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$(C_4N_2H_{12})[(GeO_2)_3(BO_{1.5}F)_2]$, a layered borogermanate containing three- and nine-membered rings

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A new borogermanate, *viz*. piperazine-1,4-diium difluorononaoxotrigermaniumdiboron, $(C_4H_{12}N_2)[(GeO_2)_3(BO_{1.5}F)_2]$, was solvo/hydrothermally synthesized. The crystal structure consists of layers composed of three-membered-ring Ge_3O_9 subunits and nine-membered-ring channels formed by six GeO_4 tetrahedra and three BO_3F tetrahedral pairs. The diprotonated piperazine cations, which lie about inversion centres, are located between adjacent layers and connect the layers *via* hydrogen bonds.

Comment

Porous materials are widely used in industry owing to their sorption, ion-exchange and catalyst properties (Chen *et al.*, 1989; Jansen *et al.*, 1994), and these materials often show great structural diversity (Smith, 1988). During the past decade, the number of known porous materials consisting of pure tetrahedra or mixed polyhedra has increased because of the inclusion of various framework-forming elements (Cheetham *et al.*, 1999). Recent studies have shown that germanium oxides can be crystallized by solvo/hydrothermal synthetic methods in basic solutions, thus forming open frameworks with tetrahedral or mixed-polyhedral Ge—O coordinations, for example, in ICMM2 (Cascales *et al.*, 1999), ASU-16 (Plevert *et al.*, 2001), ASU-14 (Li *et al.*, 1999) and $Ge_{10}O_{21}(OH)\cdot C_6H_{21}N_4$ (Beitone *et al.*, 2002). Although more than 20 elements have been incorporated successfully into silicate frameworks, there are only a few reports of elements being incorporated into germanates. One of the elements that has been incorporated is boron, although up to now only two borogermanates, prepared *via* molecular templating methods, have been reported. The first is $(C_2H_{10}N_2)_2[(GeO_2)_3(BO_{2.5})_2]$, a layered structure containing nine-membered-ring channels templated by ethylenediamine (Dadachov *et al.*, 2000), and the second is $KBGe_2O_6$, a chiral borogermanate with seven-membered-ring channels (Lin *et al.*, 2003). We report here another layered borogermanate containing nine- and three-membered-ring channels (templated by piperazine), *viz*. the title compound, (I), which is also denoted SU-13 (Stockholm University No. 13).

The asymmetric unit of (I) contains two unique Ge atoms and one unique B atom (Fig. 1). All of the Ge and B atoms are tetrahedrally coordinated, Ge by four O atoms, and B by three O atoms and one F atom (Table 1). The GeO_4 and BO_3F groups are vertex-connected *via* the O atoms, as is also seen in zeolites. Three GeO_4 tetrahedra are connected to form a three-unit ring, a configuration that is very common in germanates. Three such rings are connected *via* three pairs of BO_3F tetrahedra, in an alternating manner, to form a layer containing nine-unit rings composed of six GeO_4 tetrahedra and three pairs of BO_3F tetrahedra (Fig. 2).

The diprotonated piperazine cations lie about inversion centres and are located between the adjacent layers, inside the nine-membered-ring channels (Fig. 2). The cations balance the framework charge and connect the layers, *via* hydrogen bonds (Table 2), into a three-dimensional structure. The Ge and B tetrahedra have average angles close to that of an ideal tetrahedron (109.5°). The Ge—O—Ge and B—O—Ge angles

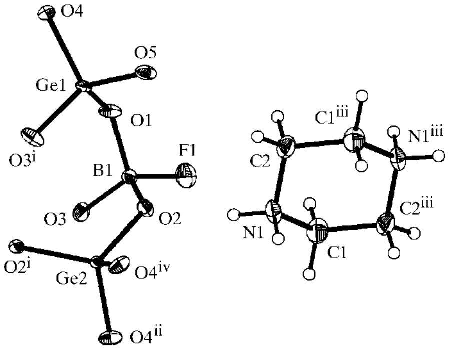

Figure 1
A view of (I), showing the atomic labelling scheme and displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-x, -y, 1 - z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, z$.]

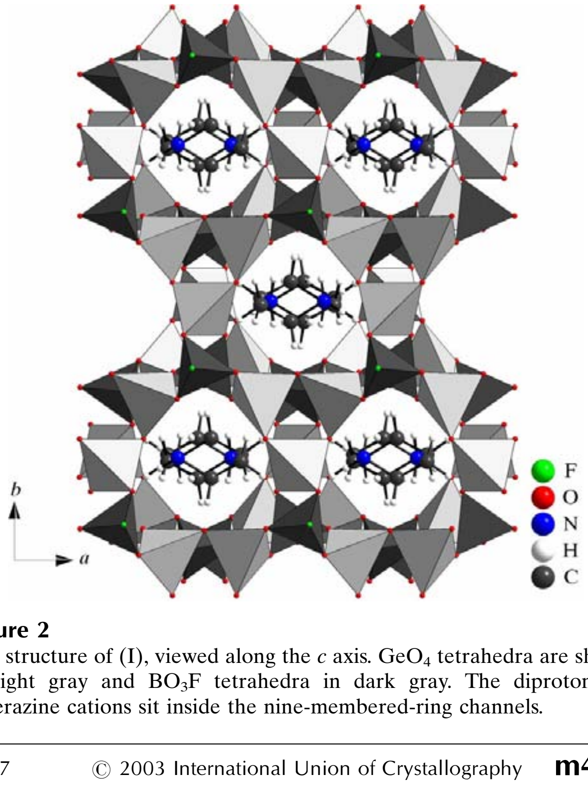

Figure 2
The structure of (I), viewed along the *c* axis. GeO_4 tetrahedra are shown in light gray and BO_3F tetrahedra in dark gray. The diprotonated piperazine cations sit inside the nine-membered-ring channels.

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are all smaller than, but still close to, the Ge—O—Ge angles reported for other germanates (130°; O'Keeffe & Yaghi, 1999).

The $[(GeO_2)_3(BO_{1.5}F)_2]$ layer in (I) is the same as that in $(C_2H_{10}N_2)_2[(GeO_2)_3(BO_{2.5})_2]$ (Dadachov *et al.*, 2000), although the relative positions of the adjacent layers are different as a result of the shape and size differences of the organic cations in these two compounds. The distances between the layers are also different, *viz*. 8.0 Å in (I) and 7.2 Å in $(C_2H_{10}N_2)_2[(GeO_2)_3(BO_{2.5})_2]$. The $[(GeO_2)_3(BO_{1.5}F)_2]$ layers in both borogermanates are also similar to the $[(GeO_2)_3(GeO_{1.5}F_3)_2]$ layer in several pure germanate compounds, for example, $K_4[(GeO_2)_3(GeO_{1.5}F_3)_2]$ (Bu *et al.*, 1999) and $(NH_4)[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot 0.67H_2O$ (Conradsson *et al.*, 2000). The main structural difference between the borogermanates and the germanates is that the BO_3F tetrahedral pair in $[(GeO_2)_3(BO_{1.5}F)_2]$ is replaced by the GeO_3F_3 octahedral pair in $[(GeO_2)_3(GeO_{1.5}F_3)_2]$.

Experimental

Compound (I) was synthesized *via* a solvo/hydrothermal route using a mixture of pyridine and water. In a typical synthesis, GeO_2 (0.25 g), H_3BO_3 (0.75 g) and piperazine (2.4 g) were dissolved in a mixed solution of pyridine (7.7 ml) and water (1.7 ml). HF (0.17 ml, 40 wt%) was added and the mixture was stirred continuously for 3 h. The final solution had a GeO_2/pyridine/H_2O/H_3BO_3/piperazine/HF molar ratio of 1:40:38:5:12:2 and a pH higher than 13. The solution was sealed in a Teflon-lined autoclave, heated and kept at 438 K for 3 d. The autoclave was left to cool to room temperature and the products were then filtered off, washed with distilled water and dried. Two distinct kinds of large colourless crystals were obtained, *viz*. (I) and ASU-14 (Li *et al.*, 1999). All reagents (Aldrich) were of analytical grade and were not further purified before use.

Crystal data

$(C_4H_{12}N_2)[(GeO_2)_3(BO_{1.5}F)_2]$
$M_r = 509.54$
Orthorhombic, *Pbcn*
$a = 6.9776$ (14) Å
$b = 11.779$ (2) Å
$c = 15.997$ (3) Å
$V = 1314.8$ (4) Å^3
$Z = 4$
$D_x = 2.574$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 3.4$–25.9°
$\mu = 6.89$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.15 × 0.10 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*XRED*; Stoe & Cie, 1997)
$T_{\min} = 0.444$, $T_{\max} = 0.558$
8492 measured reflections
1278 independent reflections

1092 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 25.9°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.046$
$S = 1.00$
1278 reflections
101 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

All H atoms were positioned geometrically and allowed to ride on their parent atoms (C—H = 0.97 Å and N—H = 0.90 Å).

Table 1
Selected geometric parameters (Å, °).

Ge1—O1	1.7376 (18)	Ge2—O4$^{\rm ii}$	1.7524 (18)
Ge1—O3$^{\rm i}$	1.7186 (18)	B1—F1	1.419 (3)
Ge1—O4	1.7575 (18)	B1—O1	1.465 (3)
Ge1—O5	1.7529 (12)	B1—O2	1.488 (3)
Ge2—O2	1.7299 (17)	B1—O3	1.460 (3)
B1—O1—Ge1	122.06 (16)	Ge1—O5—Ge1$^{\rm iv}$	125.94 (15)
B1—O2—Ge2	124.31 (16)	Ge2$^{\rm v}$—O4—Ge1	124.98 (10)
B1—O3—Ge1$^{\rm i}$	127.59 (16)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2	0.90	1.88	2.754 (3)	165
N1—H1B···O1$^{\rm vi}$	0.90	1.98	2.822 (3)	155

Symmetry code: (vi) $\frac{1}{2} - x, y - \frac{1}{2}, z$.

Data collection: *EXPOSURE* in *IPDS Software* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1066). Services for accessing these data are described at the back of the journal.

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