

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(1-adamantylammonium) hexafluoridogermanate

Liyang Cheng,^a Xin Xu^b and Yan Xu^{a*}

^aInstitute of Chemistry for Functionalized Materials, College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China, and ^bHeavy Oil Company, Liaohe Petroleum Filiale, China National Petroleum Corporation (CNPC), Shiyou Street No. 96, Panjin 124010, People's Republic of China

Correspondence e-mail: yanxu@lnnu.edu.cn

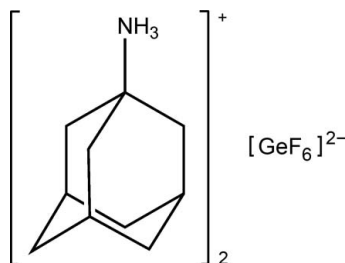
Received 26 October 2007; accepted 27 November 2007

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in main residue; R factor = 0.057; wR factor = 0.144; data-to-parameter ratio = 12.1.

The title compound, $(\text{C}_{10}\text{H}_{18}\text{N})_2[\text{GeF}_6]$, was obtained hydrothermally from an aqueous solution of GeO_2 , H_3BO_3 , NiCl_2 , adamantylammonium chloride, butanol and hydrofluoric acid. The structure consists of discrete bis(1-adamantylammonium) cations lying on crystallographic mirror planes and hexafluoridogermanate anions disordered about sites of $2/m$ point symmetry. In the latter, the Ge atom lies on the site of $2/m$ symmetry, one F atom lies on the mirror plane and two further F atoms are included in general positions with 50% site occupancy. The cations and anions lie in layers with $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds formed between them.

Related literature

For related literature concerning germanium framework materials, see: Li *et al.* (1998); Plévert *et al.* (2001); Xu, Fan, Chino *et al.* (2004); Xu, Fan, Elangovan *et al.* (2004); Xu *et al.* (2006).



Experimental

Crystal data

$(\text{C}_{10}\text{H}_{18}\text{N})_2[\text{GeF}_6]$
 $M_r = 491.10$
 Monoclinic, $C2/m$
 $a = 11.099$ (2) Å
 $b = 6.7458$ (13) Å
 $c = 14.179$ (3) Å
 $\beta = 97.844$ (3)°

$V = 1051.7$ (4) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.52$ mm⁻¹
 $T = 293$ (2) K
 $0.20 \times 0.18 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.751$, $T_{\max} = 0.863$

2694 measured reflections
 1037 independent reflections
 955 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.144$
 $S = 1.07$
 1037 reflections

86 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.00$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.69$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1B}\cdots\text{F2}^{\text{i}}$	0.90	1.80	2.639 (5)	155
$\text{N1}-\text{H1C}\cdots\text{F1}^{\text{ii}}$	0.90	2.04	2.920 (4)	166

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

This work was supported by the Natural Science Foundation of Liaoning Province (20062139).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: B12261).

References

- Bruker (1997). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2005). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Li, H., Eddaoudi, M., Richardson, D. A. & Yaghi, O. M. (1998). *J. Am. Chem. Soc.* **120**, 8567–8568.
 Plévert, J., Gentz, T. M., Laine, A., Li, H., Young, V. G., Yaghi, O. M. & O'Keeffe, M. (2001). *J. Am. Chem. Soc.* **123**, 12706–12707.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). SADABS. University of Göttingen, Germany.
 Xu, Y., Cheng, L. & You, W. (2006). *Inorg. Chem.* **45**, 7705–7708.
 Xu, Y., Fan, W., Chino, N., Uehara, K., Hikichi, S., Mizuno, N., Ogura, M. & Okubo, T. (2004). *Chem. Lett.* **33**, 74–75.
 Xu, Y., Fan, W., Elangovan, S. P., Ogura, M. & Okubo, T. (2004). *Eur. J. Inorg. Chem.* pp. 4547–4549.

supporting information

Acta Cryst. (2008). E64, m82 [https://doi.org/10.1107/S1600536807063702]

Bis(1-adamantylammonium) hexafluoridogermanate

Liyang Cheng, Xin Xu and Yan Xu

S1. Comment

Over the past decades, germanium has been used to synthesize inorganic framework materials (Li *et al.*, 1998; Plévert *et al.*, 2001; Xu, Fan, Chino *et al.*, 2004; Xu, Fan, Elangovan *et al.*, 2004; Xu *et al.*, 2006). In this work, we used a typical method to synthesize germanate frameworks under hydrothermal conditions, but obtained instead a simple salt of adamantamine and germanium fluoride.

S2. Experimental

Colorless plate-like crystals were synthesized hydrothermally from a mixture of GeO₂, H₃BO₃, NiCl₂, (C₁₀H₁₈N)Cl, C₄H₉OH, HF and H₂O. In a typical synthesis, GeO₂ (0.100 g), H₃BO₃ (0.006 g), NiCl₂ (0.23 g), and (C₁₀H₁₈N)Cl (0.300 g) were dissolved in a mixture of C₄H₉OH (2.170 g), 47% HF (0.10 ml) and 1 ml water with constant stirring. The mixture was kept in a 25 ml Teflon-lined steel autoclave at 443 K for 7 days. The autoclave was slowly cooled to room temperature, then the product was filtered, washed with distilled water, and dried at room temperature.

S3. Refinement

The GeF₆²⁻ anion is disordered about a site of 2/m point symmetry. Atoms F2 and F3 are included with site occupancy factor 0.5. H atoms were placed geometrically and allowed to ride during subsequent refinement with C—H = 0.96 Å, $U_{iso}(H) = 1.2U_{eq}(C)$, and with N—H = 0.90 Å, $U_{iso}(H) = 1.5U_{eq}(N)$,

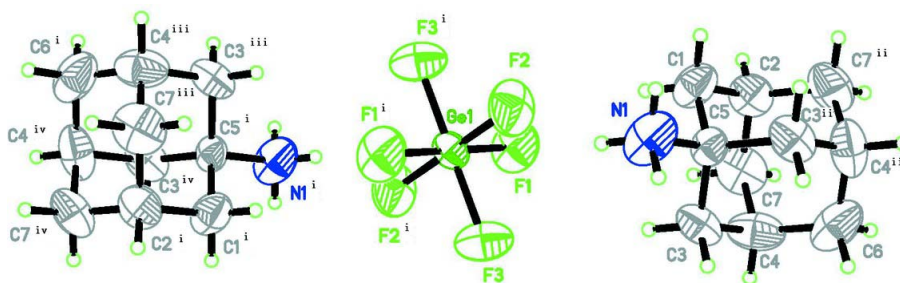


Figure 1

The molecular structure of title compound showing displacement ellipsoids at the 70% probability level for non-H atoms (the occupancy factors for F1 and F2 are 1/2).

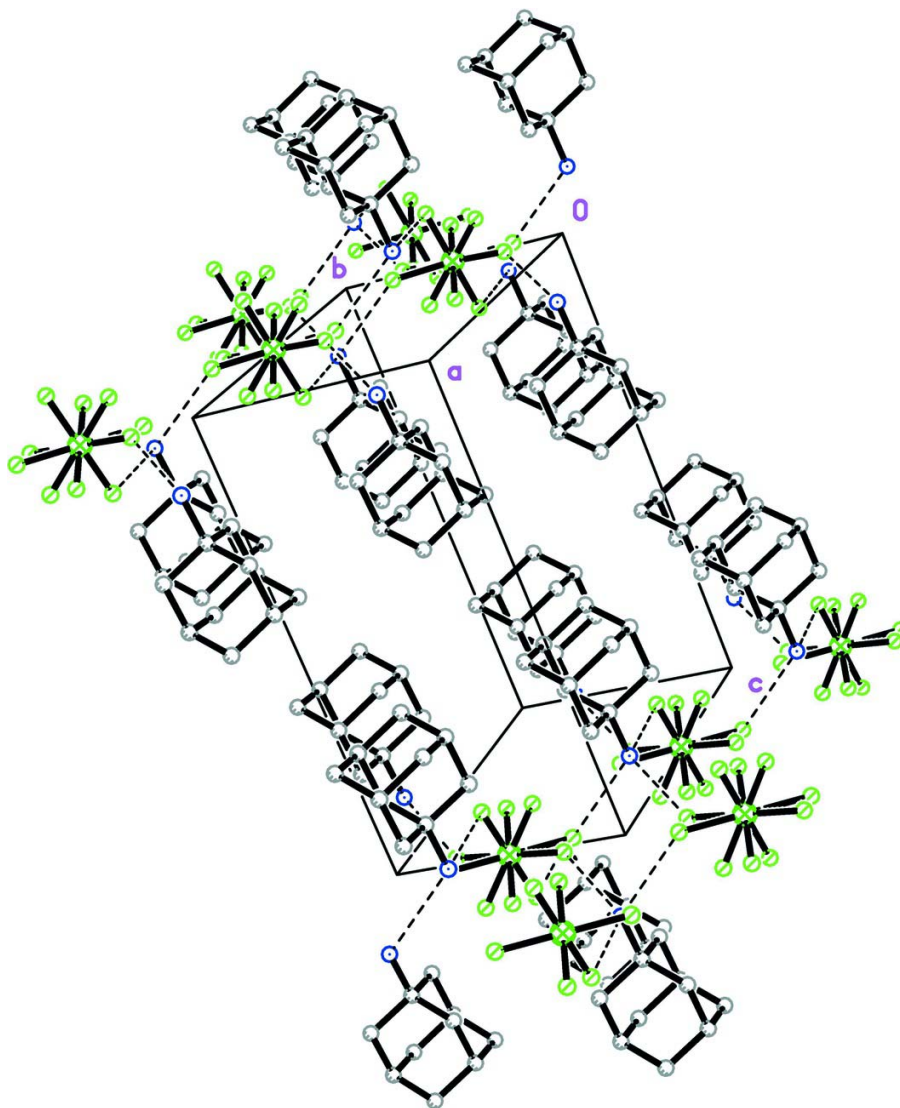


Figure 2
Unit-cell contents.

Bis(amantadinium) hexafluoridogermanate

Crystal data

$(C_{10}H_{18}N)_2[GeF_6]$

$M_r = 491.10$

Monoclinic, $C2/m$

Hall symbol: $-C 2y$

$a = 11.099 (2) \text{ \AA}$

$b = 6.7458 (13) \text{ \AA}$

$c = 14.179 (3) \text{ \AA}$

$\beta = 97.844 (3)^\circ$

$V = 1051.7 (4) \text{ \AA}^3$

$Z = 2$

$F(000) = 512$

$D_x = 1.551 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 955 reflections

$\theta = 3.5\text{--}25.1^\circ$

$\mu = 1.52 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate, colorless

$0.20 \times 0.18 \times 0.10 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	2694 measured reflections
Radiation source: fine-focus sealed tube	1037 independent reflections
Graphite monochromator	955 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.054$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$\theta_{\text{max}} = 25.2^\circ$, $\theta_{\text{min}} = 3.5^\circ$
$T_{\text{min}} = 0.751$, $T_{\text{max}} = 0.863$	$h = -10 \rightarrow 13$
	$k = -8 \rightarrow 8$
	$l = -17 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H-atom parameters constrained
$wR(F^2) = 0.144$	$w = 1/[\sigma^2(F_o^2) + (0.0862P)^2 + 0.4272P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1037 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
86 parameters	$\Delta\rho_{\text{max}} = 1.00 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.69 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ge1	-0.5000	0.0000	0.0000	0.0276 (3)	
F1	-0.5435 (3)	0.0000	0.1155 (2)	0.0516 (10)	
F2	-0.4626 (5)	-0.2563 (7)	0.0005 (6)	0.0527 (19)	0.50
F3	-0.3490 (4)	0.0578 (7)	0.0500 (4)	0.0490 (17)	0.50
C5	-0.3233 (5)	-0.5000	0.2032 (4)	0.0276 (12)	
C1	-0.4579 (5)	-0.5000	0.2134 (4)	0.0400 (15)	
H1A	-0.4963	-0.6155	0.1832	0.048*	
C2	-0.4722 (6)	-0.5000	0.3188 (4)	0.0383 (14)	
H2A	-0.5568	-0.5000	0.3265	0.046*	
C3	-0.2621 (4)	-0.3158 (6)	0.2489 (3)	0.0382 (10)	
H3A	-0.2989	-0.1991	0.2188	0.046*	
H3B	-0.1775	-0.3161	0.2414	0.046*	
C4	-0.2760 (4)	-0.3161 (7)	0.3550 (3)	0.0465 (12)	
H4A	-0.2383	-0.1998	0.3847	0.056*	
N1	-0.3085 (5)	-0.5000	0.1002 (3)	0.0495 (15)	
H1B	-0.3439	-0.6089	0.0722	0.074*	

H1C	-0.2288	-0.5000	0.0942	0.074*
C6	-0.2157 (6)	-0.5000	0.4014 (5)	0.0523 (19)
H6A	-0.2230	-0.5000	0.4681	0.063*
H6B	-0.1307	-0.5000	0.3948	0.063*
C7	-0.4110 (4)	-0.3163 (7)	0.3658 (4)	0.0478 (12)
H7A	-0.4209	-0.3142	0.4320	0.057*
H7B	-0.4490	-0.1998	0.3362	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.0296 (5)	0.0262 (5)	0.0286 (5)	0.000	0.0103 (3)	0.000
F1	0.048 (2)	0.079 (3)	0.031 (2)	0.000	0.0180 (16)	0.000
F2	0.072 (6)	0.032 (3)	0.052 (3)	0.013 (2)	0.000 (5)	-0.001 (3)
F3	0.033 (3)	0.057 (5)	0.058 (3)	-0.008 (2)	0.008 (2)	-0.016 (2)
C5	0.029 (3)	0.035 (3)	0.019 (3)	0.000	0.007 (2)	0.000
C1	0.029 (3)	0.061 (4)	0.031 (3)	0.000	0.005 (2)	0.000
C2	0.033 (3)	0.046 (4)	0.039 (3)	0.000	0.016 (3)	0.000
C3	0.039 (2)	0.030 (2)	0.048 (3)	-0.0047 (19)	0.017 (2)	0.0013 (19)
C4	0.047 (3)	0.049 (3)	0.047 (3)	-0.017 (2)	0.019 (2)	-0.021 (2)
N1	0.033 (3)	0.088 (5)	0.030 (3)	0.000	0.013 (2)	0.000
C6	0.034 (4)	0.093 (6)	0.030 (3)	0.000	0.006 (3)	0.000
C7	0.051 (3)	0.047 (3)	0.050 (3)	0.004 (2)	0.023 (2)	-0.011 (2)

Geometric parameters (Å, °)

Ge1—F1	1.769 (3)	C2—C7	1.522 (6)
Ge1—F1 ⁱ	1.769 (3)	C2—C7 ^{iv}	1.522 (6)
Ge1—F3	1.772 (4)	C2—H2A	0.960
Ge1—F3 ⁱ	1.772 (4)	C3—C4	1.532 (6)
Ge1—F3 ⁱⁱ	1.772 (4)	C3—H3A	0.960
Ge1—F3 ⁱⁱⁱ	1.772 (4)	C3—H3B	0.960
Ge1—F2 ⁱⁱ	1.778 (4)	C4—C6	1.517 (6)
Ge1—F2 ⁱⁱⁱ	1.778 (4)	C4—C7	1.527 (7)
Ge1—F2 ⁱ	1.778 (4)	C4—H4A	0.960
Ge1—F2	1.778 (4)	N1—H1B	0.900
C5—N1	1.491 (6)	N1—H1C	0.900
C5—C3	1.518 (5)	C6—C4 ^{iv}	1.517 (6)
C5—C3 ^{iv}	1.518 (5)	C6—H6A	0.960
C5—C1	1.521 (8)	C6—H6B	0.960
C1—C2	1.524 (8)	C7—H7A	0.960
C1—H1A	0.960	C7—H7B	0.960
F1—Ge1—F1 ⁱ	180.0 (2)	C5—C1—H1A	109.8
F1—Ge1—F3	89.6 (2)	C2—C1—H1A	109.8
F1 ⁱ —Ge1—F3	90.4 (2)	C7—C2—C7 ^{iv}	109.1 (6)
F1—Ge1—F3 ⁱ	90.4 (2)	C7—C2—C1	109.2 (3)
F1 ⁱ —Ge1—F3 ⁱ	89.6 (2)	C7 ^{iv} —C2—C1	109.2 (3)

F3—Ge1—F3 ⁱ	180.0 (3)	C7—C2—H2A	109.6
F1—Ge1—F3 ⁱⁱ	89.6 (2)	C7 ^{iv} —C2—H2A	109.6
F1 ⁱ —Ge1—F3 ⁱⁱ	90.4 (2)	C1—C2—H2A	110.1
F1—Ge1—F3 ⁱⁱⁱ	90.4 (2)	C5—C3—C4	108.6 (4)
F1 ⁱ —Ge1—F3 ⁱⁱⁱ	89.6 (2)	C5—C3—H3A	110.1
F3 ⁱⁱ —Ge1—F3 ⁱⁱⁱ	180.0 (4)	C4—C3—H3A	110.1
F1—Ge1—F2 ⁱⁱ	95.1 (3)	C5—C3—H3B	109.8
F1 ⁱ —Ge1—F2 ⁱⁱ	84.9 (3)	C4—C3—H3B	109.9
F3 ⁱⁱ —Ge1—F2 ⁱⁱ	90.3 (2)	H3A—C3—H3B	108.4
F3 ⁱⁱⁱ —Ge1—F2 ⁱⁱ	89.7 (2)	C6—C4—C7	109.7 (4)
F1—Ge1—F2 ⁱⁱⁱ	84.9 (3)	C6—C4—C3	109.2 (4)
F1 ⁱ —Ge1—F2 ⁱⁱⁱ	95.1 (3)	C7—C4—C3	109.3 (4)
F3 ⁱⁱ —Ge1—F2 ⁱⁱⁱ	89.7 (2)	C6—C4—H4A	109.7
F3 ⁱⁱⁱ —Ge1—F2 ⁱⁱⁱ	90.3 (2)	C7—C4—H4A	109.4
F2 ⁱⁱ —Ge1—F2 ⁱⁱⁱ	180.0	C3—C4—H4A	109.5
F1—Ge1—F2 ⁱ	84.9 (3)	C5—N1—H1B	109.4
F1 ⁱ —Ge1—F2 ⁱ	95.1 (3)	C5—N1—H1C	109.5
F3—Ge1—F2 ⁱ	89.7 (2)	H1B—N1—H1C	109.5
F3 ⁱ —Ge1—F2 ⁱ	90.3 (2)	C4 ^{iv} —C6—C4	109.7 (5)
F1—Ge1—F2	95.1 (3)	C4 ^{iv} —C6—H6A	109.6
F1 ⁱ —Ge1—F2	84.9 (3)	C4—C6—H6A	109.6
F3—Ge1—F2	90.3 (2)	C4 ^{iv} —C6—H6B	109.8
F3 ⁱ —Ge1—F2	89.7 (2)	C4—C6—H6B	109.8
F2 ⁱ —Ge1—F2	180.0 (3)	H6A—C6—H6B	108.2
N1—C5—C3	108.4 (3)	C2—C7—C4	110.0 (4)
N1—C5—C3 ^{iv}	108.4 (3)	C2—C7—H7A	109.6
C3—C5—C3 ^{iv}	109.9 (5)	C4—C7—H7A	110.0
N1—C5—C1	109.6 (4)	C2—C7—H7B	109.4
C3—C5—C1	110.3 (3)	C4—C7—H7B	109.5
C3 ^{iv} —C5—C1	110.3 (3)	H7A—C7—H7B	108.2
C5—C1—C2	109.2 (5)		

Symmetry codes: (i) $-x-1, -y, -z$; (ii) $x, -y, z$; (iii) $-x-1, y, -z$; (iv) $x, -y-1, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B \cdots F2 ^{iv}	0.90	1.80	2.639 (5)	155
N1—H1C \cdots F1 ^v	0.90	2.04	2.920 (4)	166

Symmetry codes: (iv) $x, -y-1, z$; (v) $x+1/2, y-1/2, z$.