Bis(diethylenetriamine-$\kappa^3 N$)nickel hexafluorogermanate

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The title compound, [Ni(dien)$_2$][GeF$_6$] (dien is diethylenetriamine, C$_4$H$_{13}$N$_3$), synthesized under mild solvothermal conditions, is a novel zero-dimensional material in which [GeF$_6$]$^{2-}$ building anions are connected to [Ni(dien)$_2$]$^{2+}$ cations *via* hydrogen bonds between F atoms and N—H groups. Both metal atoms are located on special positions of site symmetry 2/*m*. Furthermore, one F and one N atom (including the attached H atom) are located on a mirror plane.

Comment

Despite the rapid development in the syntheses of new materials, the field of fluorides remains undeveloped. More recently, fluoroaluminates such as (C$_4$H$_{12}$N$_2$)(H$_3$O)[Al$_3$F$_{12}$] (Tang *et al.*, 2001*c*) and (C$_4$H$_{12}$N$_2$)$_2$[Al$_2$F$_{10}$]·2H$_2$O (Tang *et al.*, 2001*e*), the fluorosilicate (C$_4$N$_2$H$_{12}$)[SiF$_6$] (Tang *et al.*, 2001*f*) and fluorotitanates such as (C$_5$H$_6$N)$_2$(H$_3$O)[Ti$_2$F$_{11}$]·H$_2$O (Tang *et al.*, 2001*d*), (C$_4$N$_2$H$_{14}$)[TiF$_4$O] (Tang *et al.*, 2001*a*), (C$_4$H$_{12}$N$_2$)[TiF$_5$(H$_2$O)]$_2$ (Tang *et al.*, 2001*b*) and (C$_4$H$_{12}$N$_2$)$_2$[Ti$_2$F$_{10}$O]·2H$_2$O (Dadachov *et al.*, 2001) have been reported. In those fluorides, the central Al, Si and Ti atoms are all coordinated by F atoms. However, considerably less work has been performed on fluorogermanates, with only a few Ge^{IV} fluorides, *viz.* K$_2$[*cis*-(CF$_3$)$_2$GeF$_4$] (Brauer *et al.*, 1980), [(CH$_3$)$_4$N][(CF$_3$)$_3$GeF$_2$] (Brauer *et al.*, 1986) and N(CH$_2$CH$_2$O)$_3$GeF (Lukevics *et al.*, 1997), structurally characterized. All these fluorogermanates are coordinated by mixed ligands. Recently, the use of hydrofluoric acid as a mineralizing agent in the synthesis of zeolite materials with novel architectures has attracted much attention (Li *et al.*, 1998; Plevert *et al.*, 2001). As part of our interest in borogermanate microporous materials, we tried to prepare novel open frameworks using organic amines in the presence of hydrofluoric acid. Unexpectedly, the novel title compound, (I), was obtained; this is the first structure of its kind.
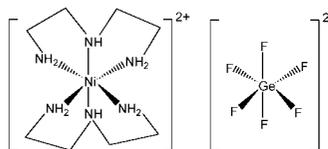
The title compound (Fig. 1) is composed of [GeF$_6$]$^{2-}$ anions and [Ni(dien)$_2$]$^{2+}$ cations. In the anion [GeF$_6$]$^{2-}$, the germanium center is coordinated by six fluoride ligands, resulting in an octahedral geometry, with Ge—F distances of 1.798 (2) and 1.799 (4) Å, which is consistent with K$_2$GeF$_6$ (Ge—F = 1.77 Å; Hoard & Vincent, 1939), other fluorogermanates (Taylor &

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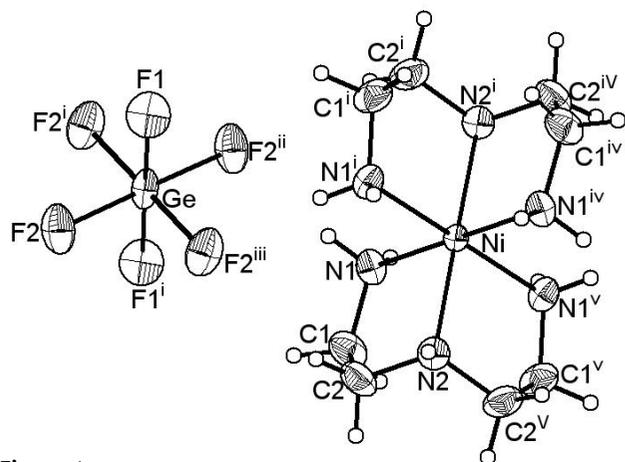
Figure 1
The cation and anion of the title complex, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$; (iii) $x, y, 2 - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (v) $x, y, 1 - z$.]
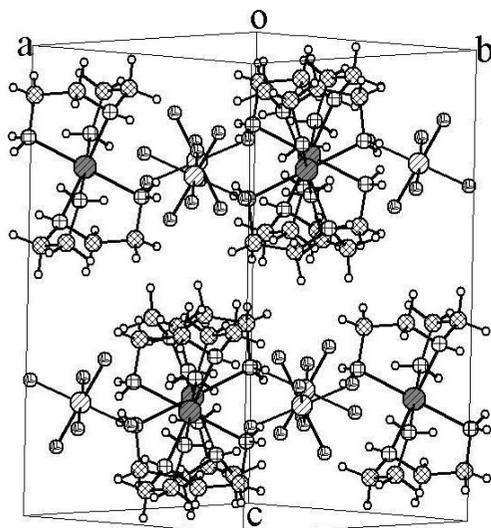
Figure 2
Packing diagram of (I), viewed down [101].

Wilson, 1973), and $[(CH_3)_4N][(CF_3)_3GeF_2]$ (Brauer *et al.*, 1986); *cis*-F—Ge—F angles lie between 89.4 (1) and 90.6 (1)°. The nickel cation displays distorted octahedral geometry and is bonded to six N atoms of two diethylene triamines with Ni—N distances of 2.110 (2) and 2.112 (4) Å, and *cis*-N—Ni—N angles in the range 83.1 (1)—96.9 (1)°. Like $[Co(dien)_2]^{2+}$ (Keene & Searle, 1974), $[Ni(dien)_2]^{2+}$ also has *s-cis*, *u-cis* and *trans* configurations, and the latter two are chiral. In the title compound, there is only one unique Ni site of *s-cis*-$[Ni(dien)_2]^{2+}$. The $[GeF_6]^{2-}$ anions interact with $[Ni(dien)_2]^{2+}$ cations both electrostatically and through weak hydrogen bonds. The hydrogen bonds are formed between the F and N atoms, with F···N distances in the range 3.060 (4)–3.180 (5) Å.

Experimental

The title compound was prepared from a mixture of germanuim dioxide (GeO₂, 0.104 g), boric acid (H₃BO₃, 0.031 g), NiCl₂·6H₂O (0.238 g), diethylenetriamine ($C_4N_3H_{13}$, 2 ml), pyridine (C_5H_5N,

2 ml), hydrofluoric acid (HF, 40%, 0.1 ml), and deionized water (2 ml), in the molar ratio 1:1:1:18:25:5:110. The mixture was mechanically stirred at room temperature with a final pH of 9.0 and then placed in an autoclave at 443 K for 7 d.

Crystal data

$[Ni(C_4H_{13}N_3)_2][GeF_6]$	Mo $K\alpha$ radiation
$M_r = 451.65$	Cell parameters from 25
Orthorhombic, $Cccm$	reflections
$a = 9.5937 (19)$ Å	$\theta = 2.5–25.0°$
$b = 15.193 (3)$ Å	$\mu = 3.17$ mm^{-1}
$c = 10.819 (2)$ Å	$T = 293 (2)$ K
$V = 1576.9 (6)$ Å^3	Polyhedron, purple
$Z = 4$	$0.48 \times 0.40 \times 0.22$ mm
$D_x = 1.902$ Mg m^{-3}	

Data collection

Bruker CCD area-detector diffractometer	739 independent reflections
	536 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SADABS*; Sheldrick, 1996)	$h = -11 \rightarrow 8$
$T_{min} = 0.238, T_{max} = 0.498$	$k = -17 \rightarrow 7$
1847 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 3.1056P]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
739 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
57 parameters	$\Delta\rho_{min} = -0.72$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ge—F2	1.798 (2)	N1—C1	1.460 (5)
Ge—F1	1.799 (4)	N2—C2	1.471 (5)
Ni—N1	2.110 (3)	C1—C2	1.542 (7)
Ni—N2	2.112 (4)		
F2^{ii}—Ge—F2	180.0	N1^{iv}—Ni—N1	90.6 (2)
F2^{i}—Ge—F2^{ii}	89.8 (2)	N1^{i}—Ni—N2	96.9 (1)
F2—Ge—F2^{i}	90.2 (2)	N1—Ni—N2	83.1 (1)
F2^{iii}—Ge—F1	89.5 (1)	N1—Ni—N2^{iv}	96.9 (1)
F2—Ge—F1	89.4 (1)	N2—Ni—N2^{iv}	180.0
F2^{i}—Ge—F1	90.6 (1)	C1—N1—Ni	111.1 (2)
F1^{ii}—Ge—F1	180.0	C2^{v}—N2—C2	116.9 (5)
N1^{i}—Ni—N1^{v}	180.0	N1—C1—C2	110.3 (3)
N1^{i}—Ni—N1	89.4 (2)	N2—C2—C1	112.2 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···F1^{vi}	0.90	2.24	3.060 (4)	152
N1—H1B···F2^{vi}	0.90	2.37	3.099 (4)	138
N1—H1A···F2^{ii}	0.90	2.23	3.123 (5)	171
N2—H2A···F2^{vii}	0.91	2.39	3.180 (5)	145
N2—H2A···F2^{viii}	0.91	2.39	3.180 (5)	145

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

All H atoms were positioned geometrically (C—H = 0.97 Å and N—H = 0.91 Å) and allowed to ride on their parent C or N atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* and *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Brauer, D. J., Burger, H. & Eujen, R. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 836–837.
Brauer, D. J., Wilke, J. & Eujen, R. (1986). *J. Organomet. Chem.* **316**, 261–269.
Bruker. (1999). *SMART*, *SAINT* and *SHELXTL*. Versions 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Dadachov, M. S., Tang, L. Q. & Zou, X. D. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 141–142.
Hoard, J. L. & Vincent, W. B. (1939). *J. Am. Chem. Soc.* **61**, 2849–2852.
Keene, F. R. & Searle, G. H. (1974). *Inorg. Chem.* **13**, 2173–2180.
Li, H., Eddaoudi, M., Richardson, D. A. & Yaghi, O. M. (1998). *J. Am. Chem. Soc.* **120**, 8567–8568.
Lukevics, E., Belyakov, S., Arsenyan, P. & Popelis, J. (1997). *J. Organomet. Chem.* **549**, 163–165.
Plevert, 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. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001*a*). *Z. Kristallogr. New Cryst. Struct.* **216**, 257–258.
Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001*b*). *Z. Kristallogr. New Cryst. Struct.* **216**, 259–260.
Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001*c*). *Z. Kristallogr. New Cryst. Struct.* **216**, 385–386.
Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001*d*). *Z. Kristallogr. New Cryst. Struct.* **216**, 387–388.
Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001*e*). *Z. Kristallogr. New Cryst. Struct.* **216**, 389–390.
Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001*f*). *Z. Kristallogr. New Cryst. Struct.* **216**, 391–392.
Taylor, J. C. & Wilson, P. W. (1973). *J. Am. Chem. Soc.* **95**, 1834–1838.