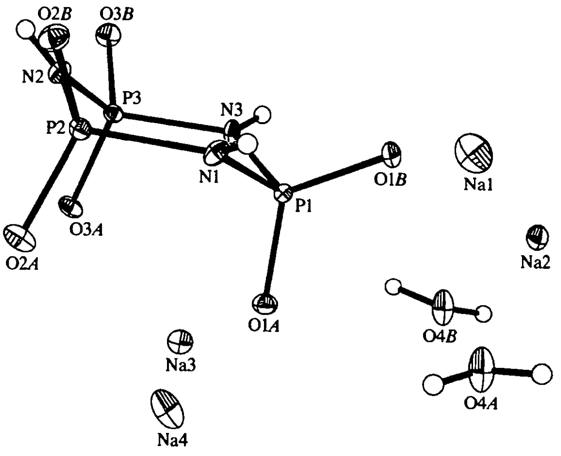


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary size.

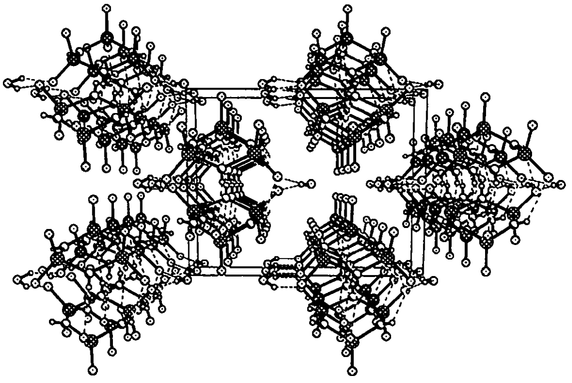


Fig. 2. View along [001] of the crystal packing of the trimetaphosphimate rings and water molecules illustrating the hydrogen bonds. The sodium ions have been omitted for clarity.