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Bis(1-adamantylammonium) hexafluoridogermanate

Liying Cheng,[a] Xin Xu[b] and Yan Xu[a]*

[a]Institute of Chemistry for Functionalized Materials, College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China, and [b]Heavy 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

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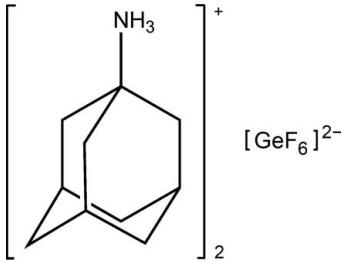
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; disorder in main residue; R factor = 0.057; wR factor = 0.144; data-to-parameter ratio = 12.1.

The title compound, $(C_{10}H_{18}N)_2[GeF_6]$, 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 N—H···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

$(C_{10}H_{18}N)_2[GeF_6]$
M_r = 491.10
Monoclinic, $C2/m$
a = 11.099 (2) Å
b = 6.7458 (13) Å
c = 14.179 (3) Å
β = 97.844 (3)°
V = 1051.7 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.52 mm^{-1}
T = 293 (2) K
0.20 × 0.18 × 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_{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
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···F2^{i}	0.90	1.80	2.639 (5)	155
N1—H1C···F1^{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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2261).

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supplementary materials

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Bis(1-adamantylammonium) hexafluoridogermanate

L. Cheng, X. Xu and Y. Xu

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.

Experimental

Colorless plate-like crystals were synthesized hydrothermally from a mixture of GeO_2, H_3BO_3, $NiCl_2$, $(C_{10}H_{18}N)Cl$, C_4H_9OH, HF and H_2O. In a typical synthesis, GeO_2 (0.100 g), H_3BO_3 (0.006 g), $NiCl_2$ (0.23 g), and $(C_{10}H_{18}N)Cl$ (0.300 g) were dissolved in a mixture of C_4H_9OH (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.

Refinement

The GeF_6^{2-} 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),

Figures

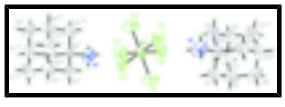

Fig. 1. The molecular structure of title compound showing displacement ellipsoids at the 70% probability level for non-H atoms (the occupancy factors for F1 and F2 are 1/2).

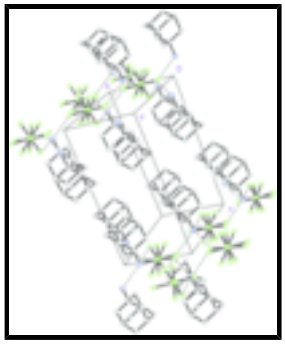

Fig. 2. Unit-cell contents.

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) Å
$b = 6.7458$ (13) Å
$c = 14.179$ (3) Å
$\beta = 97.844$ (3)°
$V = 1051.7$ (4) Å^3
$Z = 2$
$F_{000} = 512$
$D_x = 1.551$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 955 reflections
$\theta = 3.5$–$25.1°$
$\mu = 1.52$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.20 × 0.18 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 293$(2) K
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.751$, $T_{max} = 0.863$
2694 measured reflections
1037 independent reflections
955 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 25.2°$
$\theta_{min} = 3.5°$
$h = -10 \rightarrow 13$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.144$
$S = 1.07$
1037 reflections
86 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0862P)^2 + 0.4272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.00$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}
Extinction correction: none

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^2)

	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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1B···F2^{iv}	0.90	1.80	2.639 (5)	155
N1—H1C···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*.

Fig. 1

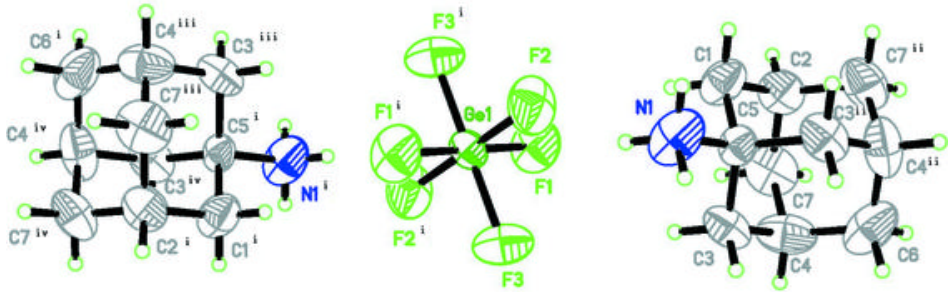
C6 i
C4 iii
C3 iii
C7 iii
C4 iv
C5 i
N1 i
C3 iv
C7 iv
C2 i
C1 i
F3 i
F2
F1 i
Ge1
F1
F2 i
F3
C1
C2
C7 ii
N1
C5
C3 ii
C4 ii
C7
C3
C4
C6

Fig. 2