

(Ethylenediamine- κ^2N)(triethylenetetramine- κ^4N)-nickel hexafluorogermanate**Guo-Ming Wang, Yan-Qiong Sun and Guo-Yu Yang***

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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$ R factor = 0.053 wR factor = 0.126

Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Ni}(\text{en})(\text{TETA})][\text{GeF}_6]$ or $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)(\text{C}_6\text{H}_{18}\text{N}_4)][\text{GeF}_6]$, was synthesized under mild solvothermal conditions in the presence of triethylenetetramine (TETA) as a base. It is a new salt composed of $[\text{GeF}_6]^{2-}$ anions and $[\text{Ni}(\text{en})(\text{TETA})]^{2+}$ cations. The ions are linked together by hydrogen bonding between F atoms and N–H groups. The complex cation and anion lie on twofold axes of the space group *Pccn*.

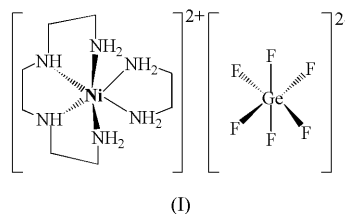
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Comment

Currently, many efforts have been dedicated to the design and synthesis of new materials. The field of fluorides, however, remains undeveloped. More recently, different fluorides including fluoroaluminates (Tang *et al.*, 2001*a,b*), fluoro-silicates (Tang *et al.*, 2001*c*) and fluorotitanates (Tang *et al.*, 2001*d,e,f*; Dadachov *et al.*, 2001) have been reported. However, less work has been performed on fluorogermanates, with only a few Ge^{IV} fluorides (Brauer *et al.*, 1980, 1986; Lukevics *et al.*, 1997; Zhang *et al.*, 2003) structurally characterized. The aim of our work is to synthesize microporous germanates templated by organic amines. Unexpectedly, the title compound, (I), was obtained, a new fluorogermanate templated by the metal complex $[\text{Ni}(\text{en})(\text{TETA})]^{2+}$. Since we did not add ethylenediamine (en) to the initial mixture, it must have been derived from the decomposition of TETA under hydrothermal conditions.



The crystal structure of (I) consists of a discrete $[\text{GeF}_6]^{2-}$ anion and an $[\text{Ni}(\text{en})(\text{TETA})]^{2+}$ cation (Fig. 1). In $[\text{GeF}_6]^{2-}$, the germanium center is coordinated by six F atoms, resulting in an octahedral geometry. The Ge–F bond distances are in the range 1.781 (3)–1.799 (3) Å, which is consistent with K_2GeF_6 (Ge–F = 1.77 Å; Hoard & Vincent, 1939) and other fluorogermanates, *e.g.* $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$ (Brauer *et al.*, 1986). In the $[\text{Ni}(\text{en})(\text{TETA})]^{2+}$ cation, the Ni^{II} atom is bonded to six N atoms of the en and TETA molecules, with Ni–N distances in the range 2.080 (4)–2.135 (5) Å. The complex cation and anion lie on twofold axes. The $[\text{GeF}_6]^{2-}$ anions and $[\text{Ni}(\text{en})(\text{TETA})]^{2+}$ cations interact with each other

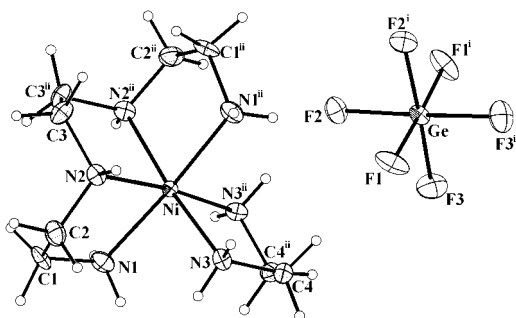


Figure 1
The ionic components of the title compound, with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, z$].

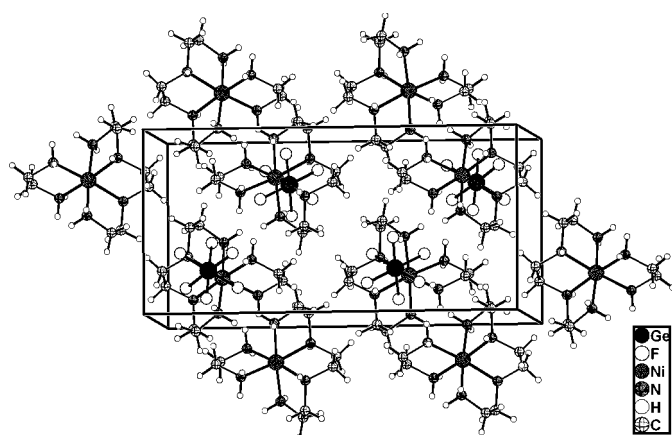


Figure 2
Packing diagram of the title compound, viewed down the *b* axis.

via weak hydrogen bonds, with $H \cdots F$ distances in the range 2.07–2.40 Å.

Experimental

In a typical synthesis, a mixture of GeO_2 (0.104 g, 1 mmol), $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), TETA (1.8 ml), pyridine (2 ml), hydrofluoric acid (40%, 0.1 ml), and H_2O (1 ml), in a 1:1:12:25:5:56 molar ratio, was sealed in a Teflon-lined steel autoclave, heated at 443 K for 7 d and then cooled to room temperature. The resulting purple crystals were recovered by filtration, washed with distilled water and dried in air.

Crystal data

$[Ni(C_2H_8N_2)(C_6H_{18}N_4)][GeF_6]$
 $M_r = 451.65$
Orthorhombic, *Pccn*
 $a = 8.9029$ (2) Å
 $b = 9.4731$ (3) Å
 $c = 18.0856$ (2) Å
 $V = 1525.30$ (6) Å³
 $Z = 4$
 $D_x = 1.967$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 2958 reflections
 $\theta = 2.2$ – 25.0°
 $\mu = 3.27$ mm⁻¹
 $T = 293$ (2) K
Prism, purple
0.22 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.630, T_{max} = 0.721$
7696 measured reflections

1315 independent reflections
1216 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.034$
 $\theta_{max} = 25.0^\circ$
 $h = -8 \rightarrow 10$
 $k = -11 \rightarrow 10$
 $l = -19 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.126$
 $S = 1.14$
1315 reflections
101 parameters
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 11.3515P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.03$ e Å⁻³
 $\Delta\rho_{min} = -0.56$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ge—F1	1.781 (3)	Ni—N3	2.080 (4)
Ge—F3	1.785 (3)	Ni—N2	2.108 (5)
Ge—F2	1.799 (3)	Ni—N1	2.135 (5)
F1—Ge—F3	91.46 (17)	N3—Ni—N2	96.04 (17)
F1—Ge—F2	89.56 (16)	N3—Ni—N1	90.72 (18)
F3—Ge—F2	89.54 (16)	N2—Ni—N1	81.90 (18)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots F3 ⁱⁱⁱ	0.90	2.19	3.005 (6)	151
N1—H1A \cdots F2 ⁱⁱⁱ	0.90	2.34	3.064 (6)	138
N2—H2C \cdots F1 ^{iv}	0.91	2.25	3.035 (5)	145
N2—H2C \cdots F3 ^v	0.91	2.40	3.176 (6)	143
N3—H3A \cdots F2 ^v	0.90	2.21	3.028 (6)	150
N3—H3A \cdots F1 ^{iv}	0.90	2.32	3.046 (5)	138
N3—H3B \cdots F2 ⁱⁱ	0.90	2.07	2.960 (6)	171
C4—H4B \cdots F1	0.97	2.33	3.198 (7)	148

Symmetry codes: (ii) $\frac{1}{2} - x, \frac{3}{2} - y, z$ (iii) $x - \frac{1}{2}, 1 - y, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, 2 - y, \frac{1}{2} - z$; (v) $1 - x, \frac{3}{2} + y, \frac{1}{2} - z$.

All H atoms were positioned geometrically ($C-H = 0.97$ Å and $N-H = 0.90$ Å) and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$. The highest peak in the difference map is located 1.14 Å from atom F3.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); 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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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 (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SMART* and *SAINT*. 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.
- Lukevics, E., Belyakov, S., Arsenyan, P. & Popelis, J. (1997). *J. Organomet. Chem.* **549**, 163–165.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001a). *Z. Kristallogr. New Cryst. Struct.* **216**, 385–386.
- Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001b). *Z. Kristallogr. New Cryst. Struct.* **216**, 389–390.
- Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001c). *Z. Kristallogr. New Cryst. Struct.* **216**, 391–392.
- Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001d). *Z. Kristallogr. New Cryst. Struct.* **216**, 257–258.
- Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001e). *Z. Kristallogr. New Cryst. Struct.* **216**, 259–260.
- Tang, L. Q., Dadachov, M. S. & Zou, X. D. (2001f). *Z. Kristallogr. New Cryst. Struct.* **216**, 387–388.
- Zhang, H. X., Yang, G. Y. & Sun, Y. Q. (2003). *Acta Cryst.* **E59**, m185–m187.